WASM: Mineral, Energy and Chemical Engineering

Design and Development of a Three Phase Semifluidized Bed Reactor for Wastewater Treatment with Reference to Steel Plant Effluent

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This thesis is presented for the Degree of Doctor of Philosophy

of Curtin University

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature:

Date: 05/08/2020

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Abstract

The present research work has been undertaken to develop and analyze the performance of a semifluidized bed as a reactor for adsorptive removal of various heavy metals and organic pollutants along with its application in real steel plant effluents treatment operation. A lab scale semifluidized bed has been developed and it's hydrodynamic parameters like minimum fluidization velocity, semifluidization velocity, packed bed formation tendency, bed pressure drops etc. have been estimated with various operating conditions. The study reveals that, the low-density particles significantly reduced the minimum fluidization velocity ranging from 0.004 - 0.01 m/s, and minimum semifluidization velocity of 0.032 - 0.006 m/s. Maximum pressure of the system was found to be 5-6 kPa which is significantly lower value. In order to replace the bed materials as bio adsorbents, novel composite adsorbent was prepared from agricultural solid biomass-based biochar and Na-alginate and used in treatment operation. The biochar was prepared from pine cone and sugarcane bagasse precursor. Both the adsorbents have high surface properties in terms of specific surface area, pore size, functional groups, surface morphology and total carbon contents which are important for adsorptive surface reaction The BET surface area of both sugarcane bagasse based biochar and its composites materials were 391.42 and 200.14 m^2/g respectively, whereas for pine cone based biochar and its composite were 144.94 and 163.87 m^2/g respectively. Experimental batch adsorptive removal of aqueous phase inorganics/organics by biochar and composite adsorbents materials were carried out to identify and optimize various process parameters and their effects on adsorption mechanism. Kinetic experiments confirmed that the batch adsorption reaction was fast and equilibrium was attended within 3 hours' time. The pseudo-first-order and pseudo-second-order kinetic models were fit to the experimental data and various kinetic model parameters were determined by both linear and

non-linear regression methods. Weber-Morris diffusion model confirmed the nature of adsorption and some other studies like thermodynamic, activation energy of the system showed the type of adsorption. Later these adsorbent materials are used as the solid phase of the semifluidized bed to evaluate the bed performance. Real steel plant effluents were collected from DSP, SAIL, W.B. and its was treated through the same semi-fluidized bed reactor as case study. The equilibrium time for the system is 240-300 minutes which is satisfactorily lower with compared to other systems like the packed bed or fluidized bed. Maximum capacity for Zn²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Cd²⁺ MB dye and Phenol for the bed operation were found to be 42.4, 43.27, 46.12 54.4, 36.8 37.5 and 89.35 mg/g respectively. The experimental data were optimized by RSM analysis to find out the optimum operating condition at which the system gives maximum bed efficiency. A real-time dynamic mass transfer model for the novel system was also obtained from the developed model and accordingly validated with the experimental data.

Keywords: semifluidized bed, wastewater treatment, steel plant effluent, adsorption, heavy metal removal, MB dye removal, Phenol removal, dynamic modeling.

List of publications from Thesis

- 1. Subrata Biswas, Bhim Charan Meikap, Tushar Sen, "Adsorptive removal of aqueous phase copper (Cu2+) and nickel (Ni2+) metal ions by synthesize Biochar-biopolymeric hybrid adsorbents and process optimization by response surface methodology (RSM)", Water, Air, & Soil Pollution, 2019, 230, 197.
- 2. Subrata Biswas, Saumya S Mohapatra, Usha Kumari, Bhim Charan Meikap, Tushar Sen, "Adsorptive Removal of MB Dye using low-cost Sugarcane Bagasse Biochar and its Alginate Composite in Batch and Closed Circuit Semifluidized Bed Reactor' Journal of Environmental Chemical Engineering, 2020, 8(1).
- 3. Subrata Biswas, Tushar Sen, Bhim Charan Meikap, *Experimental Hydrodynamic and bed Characteristics of Co-current Gas-Liquid-Solid Three Phase Semifluidization with liquid as the continuous phase*, Particulate Science and Technology, 2019, 1–13.
- 4. Subrata Biswas, Tushar Sen, Anteneh Mesfin Yeneneh ,Bhim Charan Meikap, Synthesis and characterization of a novel Ca-alginate-biochar composite as efficient zinc (Zn²⁺) adsorbent: Thermodynamics, process design, mass transfer and isotherm modeling, Separation Science and Technology, 2019, 54(7).
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- 6. Subrata Biswas, Hammad Siddiqi, Bhim Charan Meikap, Tushar Sen, Mahadi khidani, *Preparation and characterization of raw and inorganic acid activated pine cone biochar and its application in the removal of aqueous phase Pb2+ metal ions by adsorption*, Water, Air, & Soil Pollution, 2019, 231 (1),
- Subrata Biswas, Shubham Sharma, Subhrajit Mukherjee, Bhim Charan Meikap, Tushar Sen, Process modelling and optimization of a novel Semifluidized bed adsorption column operation for divalent heavy metal removal, Journal of Water Process Engg. 2020, 37, 101406

List of Figures

Figure	Caption	Page No.
No		
Fig.1.1	Source and sink of heavy metals	4
Fig.1.2	Summary of heavy metals enter into the human body and other living creatures	6
Fig. 1.3	Mechanism of Photocatalysis	13
Fig. 1.4	Concept of Membrane separation	15
Fig. 1.5	Mechanism of Electrodialysis process	19
Fig. 1.6	Flow diagram of the overall work	38
Fig. 2.1	The bed of particles and the force balance	46
Fig. 2.2	Schematic of experimental setup	48
Fig. 2.3	Pictorial view of the experimental setup	49
Fig. 2.4	Pictorial view of the air-water distribution section	49
Fig. 2.5	Variation of minimum fluidization velocity $U_{lmf}(m/s)$ with different gas velocity, $U_g(m/s)$ (a) for different static bed height (H_s) at $d_p=3.86mm$, (b) for different particle size (d_p) where $H_s = 0.25m$.	52
Fig. 2.6	Variation of minimum semifluidization velocity U_{sfm} , (m/s) with different gas velocity $U_g(m/s)$ (a) for different particle size (d_p) at $H_s = 0.25m$,(b) for different static bed height (H_s) , at $d_p = 3.86$ mm.	54
Fig. 2.7	Variation of packed bed formation $H_{pa}(cm)$ with superficial liquid velocity $U_{sl}(m/s)$ (a) for different static bed height $H_s(cm)$ for $d_p =$ 3.86 mm, $U_g = 0.004246m/s$, (b) for different particle sizes d_p at static bed height $H_s = 25 cm$, $U_g = 0.004246m/s$, (c) for different bed expansion ratio (R), particle size $d_p = 3.86$ mm.	56
Fig. 2.8	Variation of packed bed to static bed ratio H_{Pa}/Hs with superficial liquid velocity $U_{SL}(m/s)$ (a) for different particle sizes, at $Hs = 25$ cm, (b) for different bed expansion ratio (R) at particle size d_p 3.86 mm	57
Fig. 2.9	Variation of Pressure drop $\Delta P(kPa)$ with superficial liquid velocity $U_{SL}(m/s)$ (a) at static bed height $H_s = 25$ cm, $d_p = 3.86$ mm and $U_g = 0.004246 m/s$, (b) for different static bed height H_s at $d_p = 3.86$ mm $U_g = 0.004246m/s$, (c) for different particle sizes d_p , static	59

	bed height H_s 25 cm, (d) for different superficial gas velocity U_g ,	
Fig 2.10	particle size a_p =5.80, static bed height $H_S = 25$ cm. Experimental vs Calculated values for minimum fluidization value ity	60
Fig. 2.10	Experimental vs calculated values for minimum semifluidization	61
Fig. 2.11	velocity	01
Fig. 2.12	Experimental vs calculated values for top packed zone formation	62
Fig. 2.13	Experimental vs calculated values for a pressure drop of semifluidized bed	63
Fig.2.14	Experimental vs predicted values for dimensionless top packed zone formation	64
Fig. 2.15	Experimental vs predicted values for a dimensionless pressure drop of semifluidized bed	65
Fig. 3.1	(a) Preparation of Alginate biochar composite beads, (b) composite adsorbent in distilled water	71
Fig. 3.2	Dry adsorbent bead under the scan electron microscope	72
Fig. 3.3	Autosorb iQ BET analyzer	73
Fig. 3.4	BET isotherm plot for a) Scot pine cone biochar (PC) b) pinecone alginate composite (CAPC) (c) sugarcane bagasse biochar (SB) (d) Ca Alginate sugarcane bagasse biochar composite (CASB)	76
Fig. 3.5	Perkin Elmer Spectra 100 FT IR	77
Fig. 3.6	FTIR spectrum for a) Pinecone biochar and CAPC composite b)	78
5.05	Sugarcane bagasse biochar and CASB composite	0.0
F1g. 3./	XRD spectrum for a) Pinecone biochar b) CAPC composite c) Sugarcane bagasse biochar d) CASB composite	80
Fig. 3.8	JEOL -JSM-7610F FESEM for Surface morphology analysis	81
Fig. 3.9	FESEM images for a) Pine cone biochar b) CAPC composite c) Sugarcane bagasse biochar d) CASB composite	82
Fig. 4.1	Effect of pH on adsorption of heavy metals and Phenol	95
Fig. 4.2	Effect of time and initial adsorbate concentration on adsorption	98
Fig. 4.3	Effect of adsorbent dose on the adsorption process	100
Fig. 4.4	Effect of system temperature on adsorption	101
Fig. 4.5	Typical Pseudo-second –order kinetic model for a) Liner fit model b) non-linear fit model	104
Fig. 4.6	Intra-particle diffusion model and mechanism of adsorption	109
Fig. 4.7	Example of Linear fit and non-linear fit of isotherm models	112
Fig. 4.8	Surface morphology changed for CASB after interaction with adsorbent a) Zn^{2+} b) Cu^{2+} c) Ni^{2+} d) Cd^{2+} e) Pb^{2+} f) Phenol	117
Fig. 4.9	Surface morphology changed for CAPC after interaction with adsorbent	118

	a) Zn^{2+} b) Cu^{2+} c) Ni^{2+} d) Cd^{2+} e) Pb^{2+} f) Phenol	
Fig. 4.10	Surface morphology changed for (a) CASB and (b)CAPC after interaction with MB dye	119
Fig. 5.1	Pictorial view of Semifluidized bed under operation (a) complete experimental set up (b) semifluidized bed only reacting section	125
Fig. 5.2	Effect of initial metal ion concentration on performance of Semifluidized bed reactor (a) Cu^{2+} (b) Ni^{2+} (c) Pb^{2+} and (d) Cd^{2+} at initial adsorbent bed height 10 cm, Feed flow rate 2 LPM	129
Fig. 5.3	Effect of initial adsorbent loading on performance of Semifluidized bed reactor (a) Zn^{2+} (b) Cu^{2+} (c) Ni^{2+} and (d) Pb^{2+} at initial concentration 20 mg/L, Feed flow rate 2 LPM	131
Fig. 5.4	Effect of Liquid flow rate on performance of Semifluidized bed reactor (a) Zn^{2+} (b) Ni^{2+} (c) Pb^{2+} and (d) Cd^{2+} at initial concentration 20 mg/L, initial adsorbent bed height.	134
Fig. 5.5	Effect of a) initial adsorbent bed height b) initial phenol concentration c) Liquid flow rate on performance of Semifluidized bed reactor, d) Performance of SFBR on removal of phenol from steel plant effluent	136
Fig. 6.1	A pictorial view of CCD design	143
Fig. 6.2	(a) Interaction effect of Bed height (X_1) and Concentration (X_2) on Zn^{2+} removal (b) Interaction effect of Bed height (X_1) and flow rate (X_3) on Zn^{2+} removal (c) Interaction effect of Flow rate (X_3) and Concentration (X_2) on Zn^{2+} removal (d) Couture plot at optimum condition for Zn^{2+} removal (e) The normal probability vs studentized residual plot (f) Actual vs predicted Zn^{2+} removal	156
Fig. 6.3	(a) Interaction effect of Bed height (X_1) and Concentration (X_2) on Pb^{2+} removal (b) Interaction effect of Bed height (X_1) and flow rate (X_3) on Pb^{2+} removal (c) Interaction effect of Flow rate (X_3) and Concentration (X_2) on Pb^{2+} removal (d) Couture plot at optimum condition for Pb^{2+} removal (e) The normal probability vs studentized residual plot (f) Actual vs predicted Pb^{2+} removal	157
Fig. 6.4	Validation of dynamic model for the performance of Semifluidized bed reactor for Pb^{2+} (a-c)/Cd ²⁺ (d-f) removal at various operating conditions.	158

List of Tables

Table No	Caption	Page No.
Table 1.1	Sources and effects of various heavy metals	4
Table 1.2	Toxic effect and threshold limit of various heavy metals	6
Table 1.3	Example of heavy metal removal by chemical precipitation	9
Table 1.4	Examples of heavy metal removal by ion exchange	11
Table 1.5	Example of heavy metal removal by membrane separation (MEUF & PEUF)	16
Table 1.6	Example of heavy metal removal by membrane separation (RO & NF)	18
Table 1.7	Example of heavy metal removal by the agricultural waste-based adsorbent	22
Table 1.8	Example of heavy metal removal by Aquatic and terrestrial biomass- based adsorbent	26
Table 1.9	Removal of various heavy metals by Nano based adsorbent	30
Table 1.10	Adsorption capacity of various adsorbent for phenol	32
Table 1.11	Drawbacks of various treatment technologies	33
Table 2.1	Operational conditions for hydrodynamic studies of a semifluidized bed	50
Table 2.2	A comparative study of other reported results of hydrodynamic parameters of the semifluidized bed system	63
Table 3.1	Proximate analysis data for the adsorbents	72
Table 3.2	Ultimate analysis data for all the adsorbent materials	73
Table3.3	Physical properties of the adsorbent materials	75
Table 4.1	Pseudo-Second-order kinetic parameters at different initial adsorbate	105
Table 4.2	concentration, temperature 308K, adsorbent dose 1g/L.	107
1 able 4.2	intra-particle diffusion model parameters	10/

Table4.3	Langmuir isotherm model parameters	113
Table 4.4	Freundlich isotherm model parameters	113
Table 4.5	Thermodynamic parameters for all the adsorbate at various system	114
	temperature	
Table 4.6	The adsorption capacities of both the adsorbents at identical	116
	experimental conditions at initial adsorbate Volume 50 mL, adsorbent	
	dose 1g/L, temperature 308K	
Table 4.7	Adsorption desorption study for Zn^{2+} (CAPC adsorbent) and	120
	Pb ²⁺ (CASB adsorbent)	
Table 5.1	Range of the operating parameters for the semifluidized bed operation	126
Table 5.2	Characterization of Steel Plant waste water before and after treatment	135
Table 5.3	Performance of packed/fixed bed and fluidized bed adsorption column	138
	for heavy metal removal	
Table 6.1	The coded form and the actual level of the independent variables	149
Table 6.2	Detail scope of experiments and range of the operating parameters	149
Table 6.3	Response values Experimental and model predicted at optimized	153
	condition (SFBR operation)	
Table 6.4	Level of the experimental conditions for the optimization for the batch	154
	studies of heavy metals	
Table 6.5	Response values Experimental and model predicted at optimized	155
	condition (batch operation)	
Table 6.6	Parameters obtained from the model fitting	160

List of symbols

Symbols

A _c	Area of the column, m ²
A_r	Archimedes number
C_e	Equilibrium concentration, mg/L
C_D	Drag coefficient
D_c , d_c	Diameter of the column, cm,m
D_z	Axial dispersion coefficient, m ²
d_p	Particle diameter, mm
d_{pav}	Average particle diameter, mm
G_{sfg}/G_{mfl}	superficial gas mass velocity ratio
G_{sfl}/G_{mfl}	superficial liquid mass velocity ratio
H_{pa}	Height of the packed section, cm
H_f	Height of the fluidized section, cm
H _s	Static bed height, cm
H _{sf}	Height of the semifluidized bed
<i>K</i> ₁	First order kinetic constant min ⁻¹
<i>K</i> ₂	Second order kinetic constant, g/mg. min
K _{id}	Intraparticle diffusion coefficient
K_L	Freundlich constant, L/g
M_b	Mass of the bed material, g
n	Dimensionless no used in Freundlich isotherm
Q_{rel}	Relative volumetric flowrate, m ³ /s
q_e	Adsorption capacity at equilibrium, mg/g
q_m	Maximum adsorption capacity, mg/g
q_t	Adsorption capacity at any time,
R	Bed expansion ratio
R _{emf}	Reynolds number at minimum fluidization
R_L	Separation factor
U_g	Superficial gas velocity, m/s
U _{lmf}	Minimum fluidization velocity of liquid, m/s
$U_{Lsf}(\min)$	Minimum semifluidization velocity of liquid, m/s
U_{SL}	Superficial liquid velocity, m/s
U_{sfg}/U_{mfl}	Superficial gas velocity ratio
U_{sfg}/U_{mfl}	Superficial liquid velocity ratio

U _t	Terminal velocity of particle, m/s
v_b	Volume of the bed, m ³
v_p	Volume of the particle, m ³
ΔG	Change in Gibb's free energy, KJ/mole
ΔH	Change of Enthalpy KJ/mole
ΔP_f	Pressure drop across the fluidized section, Pa
ΔP_{pa}	Pressure drop across the packed section, Pa
ΔP_r	Pressure drop across the restraint section, Pa
ΔP_{sf}	Pressure drop across the semifluidized bed, Pa
ΔS	Change of entropy, J/mole K
Greek Symbols	
ε _f	Void fraction of fluidization section
ε_p	Void fraction of Packed section
ρ_L	Density of liquid, kg/m ³
ρ_S	Density of solid, kg/m ³
μ_{g}	Viscosity of gas, cP
μ_L	Viscosity of liquid, cP
φ_S	Sphericity of particle
Abbreviation	
BET	Brunauer–Emmett–Teller
BJH	Barrett, Joyner, and Halenda
CASB	Ca Alginate Sugarcane Bagasse Adsorbent
CAPC	Ca Alginate Pine Cone Adsorbent
CCD	Central Composite Design
CMC	Carboxy Methyl Cellulose
FT IR	Fourier Transform Infra-Red
FESEM	Field Emission Scan Electron Microscope
HPLC	High Pressure/Performance Liquid Chromatography
ICP-OES	Inductive Coupled Plasma Optical Emission Spectroscopy
MCL	Maximum Contaminant Level
MEUF	Micellar Enhanced Ultra filtration
MWCO	Molecular Wight Cut Off
NF	Nano Filtration
PAH	Polycyclic Aromatic Hydrocarbons
PBDE	Poly Brominated Diphenyl Ethers
PC	Poly Carbonate/ Pine Cone

PCB	Poly Chloro Benzene
RO	Reverse Osmosis
SB	Sugarcane Bagasse
XRD	X-Ray Diffraction

CONTENTS

Title p	bage		i
Declar	ration		ii
Ackno	owledgem	nents	iii
Abstra	act		v
List of	f Publicat	ions	vii
List of	f Figures		viii
List of	f Tables		xi
List of	f Symbols	S	xiii
Conte	nts		xvi
Chap	ter 1	Introduction and Literature Survey	1-35
1.0		Introduction	1
1.1		Types of pollutants and their sources	1
1.1.1		Inorganic pollutants, their sources and their effects	2
1.1.2		Organic pollutants and their sources	5
1.2		Treatment technologies for removal of heavy metals and	6
		organic pollutants	
1.2.1		Chemical precipitation	6
	1.2.1.1	Hydroxide Precipitation	6
	1.2.1.2	Sulphide Precipitation	7
1.2.2		Polymerization	9
1.2.3		Ion-exchange	9
1.2.4		Photocatalysis	11
1.2.5		Membrane Separation	13
	1.2.5.1	Ultrafiltration	14

	1.2.5.2	Reverse osmosis	16
	1.2.5.3	Nanofiltration	17
1.2.6		Electrodialysis	18
1.2.7		Electrocoagulation	19
1.2.8		Adsorption	19
	1.2.8.1	Agricultural waste-based adsorbent	20
	1.2.8.2	Aquatic and terrestrial biomass-based adsorbent	23
	1.2.8.3	Zeolite and Clay material	26
	1.2.8.4	Industrial solid waste	27
	1.2.8.5	Nano based materials in water treatment	27
1.2.9		Biological treatment methods	30
1.2.10		Advanced oxidation process	31
1211		Application of fixed/packed bed and fluidized ben in	31
1.2.11		continuous wastewater treatment	51
1.3		Scope of this research	33
1.4		Objective of this research work	34
1.5		Organization of the thesis	34
Chapt	ter 2	Design and Development of a Gas-Liquid-Solid Three-	
		Phase Semifluidized Bed Reactor and it's Hydrodynamic	37-66
		Studies	
2.0		Introduction	39
2.1		Fundamental and Theory of Semifluidization Technology	40
2.2		Materials and Methods	46
	2.2.1	Design and Development of a Gas-Liquid-Solid Three-	46
		Phase Semifluidized bed column	
	2.2.2	Bed materials and process parameter measurement	49
2.3		Results and Discussion	50

	2.3.1	Effect of bed characteristic parameters on Minimum	50
		Fluidization Velocity of a Semifluidized bed operation	
	2.3.2	Effect of medium and bed characteristic parameters on	52
		Minimum Semifluidization velocity (U_{sfm})	
	2.3.3	Effect of various operating parameters on the height of	53
		packed zone formation	
	2.3.4	Bed Pressure Drop	55
2.4		Development of various bed characteristics Correlations	58
	2.4.1	Minimum fluidization velocity (U_{lmf})	59
	2.4.2	Minimum Semifluidization velocity (U_{Sfm})	59
	2.4.3	Top packed zone formation H_{pa}	60
	2.4.4	Pressure drop of Semifluidized bed $\left(\frac{\Delta P_{sf}}{\Delta P_{mf}}\right)$	61
2.5		Conclusion	64
Chapte	er 3	Synthesis and Characterization of Composite Adsorbent	67-84
		from Biochar as the Solid Phase of the Semifluidized Bed	
		Reactor	
3.0		Introduction	69
3.0 3.1		Introduction Materials and method	69 71
3.0 3.1	3.1.1	Introduction Materials and method Synthesis of bed materials	69 71 71
3.0 3.1	3.1.1 3.1.2	Introduction Materials and method Synthesis of bed materials Ca-alginate –biochar composite preparation	69 71 71 71
3.0 3.1 3.2	3.1.1 3.1.2	Introduction Materials and method Synthesis of bed materials Ca-alginate –biochar composite preparation Adsorbent characterization	69 71 71 71 71 72
3.0 3.1 3.2	3.1.13.1.23.2.1	Introduction Materials and method Synthesis of bed materials Ca-alginate –biochar composite preparation Adsorbent characterization Physicochemical characterization	 69 71 71 71 72 72
3.0 3.1 3.2	3.1.13.1.23.2.13.2.2	Introduction Materials and method Synthesis of bed materials Ca-alginate –biochar composite preparation Adsorbent characterization Physicochemical characterization FTIR analysis	 69 71 71 71 72 72 72 77
3.0 3.1 3.2	 3.1.1 3.1.2 3.2.1 3.2.2 3.2.3 	Introduction Materials and method Synthesis of bed materials Ca-alginate –biochar composite preparation Adsorbent characterization Physicochemical characterization FTIR analysis XRD analysis	 69 71 71 71 72 72 72 77 79
3.0 3.1 3.2	 3.1.1 3.1.2 3.2.1 3.2.2 3.2.3 3.2.4 	Introduction Materials and method Synthesis of bed materials Ca-alginate –biochar composite preparation Adsorbent characterization Physicochemical characterization FTIR analysis XRD analysis Surface morphology Analysis by FESEM Imaging	 69 71 71 71 72 72 72 77 79 81
3.0 3.1 3.2	 3.1.1 3.1.2 3.2.1 3.2.2 3.2.3 3.2.4 3.2.5 	Introduction Materials and method Synthesis of bed materials Ca-alginate –biochar composite preparation Adsorbent characterization Physicochemical characterization FTIR analysis XRD analysis Surface morphology Analysis by FESEM Imaging Effect of pH and temperature on the stability of composite	 69 71 71 71 72 72 72 77 79 81 82
3.0 3.1 3.2	 3.1.1 3.1.2 3.2.1 3.2.2 3.2.3 3.2.4 3.2.5 	Introduction Materials and method Synthesis of bed materials Ca-alginate –biochar composite preparation Adsorbent characterization Physicochemical characterization FTIR analysis Surface morphology Analysis by FESEM Imaging Effect of pH and temperature on the stability of composite adsorbent	 69 71 71 71 72 72 72 77 79 81 82

Chapter 4	Batch Adsorption Studies for Removal of Heavy Metals,	85-124
	MB Dye and Phenol from Wastewater by the	
	Synthesized Composite Adsorbents	
4.0	Introduction	87
4.1	Materials and method	89
4.1.1	Adsorbate and other chemicals	89
4.1.2	Synthesis of composite hybrid adsorbents and its	89
	characterization	
4.1.3	Batch Adsorption Experiments	89
4.2	Theory of adsorption	91
4.2.1	Kinetics studies of adsorption	91
4.2.2	Equilibrium isotherm	93
4.2.3	Thermodynamics studies of adsorption	94
4.3	Results and discussion	95
43.1	Effect of solution pH on metal ion and organic compound	95
	adsorption	
4.3.2	Effect of time and initial adsorbate concentration on	98
	adsorption kinetics	
4.3.3	Effect of adsorbent dose on adsorption of metal ions, MB	101
	dye and Phenol	
4.3.4	Effect of system temperature on adsorption kinetics	102
4.3.5	Effect of the presence of salts/ Electrolytes on adsorption	104
4.3.6	Adsorption Kinetics and Mechanism of Adsorption	105
4.3.6.1	Pseudo first order and Pseudo-second order kinetic models	105
4.3.6.2	Intra-particle diffusion model and mechanism of adsorption	108
4.3.7	Pore diffusion model	111
4.3.8	Activation energy of heavy metal adsorption and concept of the adsorption mechanism	113

4.3.9	Adsorption isotherm studies	114
4.3.10	Adsorption thermodynamics and nature of adsorption	117
4.4	A comparative study for both the adsorbents	118
4.5	Recycling of the adsorbent	122
4.6	123	
Chapter 5	125-144	
	Heavy Metal, Phenol and Steel Plant Effluent Treatment	
5.0	Introduction	127
5.1	Materials and method	128
5.2	Results and discussion	130
5.2.1	Effect of initial metal ion and phenol concentration on	132
	SFBR performance	
5.2.2	Effect of initial bed height or adsorbent dose on SFBR	134
	performance	
5.2.3	Effect of liquid flow rate on SFBR performance	136
5.2.4	5.2.4 Performance analysis of the Semifluidized bed reactor for	
	Real Industrial effluent	
5.2.5	Effect of Airflow on the performance of SFBR	141
5.2.6	Comparison of performance of SFBR with fixed/Packed bed	142
	and fluidized bed adsorption column	
5.3	Conclusion	144
Chapter 6	Mass Transfer Dynamic Modelling and Process	145- 168
	Optimization of SFBR Performance	
6.0	Introduction	147
6.1	Theory of Response Surface Methodology (RSM)	147
	optimization technique	147
6.2	Development of an unsteady-state mass transfer adsorptive	150
	model for the closed-circuit Semifluidized bed reactor	150
6.3	Solution for the developed model	153

6.4		Results and discussion	153
	6.4.1	Individual and Combined effect of operating parameters on	154
		SFBR Performance	
	6.4.2	Statistical Model development	155
	6.4.3	Process optimization for the batch experiments	159
6.5		Model validation and kinetic parameter estimation	165
6.6		Scale-up calculation	166
6.7		Spent adsorbent management	166
6.8		Conclusion	167
Chapter	7	Conclusion and Future Scope of Work	169-178
7.0		Introduction	171
7.1		Hydrodynamic and bed characteristic of multiphase	172
		Semifluidized bed system	
7.2		Synthesis and characterization of novel composite adsorbent	173
		as the solid phase of the Semifluidized bed reactor column	
7.3		Performance analysis of synthesized adsorbent for heavy	174
		metal and Phenol removal under various operation	
		conditions	
7.4		Performance analysis of Semifluidized bed reactor with	175
		synthetic and actual industrial effluent	
7.5		Process optimization, dynamic model development system	176
		scale up and waste adsorbent management method	
7.6		Future scope of work	177
Referenc	es		179-203

Appendix 1

Chapter 1

Introduction and Literature Survey

Chapter 1

Introduction and Literature Survey

1.0 Introduction

Over the last few decades, the civilization is continuously improving and it reaches at its best in the current century, with technical know-how and scientific information and continuously striving to improve the lifestyle of mankind in every aspect. To achieve this, damages caused to the environment are most of the time overlooked. Industrialization is such a process that causes huge cost on the world's environment. Among all the basic component of the environment, like soil, air and water, the water sources are contaminated severely and it has become an alarming threat to mankind globally. Various inorganic and organic pollutants are released to the water bodies mostly by human activities via increased population, industrialization, unplanned urbanization, agricultural activities including expended use of chemicals has become an increasingly serious problem worldwide. The severe water pollution is caused mainly by the industrial discharge of toxic pollutant laden effluent directly into water bodies including heavy metals and many organic substances. Therefore, it has become a global issue for the researchers and scientists to save the water resources from the hazardous effect of such toxic pollutants by treating the pollutant laden effluent in an efficient but cost-effective way.

1.1 Types of pollutants and their sources

Pollutants are the naturally occurring substances or foreign matters that causes adverse changes to the water quality when coming in contact with water sources. Various types of pollutants cause water pollution. These are primarily classified into three types namely, inorganic, organic and biological pollutants. Irrespective of the category all of them are very dangerous and received considerable attention due to its impact on living organisms(Vhahangwele and Khathutshelo L 2014).

1.1.1 Inorganic pollutants, their sources and their effects

Industrial and agricultural wastes are primary sources of inorganic pollutants. Inorganic pollutants are entered into the water bodies by human activities via mining activities, mine drainage, smelting, metallurgical and also from various chemical processes in the form of heavy metals. Among all the inorganic pollutants heavy metals draw the attention of researchers and scientists because of its acute toxicity even if at very low concentration in water. Although there are no exact definitions of heavy metals, literatures have defined the metals having atomic mass 63-200 unit is categorised as heavy metals (Kara et al. 2017). Some report also states that element having high atomic weight and high density which is more than five times of water can be classified as heavy metals (Cellular Effects of Heavy Metals). Lead (Pb), Copper (Cu), Arsenic (As), Nickel (Ni), Cadmium (Cd), Mercury (Hg) and Zinc (Zn) are identified as the major heavy metals that are commonly found in the surface water. Some of these metals are also known as essential elements for human health and some other living organisms up to a certain concentration. Above the threshold value determined by various health organisation recognized globally, they are very carcinogenic and lethal for human and various aquatic and marine creatures (He and Chen 2014). These hazardous metals get into the surface water like river, lakes and ponds by some natural causes like weathering, volcanic eruptions etc. Various industries release a large amount of wastewater containing heavy metals. For example, the primary sources of Zn^{2+} metal ions in wastewater are metal processing, brass, iron and steel plants, paint, galvanizing and rubber industries, pulp and paper etc. (Arias and Sen 2009). Copper (Cu^{2+}) and Nickel (Ni^{2+}) are very common metals handle by many industries and release with wastewater. Such heavy

metals mainly come from industries like electroplating, galvanizing, paints, steel plant byproducts etc.(Aydin, Bulut, and Yerlikaya 2008; Mobasherpour, Salahi, and Pazouki 2011; Randhawa et al. 2015; Randhawa, Das, and Jana 2014). Lead (Pb²⁺) and Cadmium (Cd²⁺) are two deadly heavy metals recognised by many international organizations. Primary sources of Lead are industries like batteries, metal finishing, electroplating, glass manufacturing, iron and steel plants (Momčilović et al. 2011). Cadmium is released from various industries like metal plating, CD-Ni battery, phosphate fertilizers, mining, paint and pigment and alloys etc. (Balkaya and Cesur 2008). The sources of various metal ions in industrial effluents and their adverse effects are presented in Table 1.1.

Heavy metal	Sources	Effects	
Zinc (Zn ²⁺)	Steel plants, metal alloys like brass manufacture paint, galvanization and rubber industries, pulp and paper industries	Anaemia, skin irritation, vomiting, stomach problems	
Copper (Cu ²⁺)	Water pipes, copper water heaters, pesticides, Copper cooking pots, electroplating, galvanizing, paints, steel plant by-products, Fungicides, Alcoholic beverage waste from copper brewery equipment	Mental disorder, Arthritis, stress/hypertension, vomiting &unconsciousness, Hyperactivity, Schizophrenia, Sleeplessness, Autism, Irritation and expansion of liver, heart problem	
Nickel (Ni ²⁺)	The effluent of silver refineries, electroplating, Nickel base casting, ore handling industries	Dermatitis issues, Myocarditis, encephalopathy, Pulmonary, Fibrosis, lung cancer, headache, dizziness, chest pain, nausea, vomiting	
Lead (Pb ²⁺)	Mining industries, steel plant, automobiles, batteries, paints,	Nausea, Encephalopathy, headache and vomiting, learning difficulties, Mental retardation, hyperactivity, Vertigo, kidney damage, Birth defects, Muscle weakness, Anorexia, Cirrhosis of the liver, Thyroid dysfunction, Insomnia, Degeneration of motor neurons	
Cadmium (Cd ²⁺)	Metal plating, CD-Ni battery, phosphate fertilizers, mining, paint and pigment and alloys	Mental disorder, Arthritis, hypertension, nausea/vomiting, Hyperactivity, liver and kidney damages	

Table 1.1 Sources and effects of various heavy metals (Hima et al. 2007)

These heavy metals releasing from industrial effluents get into various rivers and lakes and increase the heavy metal concentration of the water bodies. Dixit and Tiwari, 2008 studied the impact of various heavy metal contamination of Shahpura Lake, Bhopal, India. In their study, they have found that the concentration of Cu, Pb and Cd were higher than the permissible limit during the rainy session and the winter session. Singh et al., 2005 studied the heavy metals in water and bed sediments of Gomti River and Ganga River, India. From their study, they have concluded that the river water and the bed sediments both are moderately polluted with Pb and Cd. But it is highly polluted with Ni heavy metal. Figure 1 shows the possible ways how surface water contaminated by various heavy metals (Garbarino et al. 1995).



Figure 1.1: Source and sink of heavy metals

The main issue with the heavy metals is that they are not biodegradable and directly entered into the food. Therefore, it accumulated in human bodies and other aquatic and other flora and fauna as shown in Figure 1.2. Some of the heavy metals like As, Pb, Cd, Hg, are dangerous with direct exposures only. The effects of the metals are both long term and short term and long exposure to a high concentration is sometimes lethal also. Various dangerous effects on the human body have been given in Table 1.2 (Babel 2003).

Heavy metal	Toxic effects	MCL (mg/L)
As ⁵⁺	Skin appearances, primitive cancers, vascular diseases	0.050
Cd^{2+}	Kidney disorder, renal damages, a human carcinogen	0.01
Cr^{6+}	Annoyance, diarrhoea, vomiting, carcinogenic	0.05
Cu^{2+}	Liver mutilation, sleeplessness	0.25
Ni ²⁺	Dermatitis, seasickness, breathing shortness, coughing,	0.20
Zn^{2+}	Depressive disorder, tiredness, a neurological disorder	0.80
Pb ²⁺	Brain cell damage, kidney failure, nervous system disorder	0.006
Hg ²⁺	Kidney failure, the effect on the central nervous system, arthritis	0.00003

Table 1.2 Toxic effect and threshold limit of various heavy metals (Babel 2003)



Figure 1.2: Summary of heavy metals enter into the human body and other living

creatures

1.1.2 Organic pollutants and their sources

Organic pollutants are defined as the biodegradable contaminants' materials present in the air, water or soil. They are found naturally but anthropogenic activities increase the limit of pollutants in the natural resources. Main organic pollutants are Phenol, Cresol, Bi-Phenol A (BPA), PCB, paints, PAHs, PBDEs and many more. All the chemicalpharmaceutical, food processing, industries release a very high volume of such contaminants. Among the organic pollutants, commercial dyes like MB, Congo reds are the leading ones while the main inorganic pollutants of concern are heavy metals (Zn, Cu, Ni, As, Pb, Cd Cr) in nature.

1.2 Treatment technologies for removal of heavy metals and organic pollutants

1.2.1 Chemical precipitation

One of the oldest and most traditional techniques of heavy metal removal from aqueous phase is Chemical precipitation (Fu and Wang 2011). This process is costeffective and easy to handle. In precipitation operation, some chemical reagents are added and it reacts with heavy metal ions to form insoluble precipitates. The precipitates later separate by filtration or sedimentation. Chemical precipitation classified in Hydroxide precipitation and Sulphide precipitation.

1.2.1.1 Hydroxide Precipitation

Hydroxide precipitation is the most convenient technique in terms of operation cost for the removal of heavy metals. Lime is the most widely used chemical reagent for hydroxide precipitation operation and an optimum pH for the solubility for various metals were reported as 8-11. Mirbagheri and Hosseini, 2005 removed Cr(VI) and Cu(II) by using Ca(OH)₂ and NaOH from wastewater. They reported that the maximum precipitation occurs at pH 8.7 and concentration for Chromate and copper ion was reduced from 30 mg/L to 0.01 mg/L and 48.51 mg/L to 0.694 mg/L respectively. In another study, fly ash was introduced with lime to enhance the precipitation for

chromium, Copper, Lead and zinc (Chen et al. 2009). The metal ions concentration was reduced from 100 mg/L to 0.08, 0.14, 0.03, and 0.45 mg/L respectively. The addition of various coagulant such as alum, organic polymers, iron salts may enhance the precipitation process (Charerntanyarak 1999). Charerntanyarak employed chemical coagulant to remove Zn, Cd, Mn, and Mg from the synthetic wastewater at a very high concentration of 450, 150, 1085 and 3154 mg/L respectively. The author had reported that the treated water has metal concentration below the threshold value. By using chemical coagulants, the concentration of the residual heavy metal can be reduced which make the separation process easy.

However, being very easy operation Hydroxide precipitation has some serious drawbacks. In this process, a huge amount of low-density sludge is generated which is very difficult to remove (Kongsricharoern and Polprasert 1995). Many metal hydroxides are amphoteric and are a complex of various metals. Therefore, it is very difficult to separate the valuable metals for further use. The optimum pH is also a problem. An optimum pH for any metal may put another metal into the solution

1.2.1.2 Sulphide Precipitation

Another effective technique is sulphide precipitation. The low-density precipitate problem of hydroxide precipitation can be taken care as the sludge formed in this method is relatively high density and not amphoteric. Therefore, a high volume of metal can be removed over a wide range of pH in this method. An investigation has been made by Özverdi and Erdem 2006 (Özverdi and Erdem 2006) to remove Cu^{2+} , Cd^{2+} and Pb^{2+} by using pyrite and synthetic sulphide. Sulphide precipitation mechanism is reported to be governed by chemical precipitation (Eqn. 1.1) at low pH (pH<3) and higher pH (4-6) it is governed by adsorption (Eqn. 1.2).

$$FeS_{(s)} + 2H^+_{(aq)} \to H_2S_{(g)} + Fe^{2+}_{(aq)}$$
 (1.1)

$$M_{(aq)}^{2+} + H_2 S_{(g)} \to M S_{(s)} \downarrow + 2H_{(aq)}^+$$
(1.2)

In recent years, sulphide precipitation has been modified by Sulphate Reducing Bacteria (SRB). SRB transform simple organic compound into hydrogen sulphide in the first stage and later stage, the hydrogen sulphide reacts with metals and form insoluble metal sulphide (Fu and Wang 2011; Kousi et al. 2007).

Despite having some advantages, sulphide precipitation encounters some dangerous problems. Many metal solutions are acidic and in acidic medium there is a high chance of formation of toxic H_2S gas. Therefore, it is always recommended to operate the process in basic or neutral medium. Metal sulphides sometimes form a colloidal solution which is very difficult to separate by sedimentation or filtration technique.

Apart from these two precipitation techniques, there are some reports on precipitation combined with another method like ion exchange. Papadopoulos et al. 2004, found 20% enhancement in the removal of Nickel by combined treatment of ion exchange followed by precipitation (Papadopoulos et al. 2004). Chelating precipitation also tried by many researchers as an effective method which can overcome some limitation (Matlock, Howerton, et al. 2002; Matlock, Henke, and Atwood 2002). Some reported data of heavy metals removal by chemical precipitation has been listed in Table 1.3.

Metal ion	Initial conc.	Precipitants	Efficiency (%)	Reference
	(mg/L)			
Zn^{2+}	32	CaO	99	(Ghosh, Samanta,
				and Ray 2011)
$\operatorname{Zn}^{2+}\operatorname{Cu}^{2+}$,	100	CaO	99.37-99.6	(Chang, Zhang,
Cr^{3+}, Pb^{2+}				and Wang 2009)
$Zn^{2+} Cu^{2+}, Pb^{2+}$	0.018, 1.34, 2.3	H_2S	100,>94, >92	(Alvarez, Crespo,
				and Mattiasson
				2007)
Cr ³⁺	53.63	Cao and MgO	>99	(Guo et al. 2006)

Table 1.3 Example of heavy metal removal by chemical precipitation

1.2.2 Polymerization

Polymerization is a very old and traditional technique for removal of the phenolic compound from the aqueous solution in the presence of an enzyme. Hydrogen peroxide (H₂O₂) is one of the most common chemicals that had been used along with peroxide enzyme derived from horseradish. The system achieved 90% efficiency for this operation (Stanisavljevic and Neldic 2004). Another investigation it was found that 90% precipitation for Phenol has been achieved in 10 minutes. The precipitation efficiency increases with peroxide concentration and reduces with phenol concentration (Vasudevan and Li 1996). Polyethene glycol is another polymerizing additive that has been used successfully for enhanced phenol removal by polymerization and precipitation at very high initial concentration range (Nicell, Saadi, and Buchanan 1995).

1.2.3 Ion-exchange

Ion exchange is also a widely adopted treatment technology for heavy metalcontaining wastewater. It has some advantages like high treatment capacity, high efficiency and faster kinetics (Kang et al. 2004). Ion exchange resins are solid material either natural or synthetically fabricated with the ability to interchange its cations with metal ions in the wastewater. Cation exchange resins are classified as strongly acidic resins having sulfonic acid groups (-SO₃H) and weakly acidic with carboxylic acid (-COOH). The hydrogen ions present in both the groups works as the interchangeable ion with the metal ions. Ion exchange process largely depends upon the various process parameters like pH, system temperature, initial metal concentration and contact time (Gode and Pehlivan 2006). Abo Farha et al.2009 investigated the effect of ionic charge for the removal of Pb²⁺, Fe³⁺ and Ce⁴⁺ from its aqueous solution by Purolite C100 synthetic cation exchange resin. The same phenomenon was also earlier reported by Kang et al. 2004 with Amberlite IRN-77 for removal of Co²⁺, Ni²⁺ and Cr³⁺ (Kang et al. 2004).

Along with synthetic resin, some natural resin, like natural zeolite, silicate materials were also investigated as the cation exchange resin for heavy metal removal by many researchers due to its low cost and availability (Motsi, Rowson, and Simmons 2009; Ostroski et al. 2009; Taffarel and Rubio 2009). Clinoptilolite had exhibited interesting performance as a natural zeolite. Clinoptilolite doped with Fe-oxide had been used for removal of Cu, Mn and Zn from drinking water and the result shows that in the treated water metal ion concentration is under the prescribed value (Doula 2009; Doula and Dimirkou 2008).

However, having a lot of positive sides, still, this process is at the laboratory scale. No pilot plant or industrial-scale application has been reported so far. Table 1.4 represents some ion exchange-based metal removal system.

Metal	Initial	Clinoptilolite	Capacity	Efficiency	Reference
ion	conc.	(g/L)	(mg/g)	(%)	
	(mg/L)				
Pb^{2+}	2072	20-40	021-1	-	(Inglezakis and
					Grigoropoulou 2003)
Pb^{2+}	1036	20	-	55	(Inglezakis et al. 2007)
Ni ²⁺	2900	50	0.5-1.77	-	(Rodríguez-Iznaga et al.
					2002)
Ni ²⁺	25	15	0.11	93.6	(Argun 2008)
Zn^{2+}	65.4-654	25	2.41	100	(Athanasiadis and
					Helmreich 2005)

Table 1.4 Examples of heavy metal removal by ion-exchange

1.2.4 Photocatalysis

In recent years, the photocatalysis process for remediation of pollutants has drawn significant attention by many researchers as an efficient technology. In this technology, a semiconductor catalyst receives energy in the form of the photon from the light source and generates free radicals, like OH. As the light energy is greater than the bandgap energy of the semiconductor catalyst it creates an electron/hole pair in the conduction and valance band respectively(Bolisetty, Peydayesh, and Mezzenga 2019; Herrmann 1999). The holes formed in the valance band traps (OH⁻) which is a highly oxidizing agent and plays a major role in removing pollutants by photodegradation. The electron traps adsorbed oxygen species which is very unstable and reactive may evolve in various ways(Zhang and Itoh 2006).

$$TiO_2 + h\nu = TiO_2 + e_{CB}^- + h_{VB}^+$$
(1.3)

$$TiO_{2(substrate)} - OH^{-} + h^{+} = TiO_{2(substrate)} - OH_{ads}^{\cdot}$$

$$(1.4)$$

 $O_{2(ads)} + e^{-} = O_2^{-(ads)} \tag{1.5}$

Most popular semiconductor materials used for photocatalysis are TiO₂, CeO₂, CdS, ZnS, etc. Among all, TiO₂ has been reported as the most efficient catalyst as it produces maximum quantum. TiO₂ has been successfully applied for photocatalytic degradation of Arsenite to Arsenate(Zhang and Itoh 2006). In this degradation Arsenite first oxidized to Arsenate and later it removed by adsorption. Another investigation has reported that TiO₂ degrade complex Cyanide (CN⁻) and Copper (Cu²⁺) completely in 3 hours (Barakat, Chen, and Huang 2004). Photocatalytic remediation of chromium had been widely studied by many researchers. Cr(VI) is very mobile and highly toxic, but reduced Cr(III) is immobile and less harmful. Therefore TiO₂ has been used in modified and unmodified form for degradation of Cr(VI). For example, a thin film of TiO₂ has been prepared and placed on the glass plate by sol-gel method and applied for the efficient remediation of Cr(VI) (Kajitvichyanukul, Ananpattarachai, and Pongpom 2005). The same catalyst was also modified with sulphate and Zirconium phosphate. The synthesis report revealed that samples prepared in acidic condition exhibit more surface area and reactivity than the one prepared at higher pH (Das, Parida, and De 2006). Polyoxometalates (PO) and Salicylic acid treatment also improve the performance of TiO₂ photocatalyst for reduction of Cr(VI) over a wide range of 5 to 100 mg/L up to 100% (Gkika et al. 2006). Synergistic effect for remediation of Cr(VI) was found by the same catalyst in the presence of some organic or inorganic modifying compound (Papadam et al. 2007). A large surface area was obtained by the modification. The investigation also concluded that photocatalysis by TiO₂ depends on both the specific surface area and the crystal structure of the catalyst when there is no modifying compound used but dominated by the specific surface area in presence of the organic compound. This study also revealed that the synergistic effect was achieved due to the reduction of Cr(VI) to Cr(III) and oxidation of organic compound. Another novel way to

modify the catalyst was done by doping Neodymium on TiO_2 by sol-gel method and used for Cr(VI) removal in the presence of UV light. The doped surface of TiO_2 behave as electron accumulating site and enhance the overall efficiency of the system. Metalorganic frameworks are some advanced example of the photocatalytic system. Specifically, iron-based MOFs are worked as stable and much efficient photocatalysts for the treatment of Cr(VI) loaded wastewater under visible light irradiation (Li et al. 2015; Liang et al. 2015; Shi et al. 2015; Wu et al. 2017).



Figure 1.3: Mechanism of Photocatalysis

With successful removal of heavy metals, photocatalysis or photodecomposition also used for the removal of organic pollutant like phenol. Heterogeneous degradation of phenol by UV irradiated aqueous TiO_2 is capable of removing up to 70% (Ilisz, László, and Dombi 1999). Addition of hydrogen peroxide with the same catalyst can improve the phenol removal efficiency

1.2.5 Membrane separation

Membrane separation is the most promising and trending technology in recent years with various types of membranes for their excellent efficiency, easy operation and
space-saving. This technology was used to separate heavy metals, dissolved solids and some organic pollutants by ultrafiltration, reverse osmosis, Nanofiltration and Electrodialysis.

1.2.5.1 Ultrafiltration

Membranes are classified based on the pore size. Ultrafiltration (UF) membranes have a pore size in the range of 10 to 100 nm works at low trans-membrane pressure and used for removal of viruses, bacteria, pigments, organic colloids, metal ions. As the size of the hydrated metal ions or as low molecular weight complexes this will easily pass through the UF membranes. A Schematic of the process has been presented in Figure 1.4. To enhance the performance of the UF membrane, the micellar enhanced UF and Polymer enhanced UF are suggested. MEUF had been proved to be a-very effective separation technique. In this technique, a surfactant is added with the wastewater. When the surfactant concentration exceeds the critical micelle concentration (CMC), the surfactant aggregates and binds the metal ions to form a large metal surfactant structure. The surfactant metal complex easily retain by the UF membrane as its particles size is much higher than the pore size of the membrane(Landaburu-Aguirre et al. 2009, 2010). To achieve high efficiency, the surfactant should have the opposite electric charge to the target pollutant that needs to be removed. Sodium dodecyl sulphate (SDS) is one of the most widely used anionic surfactants in MEUF. The efficiency of this kind of membrane depends on the concentration of metal and surfactant, ionic strength, and membrane parameters. MEUF has been found to achieve 99% efficiency or a rejection coefficient for the removal of Cd^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} from a synthetic solution by using a surfactant to metal mole ratio above 5 (Samper et al. 2009).

The retentate obtained is a mixture of metal and surfactant which is a secondary pollutant. Therefore, it is necessary to develop some technique to recover both as the cost of an operation mainly depend on the cost of surfactant. To overcome the problem chelation and acidification followed by UF for recovering Cd^{2+} and Zn^{2+} was investigated (Li et al. 2009). The result showed that 90.1% Cd^{2+} and 87.1% Zn^{2+} was recovered. At the same time SDS recovered was 65.5% for Cd^{2+} and 68.5% Zn^{2+} respectively.



Figure 1.4: Concept of Membrane separation

PEUF is also an effective process to recover a variety of metal ions from aqueous solution. PEUF uses water-soluble polymer to form a complex with metal ions to form macromolecules of higher molecular weight than the molecular cut off to the membrane. Various complexing agents have been used by many researchers like polyacrylic acid (PAA) (Labanda, Khaidar, and Llorens 2009), polyethyleneimine (PEI) (Aroua, Zuki, and Sulaiman 2007; Molinari, Poerio, and Argurio 2008), dimethylamino methylcellulose (Trivunac and Stevanovic 2006), Humic acid (Kim et al. 2005) etc. for successful removal of various heavy metals. The main advantage of this method is high removal efficiency, high binding selectivity and reuse of metal and a modifying agent. However, there are a lot of studies on lab-scale operation on this separation but the large-scale

application is still not investigated. Some reported examples of such treatment techniques are given in Table 1.5.

Membrane type	Heavy metal	Efficiency (%)	References
	71.21	T	
MEUF (ceramic)	Pb^{2+}, AsO^{-}_{4}	Pb>99, As 19	(Ferella et al. 2007)
MEUF (Polysulphone)	Cd^{2+} , Zn^{2+}	92-98	(Huang et al. 2010)
MEUF(Amicon	Cd^{2+} , Zn^{2+}	99	(Landaburu-Aguirre et al.
Regenerated Cellulose)			2010)
PEUF(Polyethersulfone)	Cu^{2+} , Ni^{2+}	94,100	(Molinari et al. 2008)
PEUF(Polyethersulfone)	Cu ²⁺ , Cr ³⁺ , Ni ²⁺	98,99,99	(Barakat and Schmidt 2010)
PEUF(Ceramic)	Cu^{2+}	99.5	(Camarillo et al. 2010)
PEUF(Polysulfone)	Cd^{2+}	99	(Jellouli Ennigrou et al.
			2009)

Table 1.5 Example of heavy metal removal by membrane separation (MEUF & PEUF)

1.2.5.2 Reverse osmosis

Reverse osmosis is the most emerging desalination technology of the current century (Anis, Hashaikeh, and Hilal 2019; Jiang, Li, and Ladewig 2017; Lee, Arnot, and Mattia 2011) and is growing fast for the future. In this process a semipermeable membrane is used, where the fluid is passed through and the contaminants are rejected through a hydrostatic force higher than that of the osmotic pressure (Wenten et al. 2017). A wide series of metal ions were removed by this process like Cu²⁺, Ni²⁺ (Mohsen-Nia, Montazeri, and Modarress 2007), As(V)(Chan and Dudeney 2008), Zn²⁺ (Ipek 2005), up to 99%. Over the last few decades, a lot of works are going to improve the technology like low-cost membrane material fabrication, fouling minimization, concentration polarization issues and power consumptions (Bolisetty et al. 2019). Despite being such an emerging and popular technology, the RO has also some serious disadvantages like high losses of processed water, high energy consumption and large initial investments.

1.2.5.3 Nanofiltration

Nano filter membrane or Nanofiltration (NF) is classified in between UF and RO based on the pore size and molecular weight cut off ratio. The pore size of this kind of membrane is 2-5 nm and MWCO 200-1000 Da. The membrane of this type is suitable for water softening and a wide range of heavy metals can be removed by Steric and Donnan exclusion mechanism (Peydayesh et al. 2017). According to the theory, the surface of the membrane surface should be positive to achieve maximum flux and rejection and some works are going on such modification. Some reported studies showed very promising removal of various heavy metals like Nickel (Murthy and Chaudhari 2008), copper (Cséfalvay, Pauer, and Mizsey 2009), Chromium (Muthukrishnan and Guha 2008), Arsenic (Figoli et al. 2010; Nguyen et al. 2009) etc. NF process has many advantages like easy operation, reliability, low energy consumption and high efficiency for pollutant removal. Few reported examples of such systems have been tabulated in Table 1.6.

Membrane type	Heavy Metal	Efficiency (%)	References
RO	Cu ²⁺ , Ni ²⁺	99.5	(Mohsen-Nia et al. 2007)
RO	Cu^{2+}	70-95	(Zhang et al. 2009)
RO	As^{5+}/As^{3+}	99/55	(Chan and Dudeney 2008)
NF	Cu ²	47-66	(Chaabane et al. 2006)
NF	Cr^{6+}	99.5	(Muthukrishnan and Guha
			2008)
NF	Cu^{2+}	96-98	(Tanninen, Mänttäri, and
			Nyström 2006)
RO+NF	Cu^{2+}	>95	(Cséfalvay et al. 2009)
RO+NF	Cu^{2+}	95-99	(Sudilovskiy, Kagramanov, and
			Kolesnikov 2008)

Table 1.6 Example of heavy metal removal by membrane separation (RO & NF)

1.2.6 Electrodialysis

Electrodialysis (ED) is a membrane-based separation process where ionized solutions pass through an ion exchange membrane by electrical potential as a driving force. The ion-exchange membranes are made of thin polymeric shits charged with positively or negatively. When an ionized solution passes through the ionized membrane the anions present in the ionized solution attract by the anode and cation attracts by the cathode by crossing the positively and negatively charged membrane (Chen 2004). A schematic view of the ED process has been presented in Figure 1.5.



Figure 1.5: Mechanism of Electrodialysis process

Tzanetakis et al. 2003 evaluated the performance of an ED process by ion exchange membrane for the removal of Ni^{2+} and Co^{2+} ions from a synthetic solution. In this investigation, they have applied two different types of Cation exchange membrane namely, Perfluorosulfonic Naflon 117 and SPVDP under identical operating conditions. The former membrane shows a percentage removal of 90% and 69% for Ni^{2+} and Co^{2+} at the initial concentration of 0.84 and 11.72 mg/L respectively (Tzanetakis et al. 2003).

Effect of various operating parameters like feed flow rate, applied voltage and system temperature was investigated by Mohemmadi et al. 2004 for the removal of Pb²⁺ by the commercial membrane in laboratory ED cell. The authors have reported that the performance of the system responded positively with the temperature and voltage but adversely affected by the feed flow rate (Mohammadi, Razmi, and Sadrzadeh 2004). A model of the ED cell process was also developed based on basic electrochemistry rules and experimental data for Cu²⁺ ion separation. Few experiments were conducted for Zn²⁺, Pb²⁺ and Cr⁶⁺. The results showed that the system was independent of types of ions and depends on the nature of the cell and other operating conditions like voltage and system temperature (Mohammadi et al. 2005). Removal of Cd²⁺ by the same process was also investigated from sludge. Three different types of suspensions were prepared. Maximum 70% removal was obtained for sludge suspended in Citric acid solution(Jakobsen 2004).

1.2.7 Electrocoagulation

Petroleum refinery wastewater with high phenol concentration was treated by electrocoagulation process (Abdelwahab, Amin, and El-Ashtoukhy 2009). Effect of various operating parameters like system pH, current density, initial phenol concentration etc. was investigated for the performance analysis of the system. It was concluded from this study that, at high current density 97% removal was achieved in 120 minutes. Addition of some electrolyte like NaCl also enhanced the performance of the electrocoagulation process at neutral pH and low phenol concentration(Zazouli and Taghavi 2012).

1.2.8 Adsorption

The traditional methods for the removal of various organic and inorganic (heavy metals) pollutants like membrane separation, photocatalysis, chemical precipitation etc.

are not much economical and easy to handle for many developing countries. Therefore, a lot of research is going on to find out low-cost adsorbent and their ability for the removal of such noxious pollutants from wastewater. Coal-based activated carbon adsorbents are the most well known for their high specific surface area, porous nature and contains various functional groups like carboxyl, carbonyl, phenol, amine and others to bind the metal to form a surface complex (Deliyanni et al. 2015; Fu and Wang 2011). But, due to high cost and less regeneration capacity, the research focus has been shifted to the low-cost waste-based adsorbent. Based on the precursor material the adsorbents are classified as, agricultural waste-based adsorbent, Aquatic and terrestrial biomass-based adsorbent, local waste-based biomass, Zeolites, clay materials, industrial solid waste, fullerene and carbon nanotubes(Burakov et al. 2018).

1.2.8.1 Agricultural waste-based adsorbent

By-product or residuals of rice-based waste are one of the most prevalent forms of agricultural waste which are available in large volume in most of the world. The waste includes rice husk, rice bran, and rice straw. Rice bran and rice straw have been used for removal of Cu^{2+} from aqueous solution with a maximum adsorption capacity of 21 and 18.4 mg/g respectively(Singha and Das 2013). In some other studies have confirmed that rice husk can be applied for efficient removal of different heavy metals with adsorption capacity ranges from 5.5 to 58.1 mg/g. Complete removal of Cr^{+6} was achieved by rice husk waste adsorbent at low pH (<3) and adsorption capacity of 8.5 mg/g.

Peanut shell residue was also reported as an effective source of the adsorbent for removal of various heavy metals Pb^{2+} , Cr^{6+} (Ahmad et al. 2017; Taşar, Kaya, and Özer 2014). Some other heavy metals like Cr^{3+} , Cu^{2+} , and Pb^{2+} also successfully removed by

the same adsorbent with an adsorption capacity of 7.7, 10.2, 29.1 mg/g respectively (Li et al. 2007).

Several investigations have been reported the ability of cashew nut shell to remove heavy metal from water. A significant amount of 20 mg/g Cu^{2+} removed by this adsorbent (SenthilKumar et al. 2011). In another study, Ni²⁺ was removed up to 75% and maximum capacity was found for the adsorbent was 18.9 mg/g (Kumar et al. 2011).

Some other reported example of such agricultural waste-based adsorbents are Hazelnut shell and ground nut shell. Hazelnut shell used for removal of Cu^{2+} metal ion removal and maximum adsorption capacity was reported 58.3 mg/g (Demirbas et al. 2009). Groundnut shell was successfully applied for removal of Cu^{2+} , Ni²⁺, Zn²⁺ with an adsorption capacity of 4.9,8.05 and 11 mg/g respectively(Shukla and Pai 2005).

Use of various fruit waste also found in many reported studies like lemon peel orange peel, banana peel (Thirumavalavan et al. 2010), Apricot stone(Kobya et al. 2005). These low-cost adsorbents were efficiently used for removal of a wide range of heavy metal-laden wastewater.

Apart from heavy metals, many agricultural solid waste based adsorbents were also well investigated for adsorptive removal of phenol from the aqueous phase(Singh et al. 2008). Some example of such wastes are tobacco residue (Hameed and Rahman 2008), corncob (Tseng and Tseng 2005), sugar beet waste (Önal et al. 2007), apricot stone(Petrova et al. 2010). Some examples of various agricultural waste-based adsorbent used for the removal of various heavy metals and organic pollutants are given in Table 1.7. A recent article by Afroze et al. (Afroze and Sen 2018) discussed in details about the use of various adsorbents for the removal of heavy metals as well as organic pollutants.

Adsorbent	Adsorbate	Adsorption capacity	References
Devenue a sel	7 2+	(mg/g)	(This and the second se
Banana peel	Zn ²⁺	21.9	(1 mirumavalavan et al. 2010)
Casnew nut shell		5.8	(Annadurai, Juang, and Lee 2003)
Dairy manure		15.8	(Zhang 2011)
Orange peel		5.3	(Annadurai et al. 2003)
Orange peel		24.1	(Thirumavalavan et al. 2010)
Rice husk		8.1	(Krishnani et al. 2008)
Eucalyptus bark	2	250	(Afroze, Sen, and Ha Ming Ang 2016)
Apple residue	Cu ²⁺	10.8	(Thirumavalavan et al. 2010)
Cashew nut shell		20	(SenthilKumar et al. 2011)
Coconut shell		19.9	(Singha and Das 2013)
Dairy manure		27.2	(Zhang 2011)
Grape stalks		10.1	(Villaescusa et al. 2004)
Ground nutshells		4.5	(Shukla and Pai 2005)
Hazel nutshell		58.3	(Demirbas et al. 2009)
Lemon peel		70.9	(Thirumavalavan et al. 2010)
Orange peel		3.7	(Annadurai et al. 2003)
Orange peel		63.3	(Thirumavalavan et al. 2010)
Peanut shell		25.4	(Witek-Krowiak, Szafran, and Modelski 2011)
Peanut hull		21.3	(Zhu, Wang, and Chen 2009)
Peanut husk		10.2	(Li et al. 2007)
Rice bran		21	(Singha and Das 2013)
Rice husk		17.9	(Singha and Das 2013)
Rice husk		10.9	(Krishnani et al. 2008)
Rice straw		18.4	(Singha and Das 2013)
Sugar beet pulp		28.5	(Aksu and İşoğlu 2005)
Banana peel	Ni ²⁺	54.4	(Thirumavalavan et al. 2010)
Banana peel		6.9	(Annadurai et al. 2003)
Cashew nut shell		18.9	(Kumar et al. 2011)
Grape fruit peel		46.1	(Torab-Mostaedi et al. 2013)
Grape stalks		10.6	(Villaescusa et al. 2004)
Lemon peel		80	(Thirumavalavan et al. 2010)
Orange peel		6	(Annadurai et al. 2003)
Orange peel		162	(Feng et al. 2011)
Rice husk		5.5	(Krishnani et al. 2008)
Banana peel	Pb^{2+}	25.9	(Thirumavalavan et al. 2010)
Banana peel	-	7.9	(Annadurai et al. 2003)
Coconut shell		13.4	(Paranavithana et al. 2016)
Corncob		16.2	(Tan et al. 2010)

Table 1.7 Example of heavy metal removal by the agricultural waste-based adsorbent

Dairy manure		95.3	(Zhang 2011)
Lemon peel		37.9	(Thirumavalavan et al. 2010)
Orange peel		7.8	(Annadurai et al. 2003)
Orange peel		476	(Feng et al. 2011)
Orange peel		27.1	(Thirumavalavan et al. 2010)
Banana peel	Cd^{2+}	34.1	(Thirumavalavan et al. 2010)
Coconut shell		3.5	(Paranavithana et al. 2016)
Corncob		5.1	(Leyvaramos, Bernaljacome, and
			Acostarodriguez 2005)
Grape fruit peel		42.1	(Torab-Mostaedi et al. 2013)
Lemon peel		54.6	(Thirumavalavan et al. 2010)
Orange peel		48.1	(Thirumavalavan et al. 2010)
Orange peel		293	(Feng et al. 2011)
Orange peel		1.8	(Annadurai et al. 2003)
Citrus sinensis	MB Dye	96.4	(Ho, Chiang, and Hsueh 2005)
Peanut hull		68.05	(Gong et al. 2005)
Banana peel		20.8	(Annadurai, Juang, and Lee 2002)
Pineapple stem		119.05	(Hameed, Krishni, and Sata 2009)
Coffee waste		90.1	(Oliveira et al. 2008)
Walnut dust		59.17	(Ferrero 2007)
Rice husk		40.59	(Vadivelan and Kumar 2005)
Egg shell		16.43	(Tsai et al. 2006)
Orange Peel		18.6	(Annadurai et al. 2002)
Modified Pine cone1		142.86	(Yagub, Sen, and Ang 2014)
Sugar cane bagasse		113.01	(Biswas, Mohapatra, et al. 2020)

1.2.8.2 Aquatic and terrestrial biomass-based adsorbent

Various form of tree, marine plants and terrestrial biomass are very cheap and easily available in huge quantity. As an example, Moringa Olifera (MO) has exhibited very promising results for the removal of various heavy metals from its aqueous solution. Many researchers reported that MO exhibits high percentage removal for Cu^{2+} , Cd^{2+} , Cr^{3+} , Zn^{2+} and Pb^{2+} (Kansal and Kumari 2014; Shan et al. 2017). Apart from MO, tree fern is another plant-based adsorbent that has found a wide range of application. An isotherm study reported that tree ferns removed, Zn^{2+} Cu^{2+} and Pb^{2+} and the adsorption capacity were 7.6, 10.6 and 39.8 respectively(Y. S. Ho, Huang, and Huang 2002). Some other tree-based waste obtained from *Lagerstroemia speciosa*, an Indian native has been investigated for Cr^{6+} removal and maximum adsorption capacity for this material was found 20.4 mg/g (Srivastava, Agrawal, and Mondal 2015). For the removal of Pb²⁺ waste leaves of *Cinnamomum camphora* was investigated and very high adsorption capacity was achieved 77.8 mg/g (Chen et al. 2010).

Another frequently investigated tree-based adsorbent is sawdust. Various studies reported very effective removal of heavy metals by sawdust of different trees. For example, maple sawdust removes >80% Cr^{6+} (Chen et al. 2010). Another study reported simultaneous removal of Cu^{2+} , Ni²⁺, Cd²⁺ and Zn²⁺ by using beech sawdust(Božić et al. 2009). Some other examples of various sawdust that have been reported are, poplar tree sawdust, teakwood sawdust, Indian jujube tree(Ahmad et al. 2017).

Use of algae in living and non-living form is also a very effective and innovative alternative in heavy metal ion uptake(Lamai et al. 2005). Over the last few decades, environmentalists are working on algae to find out the potentiality and valuable role in the remediation of heavy metal ions from process effluent (Oswald 2003). Non-living algae, on the other hand, was found to be more effective for heavy metal removal because of its polymeric structure like cellulose glycoproteins etc. (Volesky 2007). Non-living algae in the form of algenic acids or salt of such acids are effective to metal ion adsorption because of the presence of different functional group like OH⁻, COO⁻ etc. These functional groups are responsible for the metal uptake capacities by binding positive metal ions with the group to form surface complex or by enhancing the electrostatic charge separation (Kaplan 2013). More reported example of such adsorbents is represented in Table 1.8.

Adsorbent Adsorbate Adsorption		Adsorption	References	
		capacity (mg/g)		
Brown algae	Zn^{2+}	41.2	(Romera et al. 2008)	
A. Polytricha		6.1	(Li et al. 2018)	
Beech sawdust		2	(Božić et al. 2013)	
Red algae		42.5	(Romera et al. 2008)	
Green algae		21.6	(Romera et al. 2008)	
F. Velutipes		6.3	(Li et al. 2018)	
Lignin		11.3	(Guo, Zhang, and Shan 2008)	
P .Eryngii		2.9	(Li et al. 2018)	
P.Ostreatus		5.1	(Li et al. 2018)	
Teakwood sawdust		11.1	(Shukla and Pai 2005)	
Tree fern		7.58	(Abdolali et al. 2016)	
A. polytricha	Cu^{2+}	6.6	(Li et al. 2018)	
Beech sawdust		4.5	(Božić et al. 2013).	
F. velutipes		7.2	(Li et al. 2018)	
Hyacinth root		21.8	(Singha and Das 2013)	
Meranti sawdust		32.9	(Rafatullah et al. 2009)	
Neem leaves		17.5	(Singha and Das 2013)	
P Eryngii		3.4	(Li et al. 2018)	
P Ostreatus		4.5	(Li et al. 2018)	
Teakwood sawdust		4.9	(Shukla and Pai 2005)	
Brown algae	Ni ²⁺	35.2	(Romera et al. 2008)	
Beech sawdust		4	(Božić et al. 2013)	
Red algae		34.2	(Romera et al. 2008)	
Green algae		12.9	(Romera et al. 2008)	
Lignin		6	(Guo et al. 2008)	
Meranti sawdust		36	(Rafatullah et al. 2009)	
Takewood sawdust		8.1	(Shukla and Pai 2005)	
A. Bisporus	Pb^{2+}	33.8	(Vimala and Das 2009)	
C. Indica		23.4	(Vimala and Das 2009)	
Lignin		89.5	(Guo et al. 2008)	
Meranti sawdust		34.2	(Rafatullah et al. 2009)	
P. Platypus		35	(Vimala and Das 2009)	
Poplar sawdust		7.2	(Li et al. 2007)	
S.Lychnophera		27.1	(LIU et al. 2006)	
Hance		39.8	(Abdolali et al. 2016)	
Tree fern			· · · · · · · · · · · · · · · · · · ·	
A. Bisporus	Cd^{2+}	29.7	(Vimala and Das 2009)	
Brown algae		69.7	(Romera et al. 2008)	

Table 1.8 Example of heavy metal removal by the aquatic and terrestrial biomass-based adsorbent

Red algae	65.2	(Romera et al. 2008)
C. Indica	24.1	(Vimala and Das 2009)
Green algae	21.4	(Romera et al. 2008)
H. Splendens	32.4	(Sari et al. 2008)
Juniper bark	8.6	(Shin, Karthikeyan, and
		Tshabalala 2007)
Juniper wood	3.2	(Shin et al. 2007)

1.2.8.3 Zeolite and clay material

Zeolites are naturally occurred or industrially produced crystalline alumina silicates material. Zeolite has been regarded as one of the best adsorbents as the material is made from the interlink of alumina (AlO₄) and silica (SiO₄) (Choi, Yu, and Kim 2016). High surface area, hydrophilicity and ion-exchange capability make the zeolite suitable for the adsorbent. Among all Clinoptilolite is treated as the most plentiful natural zeolite which successfully applied for the removal of a wide range of heavy metals(Argun 2008; Shaheen, Derbalah, and Moghanm 2012). It had also been reported that modified zeolites had more efficiency than the natural one. Many researchers also demonstrated a various method for modification of natural zeolite to increase its pore size and available surface area. For example, nano-sized NaX zeolite had been widely used for the treatment of Cd^{2+} laden wastewater (Ansari et al. 2014). Another investigation demonstrated Mg-modified zeolite as very advantageous due to its high surface area, low cost and availability for the removal of Ca^{2+} more than 98%.

Clay is another easily available minerals from the natural sources. They are classified as kaolinite, smectites and mica. Among all, bentonites exhibit the best cation exchange capacity, can be regenerate easily and much cheaper than commercial activated carbon (Renu, Agarwal, and Singh 2017; Tripathi and Rawat Ranjan 2015). Bentonite clay has been reported to be used for Cu^{2+} removal after calcination and adsorption

capacity achieved was 11.89 mg/g. Another investigation demonstrates that the same adsorbent used in the fixed bed column for the same metal and the maximum adsorption capacity was 19.063 mg/g (Almeida de Neto, Vieira, and da Silva 2014).

Kaolinite clay was investigated for simultaneous removal of Pb^{2+} , Cd^{2+} , Ni^{2+} , Cu^{2+} from wastewater and the process was found very fast (Jiang et al. 2010).

1.2.8.4 Industrial solid waste

Various industrial solid waste also exhibits very promising adsorption capacity and used for removal of various heavy metal. The materials are a by-product and there is no economic value, so the materials are very cheap. There are a lot of examples are available for the industrial by-products or industrial solid waste that has been used by many researchers. Most commonly used industrial waste are, fly ash (Al-Zboon, Al-Harahsheh, and Hani 2011; Bayat 2002; H. J. Wang et al. 2007; S. Wang, Li, and Zhu 2007), blast furnace sludge (Dimitrova 1996), waste slurry lignin (Demirbas 2004), red mud (Altundoğan et al. 2002; Sigdel et al. 2015).

1.2.8.5 Nano based materials in water treatment

Nano based materials or smart composites are newly introduced in this field. These materials are classified into three broad categories namely, Fullerene, carbon Nanotubes and Graphene Oxides. Fullerene was first introduced in 1985 which was discovered by the spectrometric measurement on interstellar dust(Kroto et al. 1985). They are closed caged carbon materials with pentagonal or hexagonal structure. It had been reported that the adsorption on fullerene is a surface property and the sorbet penetrates through the lattice of the adsorbent (Valcárcel et al. 2008). Fullerene has a very low tendency to get agglomerate and it has a very high surface area which makes it a good adsorbent for the purification of heavy metal-laden wastewater(Scida et al. 2011). For example, this material has been applied for the removal of Cu^{2+} with an adsorption capacity of 14.6 mg/g. In another study, it was reported that fullerene has been doped in AC's and adsorption capacity increased by 1.5 -2.5 times for Pb²⁺ and Cu²⁺ (Samonin, Nikonova, and Podvyaznikov 2014).

In the year 1991 Carbon Nanotubes were first discovered(Iijima 1991). Carbon Nanotubes are single or multi-layered cylinders in the form of rolled graphite plates where carbon forms a hexagonal network of few Nanometers. CNTs are now a new field of research because of some of its interesting characteristics like unique structure, electronic, optoelectronic, semiconductor, mechanical, chemical and properties. Moreover, high surface area and available mesopores make it a favourite material for the researchers in the wastewater treatment process (Coleman et al. 2006; Wang 2012). Modified CNT's with some other organic molecule by covalently or non-covalently have greater adsorption capacity(Gupta et al. 2016). Application of CNTs for removal of various heavy metals like Pb²⁺, Cd²⁺, Cr⁶⁺ had been studied by some researchers with various modified or unmodified CNTs (Robati 2013).

Another smart material that had been studied over the last few years is Graphene Oxides (GO). This material was first reported in 2004 as a two-dimensional hexagonal lattice made of carbon atoms. This material also has some unique properties like carbon Nanotubes (Novoselov et al. 2012). GO has been used for adsorption of Pb^{2+} and maximum adsorption capacity was found to be 406.6 mg/g within 40 minutes (Deng et al. 2007). Another study elucidated that, hydrogel lignosulfonate modified GO has an adsorption capacity of 1308 mg/g for Pb^{2+} (Li et al. 2016). Adsorption of other heavy metals like Cu^{2+} , Pb^{2+} , Cd^{2+} on magnetic GO was also studied and concluded as an efficient adsorbent(Hur et al. 2015). Some more example of this method for heavy metal removal has been given in Table 1.9.

Adsorbent	Adsorbate	Adsorption	References
		capacity (mg/g)	
Multi-walled CNTs	Zn^{2+}	32.68	(Lu and Chiu 2006)
Single-walled CNTs		43.66	(Lu and Chiu 2006)
As produced CNTs	Cu^{2+}	8.25	(Wu 2007)
NaOCL modified CNTs		47.39	(Wu 2007)
Multi-walled CNTs	Ni ²⁺	3.72	(Yang et al. 2009)
Multi-walled CNTs		7.53	(Lu and Liu 2006)
Single-walled CNTs		9.22	(Lu and Liu 2006)
NaOCL modified M/W		38.46	(Lu, Liu, and Su 2009)
CNTs			
NaOCL modified M/W		47.86	(Lu et al. 2009)
CNTs			
Acidified M/W CNTs	Pb^{2+}	49.71	(WANG et al. 2007)
CNTs			
Acidified (HNO ₃) CNTs		17.44	(Stafiej and Pyrzynska 2008)
Acidified (HNO ₃) M/W		49.95	(YH. Li et al. 2002)
CNTs		97.08	(Li et al. 2003)
CNTs	Cd^{2+}	144.48	(Anitha, Namsani, and Singh 2015)
CNTs-OH		171.36	(Anitha et al. 2015)
CNTs-CONH ₂		174.72	(Anitha et al. 2015)

Table 1.9 Removal of various heavy metals by Nano based adsorbent

Some more examples of various adsorbent that particularly used for adsorption of Phenol has been given here in Table 1.10 with their adsorption capacity over the range of the particular operating condition.

 Table 1.10 Adsorption capacity of various adsorbent for phenol

Adsorption	References
capacity (mg/g)	
216.46	(Okolo, Park, and Keane 2000)
36.9	(Streat, Patrick, and Perez 1995)
32.08	(Streat et al. 1995)
9.99	(Streat et al. 1995)
23.33	(Khan, Al-Bahri, and Al-Haddad 1997)
75.28	(Okolo et al. 2000)
84.69	(Okolo et al. 2000)
	Adsorption capacity (mg/g) 216.46 36.9 32.08 9.99 23.33 75.28 84.69

Modified bentonite	3.64	(A. Li et al. 2002)
Thermal bentonite	1.30	(Al-Asheh, Banat, and Abu-Aitah 2003)
Bentonite	0.2013	(Viraraghavan and De Maria Alfaro 1998)
Peat	0.0362	(Viraraghavan and De Maria Alfaro 1998)
Amnerlite-XAD-4-resin	0.259	(A. Li et al. 2002)
Amnerlite-XAD-16-	0.0748	(Abburi 2003)
resin		

The above methods which discuss in details have been used so far in many real field applications. However, more and more researches are still going on as all the process have some specific drawbacks and advantages over another. Therefore, some specific disadvantages and advantages of each system as found in some reported literature has been tabulated here in Table 1.11.

Table 1.11 Drawbacks of various tre	eatment technologies(Barakat 2011)
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Treatment method	Advantages	Disadvantages	References
Chemical precipitation	Low-cost simple operation	huge sludge generation	(Kurniawan et al. 2006)
Membrane filtration	small space requirement, Low pressure, high separation	High operational cost due to membrane fouling	(Kurniawan et al. 2006)
Electrodialysis	High separation selectivity	High-cost operation	(Mohammadi et al. 2005)
Photocatalysis	Removal of metal and organic Pollutants simultaneously, Less harmful by-products	long duration time, Limited application	(Barakat et al. 2004)
Adsorption	Low cost, easy operation, a wide range of operating parameters	waste production	(Babel 2003)

1.2.9 Biological treatment methods

Biological treatment technologies are mostly applicable to the remediation of organic pollutants. For the removal of aqueous phase phenol various biological technologies have been used by many researchers over the years. Activated sludge is one of the oldest treatment methods for the phenol removal which had been reported by many researchers (Aksu and Gönen 2004a; Marrot et al. 2006). Some other investigation including biological treatment followed by enzymatic treatment was performed by Bevilaqua et al. 2002. Up to 75% removal was achieved in this investigation(Bevilaqua et al. 2002). Various microbial treatments were also very well studied by several researchers to biodegrade phenol below the threshold limit (Annadurai, Ling, and Lee 2007; Bandhyopadhyay et al. 2001; Kafilzadeh and Mokhtari 2013; Kim et al. 2002; Senthilvelan et al. 2014).

1.2.10 Advanced oxidation process

The advanced oxidation process is one of the latest water treatment technology which is coupled with some other traditional technologies to enhance the removal rate of any organic or biodegradable pollutants. The investigation made by Rubalcaba et al. 2007, advanced oxidation have been used coupled with biological treatment and better results were obtained (Rubalcaba et al. 2007). A different investigation was conducted by introducing oxidizing agents like chlorides and sulphates for three different forms of phenolic compound to enhance its biodegradability(Siedlecka and Stepnowski 2005).

1.2.11 Application of fixed/packed bed and fluidized ben in continuous wastewater treatment

Fixed bed and fluidized beds are two conventional equipment for gas-liquid-solid or gas-solid or liquid-solid contact systems are used in separation technique. Both of them have some advantages and disadvantages. The packed bed has low axial dispersion coefficient, therefore high conversion rate, also there is no back mixing but high-pressure drop. On the other hand, in the fluidized bed, there is no channelling, flooding, and pressure drop is less, but due to high dispersion and back mixing conversion rate is low. However, both the reacting system have been widely used in various operation of chemical and biochemical engineering. Some application of Fluidized-bed reactor in wastewater treatment has been reported by many researchers. Adsorption modelling in liquid-solid-fluidized bed was investigated and reported that this kind of bed has shorter breakthrough time for pollutant removal (Veeraraghavan, Fan, and Mathews 1989). In another study, activated carbon was prepared from apricot stone and used in a fluidized bed adsorption column for the removal of divalent heavy metals like Pb, Cu, Cd and Zn. A dynamic model was also proposed and the model predicted results were satisfactory with the experimental results(Tsibranska and Hristova 2010). Correa et al.2007 developed a fluidized bed system for adsorptive removal of aqueous phase phenol with commercial macroporous resin(Corrêa, Calçada, and Peçanha 2007). Apart from water, air pollution was also investigated by removing various gaseous pollutants in fluidized bed adsorption column. A model was proposed by Saeed et al. 2017 for removal of CO₂ in a lab-scale reactor (Yaghoobi-Khankhajeh, Alizadeh, and Zarghami 2018). Application of fluidised bed bioreactors in various environmental engineering solution including wastewater treatment has been reviewed by Özkaya et al., 2019. Fluidized bed bioreactor has some other applications in the field of wastewater treatment that has been reported by many researchers (Charinpanitkul et al. 2010; Gómez et al. 2007; González et al. 2001; Hirata et al. 2000; Rabah and Dahab 2004; Sokol 2003; Tsuneda et al. 2002; Venu Vinod and Venkat Reddy 2006; Vinod and Reddy 2003).

The application of a packed bed or fixed bed is also enormous and well established. For example, Cd(II) and Pb(II) removal as studied in a fixed bed adsorption column by using dead Calcareous skeleton (Lim and Aris 2014). Palm shell and phonix tree leaf powder made adsorbents were successfully used in fixed bed adsorption column for the removal of basic dye. Vinodhini et al. 2010 have investigated the effectiveness of

neem sawdust as an adsorbent for removal of Cr(VI) in a fixed bed column and treated 3.75 Litter of effluent from tannery wastewater (Vinodhini and Das 2010). In some other studies performance of packed adsorption column was reported for removal of various pollutants like Pb²⁺(Sahu et al. 2016), cyanide (Mondal et al. 2019) and phenolic effluents (Aksu and Gönen 2004b; Banat et al. 2007; Murugesan and Sheeja 2005; Niladevi and Prema 2008; Sahoo, Pakshirajan, and Ghosh 2011; Sancinetti et al. 2012; Tziotzios et al. 2005, 2007; Yadzir et al. 2016) various organic dyes(Yagub et al. 2015; Zolfaghari et al. 2018).

1.3 Scope of this research

From the detail literature review, it has been found that all the traditional wastewater treatment technology has some specific disadvantages. Therefore, the research direction has been focused on some novel cost-effective technique. Adsorption based technology has drawn significant attention from researchers since the last decades. A lot of research works are going on for developing low-cost adsorbent from the wastebased precursor. But, most of the reported studies are restricted to the batch studies only. Therefore, some more investigation can be done in a continuous reactor for industrial application of such novel system. Many researchers work on the fixed bed and fluidized bed adsorption column using various adsorbent for wastewater treatment. These tworeactors have some specific advantages and disadvantages over each other. Hence, a novel system can be developed by combining these two reactors will be a novel system which can overcome many drawbacks of the reactors and exhibit synergistic advantages of those systems. A semi-fluidized bed combination of a packed bed followed by a fluidized bed in the same column will be a very promising system for investigating its performance to treat various potential pollutants using some low-cost novel adsorbent derived from locally available biomass and alginate.

1.4 Objective of this research work

This research involves a combination of experimental and model-based investigations to understand the mechanism and performance of semifluidized bed reactor for the treatment of wastewater. This research is divided into three main sections, (i) Continuous experiments on the hydrodynamics characteristic of this developed reactor and its performance analysis for various organic and inorganic pollutants removal, (ii) Synthesis, characterization and performance analysis of low-cost adsorbent for the removal of various pollutants in a batch study (iii) dynamic model development for the system based on mass transfer parameters and model validation with experimental data.

The specific objectives of this research include

- Design and development of a lab-scale semifluidized bed reactor and investigation of its hydrodynamic behaviour including determination of the minimum and maximum fluidization /semifluidization velocity, pressure drop, the packed bed formation of a co-current gas-liquid-solid three-phase semifluidized bed including the development of various hydrodynamic & bed characteristic correlations of the system and its validation with experimental data.
- Synthesis and characterization of a low-cost lightweight bio-adsorbent for the bed materials
- Performance analysis of the synthesized bio-adsorbent in a batch study to ensure its applicability as a suitable adsorbent
- Performance analysis of the Semifluidized bed reactor using the synthesized adsorbent
- Dynamic model development and validation, optimization of the operating variables for maximum efficiency and scale-up calculations.

1.5 Organisation of the thesis

This thesis has been organised into seven chapters. An overview of the summarised structure for this thesis is presented in Figure 1.6 which is a schematic block diagram showing the activities carried out in this research.



Figure 1.6: Flow diagram of the overall work

The first chapter deals with the background information, elaborate review of literature and research gap, scope and objective of the present work. Chapter 2 described development and hydrodynamic study of three-phase semifluidized reactor column. Chapter 3 focuses on the synthesis and characterization of a low-cost bio adsorbent as the solid phase of the bed. Chapter 4 focused on investigating the efficiency of the synthesized adsorbent for the removal of various organic and inorganic pollutants by adsorption in a batch operation. Kinetics, isotherm, thermodynamic and adsorption mechanism also studied in this chapter. Chapter 5 describe the performance of semifluidized bed reactor for various pollutants removal by incorporating the synthesized adsorbent. Chapter 6 studies on dynamic model development and process optimization. And chapter 7 is the overall conclusion and future scope of the study.

Chapter 2

Design and Development of a Gas-Liquid-Solid Three-Phase Semifluidized Bed Reactor and it's Hydrodynamic Studies

Chapter 2¹

Design and Development of a Gas-Liquid-Solid Three-Phase Semifluidized Bed Reactor and it's Hydrodynamic Studies

2.0 Introduction

Semifluidization is a technique for Liquid-solid or Gas-Liquid- solid contacting like a normal fluidized bed or packed bed system which was first introduced by Fan and co-workers in the early sixties to investigate the mass transfer between solid-liquid in a semifluidized bed system(Fan, Yang, and Wen 1959). In this system, a packed at the top followed by fluidized bed generation in the same reacting column has been achieved. This bed can be formed by providing sufficient space for the bed material to get it freely expand and arrest the escaping particle by the top restrain. The degree of semifluidization can be determined between the minimum semifluidization (when the first particle touches the top restrain) and maximum fluidization (all the bed material reach the top or form an inverse packed bed) (L. Fan and Wen 1961). Such a system can create substantial intimate contact between the gas-liquid and solid particles and provide significant advantages for the physical-chemical and biological processing operation. The difficulties of fluidized beds, such as solid back-mixing, particle attrition and erosion of surfaces, and those of packed bed system, like, non-uniform bed temperatures, solid's isolation, and channelling, are reduced in a semifluidized bed system(Schubert and Larachi 2009). There are two models of gas-liquid-solid semifluidized bed operation that have been reported so far in the literature as co-current and counter-current mode operation. Among them, the co-current three-phase system is most prominent with upward gas and liquid

¹This chapter work has been published, **Subrata Biswas**, Tushar Sen, Bhim Charan Meikap, *Experimental Hydrodynamic and bed Characteristics of Co-current Gas-Liquid-Solid Three Phase Semifluidization with liquid as the continuous phase*, Particulate Science and Technology,2019, 38(7), 1–13.

flow system. However, this type of three-phase semifluidized bed may offer highpressure drops due to the presence of a packed section at the top and results in higher gas hold up and the higher interfacial area in the bed(Jena, Roy, and Meikap 2009). Therefore, the main objectives of this work are to develop a novel three-phase gas-solidliquid semifluidized bed system involving relatively low density solid or,

low solid/liquid density ratio and to develop various hydrodynamic parameters correlations for an industrial-scale operation. It was found that the minimum fluidization velocity (U_{lmf}) is significantly depends on operating parameters like superficial gas velocity (U_g) and particle sizes (d_p) , but independent of initial static bed height (H_s) . Minimum semifluidization and maximum semifluidization velocities reduce with the rise in static bed height (H_s) . Top packed zone formation and bed pressure drop across the bed also strongly depends on particle diameter (d_p) , superficial gas (U_g) , liquid velocity (U_{SL}) and initial static bed height (H_s) . Various empirical correlations on hydrodynamic behaviour have been developed here using Global Pattern search Algorithm in MATLAB 2016.

2.1 Fundamental and theory of semifluidization technology

Fixed bed and fluidized bed reactors have been successfully used in various largescale industrial applications. However, despite its potential advantages, the application of a semi-fluidized bed has not been explored significantly (Chern, Fan, and Muroyama 1984). There are only a few reported literature in the large-scale application of industrial (physical, chemical and biochemical) operations, such as filtration, adsorption, catalytic reactions, removal and recovery of heavy metal, bio-oxidation, fermentation of ethanol, manufacturing of granule tablet, wastewater treatment, etc.(Dehkissia et al. 2008; Ho et al. 2002; Meikap and Roy, 1997; Narayanan and Biswas 2016). Further knowledge of fundamental characteristics such as hydrodynamics, heat and mass transfer characteristics are important for successful design and application of this three-phase semifluidized bed system for which progress is limited. The most important hydrodynamic parameters are minimum fluidization and semifluidization velocity, top packed bed height, maximum semifluidization velocity, the pressure drop across the semifluidized bed, etc. Over the last few decades, researchers articulated their interest in various aspects of the semifluidization phenomenon. Most of the studies are limited to traditional two-phase systems such as gas-solid or liquid-solid (Biswal et al. 1990; Murthy et al. 1976; Murthy and Roy 1986; Roy and Gupta 1973; Roy and Sarma 1974; Roy and Sharma 1978) systems.

There is a couple of reported literature on the dynamic characteristic of semifluidized bed (L. . Fan and Wen 1961; Fan et al. 1959). Fan et al. (1961) (L. Fan and Wen 1961) recommended that minimum fluidization, minimum semifluidization and maximum semifluidization velocity all strongly depend on fluidizing particle properties and a fluidizing agent. The minimum semifluidization velocity also depends upon the amount of particle to column diameter ratio. The particle's Reynolds number at minimum fluidization velocity for Liquid-solid two-phase system, Re_{mf} was proposed by Wen et al. (1966) (Wen and Yu 1966) which is as follow,

$$Re_{mf} = (33.7^2 + 0.0408Ar)^{0.5} - 33.7$$
(2.1)

Where, Ar = Archimedes number = $(d_P^3(\rho_S - \rho_L)g\rho_L/\mu_L^2)$

 Re_{mf} = particle Reynolds number at minimum fluidization, considering non-spherical particles

Recently some more correlations for semifluidization velocity on three-phase semifluidization have also been reported (Jena et al. 2009). Which are as follows

$$U_{LSF}(min) = 0.037 (U_g)^{-0.267} (R)^{0.0497} (d_P)^{0.228} (\mu_L)^{-0.157}$$
(2.2)

Where $U_{LSF}(min)$ minimum semifluidization velocity of liquid in three-phase semifluidized, m/s

 U_g average superficial gas velocity, m/s, d_p the diameter of solid particle, m, R bed expansion ratio μ_L liquid viscosity, Pa-s

At minimum semifluidization velocity (Gupta and Sathyamurthy 1999; Jena et al. 2009) some solids start forming the packed bed beneath the top restraint of a semifluidized bed reactor. The height of the packed bed formation can be controlled by adjusting the top restraint position, liquid flow rate, and initial static bed height.

There are also a few reported correlations to determine the packed bed height from the void fraction of a semifluidized bed. (Fan et al. 1959; L. T. Fan and Wen 1961; Mydlarz 1987) which are given below:

$$H_{pa} = (H_{sf} - H_f) \big((1 - \varepsilon_f) / (\varepsilon_f - \varepsilon_{pa}) \big)$$
(2.3)

$$(U_s - U_{mf}/U_t - U_{mf}) = \left((H_{sf} - H_{pa})/(H_{sf} - H_s) \right)^{-3.15}$$
(2.4)

Both the proposed correlations are valid for a liquid-solid two-phase system only.

However, for a three-phase semifluidized bed following correlations are available in the literature (D K Samal et al. 2014a, 2014b; D K. Samal et al. 2014; Deepak Kumar Samal et al. 2013; Samal et al. 2015; Samal and Roy 2015). The correlation is reproduced below

$$\left(\frac{H_{Pa}}{H_{s}}\right) = 0.0014 \times \left(\frac{H_{s}}{D_{c}}\right)^{-0.242} \left(\frac{d_{pav}}{D_{c}}\right)^{-0.967} \left(\frac{G_{sfl}}{G_{mfl}}\right)^{2.047} \left(\frac{G_{sfg}}{G_{mfl}}\right)^{1.547} R^{-0.967}$$
(2.5)

$$\left(\frac{H_{Pa}}{H_s}\right) = 9 \times 10^{-6} \left(\frac{\rho_s}{\rho_l}\right)^{-2.047} \left(\frac{d_{pav}}{D_c}\right)^{-4.214} \left(\frac{U_{sfl}}{U_{mfl}}\right)^{1.405} \left(\frac{U_{sfg}}{U_{mfl}}\right)^{3.260} R^{-2.544}$$
(2.6)

$$\left(\frac{H_{Pa}}{H_s}\right) = 8 \times 10^{-16} \left(\frac{H_s}{D_c}\right)^{-0.47} \left(\frac{d_{pav}}{D_c}\right)^{-9.23} \left(\frac{G_{sfl}}{G_{mfl}}\right)^{3.8769} \left(\frac{G_{sfg}}{G_{mfl}}\right)^{0.0.8344} R^{-0.776}$$
(2.7)

$$\left(\frac{H_{Pa}}{H_s}\right) = 2 \times 10^{-9} \left(\frac{H_s}{D_c}\right)^{-0.3114} \left(\frac{d_{pav}}{D_c}\right)^{-4.8757} \left(\frac{G_{sfl}}{G_{mfl}}\right)^{3.8769} \left(\frac{G_{sfg}}{G_{mfl}}\right)^{0.8344} R^{-3.166}$$
(2.8)

$$\left(\frac{H_{Pa}}{H_s}\right) = 9 \times 10^{-7} \left(\frac{H_s}{D_c}\right)^{0.185} \left(\frac{d_{pav}}{D_c}\right)^{-4.66} \left(\frac{G_{sfl}}{G_{mfl}}\right)^{2.556} \left(\frac{G_{sfg}}{G_{mfl}}\right)^{0.181} R^{-1.71}$$
(2.9)

$$\left(\frac{H_{Pa}}{H_s}\right) = 2.5 \times 10^{-14} \left(\frac{H_s}{D_c}\right)^{0.756} \left(\frac{d_{pav}}{D_c}\right)^{-10.66} \left(\frac{G_{sfl}}{G_{mfl}}\right)^{3.441} \left(\frac{G_{sfg}}{G_{mfl}}\right)^{1.195} R^{-2.15}$$
(2.10)

Where d_{pav} is the average particle diameter, $\frac{G_{sfl}}{G_{mfl}}$ superficial liquid mass velocity ratio, $\frac{G_{sfg}}{G_{mfl}}$ superficial gas mass velocity ratio, $\frac{U_{sfl}}{U_{mfl}}$ superficial liquid velocity ration, $\frac{U_{sfg}}{U_{mfl}}$ superficial liquid velocity ratio, the expansion of fluidized bed with respect to static bed. The proposed correlations are restricted for the specific operational conditions.

One of the important hydrodynamic parameters, such as bed pressure drop ΔP can be found by the following reported correlations (Jena et al. 2009).

$$\Delta P_{sf} = \frac{M_b g}{A_c} + 150 \left((1 - \varepsilon_{Pa})^2 \mu_l U_{SL} H_{Pa} / \varepsilon_{Pa}^3 \left(\varphi_S d_p \right)^2 \right) + 1.75 \left(1 - \varepsilon_{Pa} \rho_l H_{Pa} U_{SL}^2 / \varepsilon_{Pa}^3 \varphi_S d_p \right)$$
(2.11)

where, $\Delta P_f, \Delta P_{pa}, \Delta P_r$. pressure drop across the fluidized, packed, and restraint section respectively, KPa, A_c area of reactor column, m², M_b mass of solid, kg, U_{SL} average superficial liquid velocity m/s, ε_{Pa} voidage of packed section, φ_S sphericity of solid.

Few empirical correlations were reported by various researchers (D K Samal et al. 2014a, 2014b; D K. Samal et al. 2014; Deepak Kumar Samal et al. 2013; Samal et al. 2015; Samal and Roy 2015) for the prediction of bed pressure drop in dimensionless form for a three-phase semifluidized bed system. These correlations are given as

$$\left(\frac{\Delta P_{sf}}{\Delta P_{mf}}\right) = 0.195 \times \left(\frac{H_s}{D_c}\right)^{1.096} \left(\frac{d_{pav}}{D_c}\right)^{0.745} \left(\frac{G_{sfl}}{G_{mfl}}\right)^{3.234} \left(\frac{G_{sfg}}{G_{mfl}}\right)^{1.899} R^{-1.182}$$
(2.12)

$$\left(\frac{\Delta P_{sf}}{\Delta P_{mf}}\right) = 3 \times 10^{-5} \left(\frac{\rho_s}{\rho_l}\right)^{-3.924} \left(\frac{d_{pav}}{D_c}\right)^{-5.243} \left(\frac{G_{sfl}}{G_{mfl}}\right)^{1.343} \left(\frac{G_{sfg}}{G_{mfl}}\right)^{3.732} R^{-1.798}$$
(2.13)

$$\left(\frac{\Delta P_{sf}}{\Delta P_{mf}}\right) = 5 \times 10^{-16} \left(\frac{H_s}{D_c}\right)^{0.923} \left(\frac{d_{pav}}{D_c}\right)^{-10.33} \left(\frac{G_{sfl}}{G_{mfl}}\right)^{1.8289} \left(\frac{G_{sfg}}{G_{mfl}}\right)^{1.112} R^{-2.0134}$$
(2.14)

$$\left(\frac{\Delta P_{sf}}{\Delta P_{mf}}\right) = 4 \times 10^{-12} \left(\frac{H_s}{D_c}\right)^{0.8292} \left(\frac{d_{pav}}{D_c}\right)^{-0.7681} \left(\frac{G_{sfl}}{G_{mfl}}\right)^{3.32} \left(\frac{G_{sfg}}{G_{mfl}}\right)^{0.7208} R^{-1.9297}$$
(2.15)

$$\left(\frac{\Delta P_{sf}}{\Delta P_{mf}}\right) = 4.0 \times 10^{-8} \times \left(\frac{H_s}{D_c}\right)^{0.848} \left(\frac{d_{pav}}{D_c}\right)^{-6.662} \left(\frac{G_{sfl}}{G_{mfl}}\right)^{1.285} \left(\frac{G_{sfg}}{G_{mfl}}\right)^{1.099} R^{-1.085}$$
(2.16)

$$\left(\frac{\Delta P_{sf}}{\Delta P_{mf}}\right) = 8.2 \times 10^{-16} \times \left(\frac{H_s}{D_c}\right)^{0.562} \left(\frac{d_{pav}}{D_c}\right)^{-13.6} \left(\frac{G_{sfl}}{G_{mfl}}\right)^{1.963} \left(\frac{G_{sfg}}{G_{mfl}}\right)^{1.004} R^{-1.76}$$
(2.17)

Where $\left(\frac{\Delta P_{sf}}{\Delta P_{mf}}\right)$ is a dimensionless pressure drop across the system, rests are the same as described for equation 2.5- 2.10.

Some of the above correlations were fitted with my current experimental conditions and it produces a large deviation from the experimental data, which indicates the inapplicability of those correlations for the current system.

The semifluidization theory can also be explained from the force balance point of view. Forces acting on the solid particles present in the semifluidized bed are drag force, buoyant force and weight of the particles. The force balances applied to the particle can be explained in Figure 2.1.



Figure. 2.1: The bed of particles and the force balance.

When the weight of the particles W exceeds the buoyancy forces F_b and the drag forces F_d due to the superficial fluid velocity U, the particles remain fixed in place. The velocity U is the minimum fluidization velocity if a small increase of velocity, δU , causes the bed to expand by a small amount δH over its original height, H

It has been assumed that all the particles are uniformly distributed, particle movement in the suspension is completely independent of other particles(L. . Fan and Wen 1961). Hence, the force due to particle-particle interaction is neglected. Thus, the significant forces are only dragging force and forces for particle weight.

Drag force (F_d) of such a system can be expressed as

$$F_d = \frac{1}{2}\rho_l U_l^2 A_p C_D \tag{2.18}$$

Or sometimes in terms of a void fraction, which can be expressed as,

$$F_d = \Delta P A_p \tag{2.19}$$

$$\Delta P = f(U_l, \varepsilon, d_p, \varphi_s) \tag{2.20}$$

$$\varepsilon = 1 - \frac{v_p}{v_t} \tag{2.21}$$

Where ρ_l is liquid density kg/m³, U_l is fluid velocity m/s, A_p is particle size m², and C_D is the dimensionless drag coefficient, φ_s sphericity of particle, $V_t \& V_p$ are the volume of bed and volume of particle respectively. So, the net force acting completely depends on the fluid properties. Also, when the particle density is higher, more drag force will be required by the fluid to overcome the force caused by the weight of the solid and make the bed in fluidized or semifluidized conditions. This also results in a higher pressure drop across the semifluidized bed. When the upward fluid flow rate is higher, the free expansion of bed will be increased and this expansion was restricted using a top fixed bed restraint which helps to form a packed bed zone at the top and fluidized section at the bottom of the single column (L. . Fan and Wen 1961).

2.2 Materials and methods

2.2.1 Design and development of a gas-liquid-solid three-phase semifluidized bed column

A three-phase semifluidized bed reactor was fabricated in our laboratory with the help of our Central workshop facilities at IIT Kharagpur. The schematic diagram has been given in Figure 2.2 and the pictorial view of the experimental rig has been given in Figure 2.3. The reactor column is consisting of three different sections. They are identified as gasliquid distribution section, main reaction or Gas-Liquid-solid contacting section and the liquid disengagement section. The distributor section has a height of 22 cm of fructoconical shape with a divergence angle of 5.3^{0} . Water inlet nozzle diameter was 0.126 cm and outlet nozzle diameter was 10.03 cm connected with the main reacting or contacting section by flanges. Brass plate with 90 holes of 2 mm diameter was attached in between the flanges (has been shown in Figure 2.4). An air connection was entered in this section to ensure proper mixing of air-water before entering into the main section of the column Has been given in. The main section was made of a Perspex tube with an inner diameter of 10 cm and a thickness of 3 mm. pressure taps were connected at different positions of the column to monitor the be pressure at a different position. The top restraint was made of stainless steel plate with OD (outer diameter) 10 cm with holes of 2 mm to restrict the upward movement of the solid particles. At the top, there is a liquid disengagement section where the liquid accumulates just after the contact takes place. The sample collection point was connected at this point.



Figure. 2.2: Schematic of the experimental setup.



Legends

- 1. Disengagement zone
- 2. Test Section
- 3. Gas-Liquid Distributor
- 4. Water Rotameter
- 5. Air Rotameter
- 6. Sample collection tap
- 7. Recycle to feed tank

Figure. 2.3: Pictorial view of the experimental setup.



Figure. 2.4: Pictorial view of the air-water distribution section.

2.2.2 Bed materials and process parameter measurement

Acrylic polymeric beads of different diameter from 3.86-6.8 mm have been purchased from the local market has been used as the bed material. The material has been selected because of its light weight and density which very similar to biopolymer like alginate beads. The acrylic beads were filled in the column to get the desired bed height. Clean tap water and compressed air pumped from the bottom in concurrent mode. Pressure taps were fitted with the column at top and bottom such a way so that error can be minimized due its position. A U-tube manometer filled with Carbon Tetra Chloride (CCl₄) connected with the pressure taps to measure the pressure drop across the bed. The minimum liquid semifluidization velocity, based on experimental pressure drop measurement was performed and it was compared with the values based on theoretical pressure drop measurement. Table 2.1 presented the various operational conditions of hydrodynamic experiments.

Table 2.1: Operational conditions for hydrodynamic studies of a semifluidized bed.

Parameters	Values /Range
Spherical acrylic polymeric beads (solid phase)	The diameter of particles 3.9,6,7.8 mm; Sp gravity 1.1
Tap water (Liquid phase)	Flow rate range 0-30 LPM
Oil-free compressed air (gas phase)	Flow rate range 0-10 LPM
Carbon Tetra Chloride (CCl ₄) (manometer fluid)	Sp. Gravity 1.596
2.3 Results and discussion

2.3.1 Effect of bed characteristic parameters on minimum fluidization velocity (U_{lmf}) of a semifluidized bed operation

The minimum fluidization velocity and semi-fluidization velocity are two successive events in the operation of a semifluidized bed reactor. While the former deals with the initial movement of a particle in a fluid-solid or a gas-liquid-solid system, the later indicates the superficial fluid velocity at which the bed just starts forming a packed bed section at the top (Zhang, Epstein, and Grace 1998). 2.5a, 2.5b show the variations of minimum fluidization velocity with various process parameters. When a fluid passed upward through a bed of solid particles, at a low flow rate, the fluid (liquid/gas) simply passes through ugh the void space of stationary bed. With an increase in flow rate, particles start to move through a restricted region and the bed is called an expanded bed. At higher velocity, the bed particles are fully suspended by the upward flowing fluid and the bed is called an incipiently fluidized bed. At this particular point, the particle-fluid frictional force is counterbalanced by the weight of the solid particles and pressure drop across the bed has become constant.

The minimum fluidization velocity in this study has been measured experimentally (by observing) and also from the bed pressure drop measurement. In this work, both the methods give nearly the same results for minimum fluidization velocity. The minimum fluidization velocity of 0.0096 m/s was obtained for a superficial gas velocity, U_g of 0.00424 m/s, particle size d_p = 3.9 mm, static bed height (H_s) of 15 cm. Whereas, the pressure drop measurement method gives the minimum fluidization velocity of 0.0103 m/s for the same operating conditions.

It is clearly shown in Figure 2.5a that the minimum liquid velocity of fluidization reduces with the rise in gas flow rate, thus indicating a significant contribution of gas velocity to fluidization. This may be due to the reduction of lift force for the solid particles by the liquid-gas phase compared to the single system only.

Figure 2.5a and 2.5b illustrate the effect of static bed height(H_s) and bed particle size (d_p) on minimum fluidization velocity (U_{lmf}) . Figure 2.5a shows that the minimum fluidization velocity (U_{lmf}) does not depend significantly on the initial bed height. There is little difference in minimum fluidization velocity for the static bed's height at zero gas velocity and this is due to the difference in static bed height. Once the gas flow is introduced into the system, the values of minimum fluidization velocity (U_{lmf}) are almost the same for both the bed height as shown in Figure 2.5a. Whereas, Figure 2.5b shows that the minimum fluidization velocity (U_{lmf}) is strongly affected by the bed particle sizes. For the same initial static bed height the liquid minimum fluidization velocity, (U_{lmf}) is much higher for the larger particle size. Fluid needs more drag and a buoyant force is to make the bed fluidized.



Figure 2.5: Variation of minimum fluidization velocity $U_{lmf}(m/s)$ with different gas velocity, $U_g(m/s)$ (a) for different static bed height (H_s) at $d_p=3.86mm$, (b) for different particle size (d_p) where $H_s = 0.25m$.

2.3.2 Effect of medium and bed characteristic parameters on minimum semifluidization velocity (U_{sfm})

Earlier, it was mention that the velocity at which the bed is just starting forming packed section at the top is defined as minimum semifluidization velocity. Here also, this velocity was measured by visual observation as well as from pressure drop data. In both, cases the values obtained are 0.0328 m/s and 0.034 m/s respectively when the superficial gas velocity U_g was 0.00424 (m/s), particle size d_p 3.86 mm and static bed height H_s 25 cm. Figures 2.6a and 2.6b showed that the change of minimum semifluidization velocity U_{sfm} with different superficial gas (U_g) velocity. From Figure 2.6, it is very clear that the higher the gas velocity, the lower the (U_{sfm}). Hence, the gas velocity plays a significant role in occurring semifluidization in the same way as minimum fluidization at low liquid velocity.



Figure 2.6: Variation of minimum semifluidization velocity U_{sfm} , (m/s) with different gas velocity $U_g(m/s)$ (a) for different particle size (d_p) at $H_s = 0.25m$,(b) for different static bed height (H_s) , at $d_p = 3.86$ mm.

The variation of particle size (d_p) and static bed height (H_s) on (U_{sfm}) are also shown in Figure 2.6a and 2.6b respectively. It was found that the higher the particle size, the higher

the magnitude of U_{sfm} . This signifies that higher drag is required by fluid for the formation of the packed zone at the top of the column. Effect of static bed height is also illustrated in the same way, lower the static bed height means it is required more force by the working fluids to form packed bed for the same particle size.

2.3.3 Effect of various operating parameters on the height of packed zone formation

Another important parameter in the semifluidized bed reactor is packed bed zone formation. Figure 2.7a, 2.7b, and 2.7c illustrate the variation of packed zone creation H_{pa} with superficial liquid velocity U_{sL} for different static bed height (H_s) , particle sizes (d_p) , and bed expansion ratio respectively. From Figure 2.7a it is clear that with the increase in superficial liquid velocity, packed bed height was increased. At low superficial gas velocity, when liquid velocity is increased the packed bed height increased. When the formation of the packed section was 80% or more it becomes steady and there is an equilibrium between the two zones. The zone between packed and fluidized sections is a clear and very small amount of bed materials presented in the fluidized section, practically it is not possible to get a 100% top packed section. Higher the static bed height the tendency of formation packed height was also high. At a high fluid velocity and more amount of solid present in the system easily reach the top portion of the bed and formed a packed bed section. Figure 2.7b depicts that the packed bed formation which was also influenced by the particle size, d_p . Lower the particle size, higher the packed section formation compared to the larger particle size at the same superficial liquid velocity. The larger particles need more velocity to maintain the packed section, in other words for the larger size particles much drag is required as it bears more mass. Figure 2.7c depicts how packed bed height depends on different bed expansion ratios (R), for a total bed height of 50 cm, only by changing static bed height i.e. the expansion ratio. It is clear from Figure 2.7c that less the expansion ratio (higher the static bed height) the top packed bed zone formation is more.



Superficial liquid velocity USL (m/s)

Figure 2.7: Variation of packed bed formation $H_{pa}(cm)$ with superficial liquid velocity $U_{sl}(m/s)$ (a) for different static bed height $H_s(cm)$ for $d_p = 3.86 mm$, $U_g = 0.004246m/s$, (b) for different particle sizes d_p at static bed height $H_s = 25 cm$, $U_g = 0.004246m/s$, (c) for different bed expansion ratio (R), particle size $d_p = 3.86 mm$.

The effect of packed bed height to static bed ratio on superficial liquid velocity is shown in Fig 2.8a. The velocity at which $H_{Pa}/Hs = 1$ is called the maximum semifluidization velocity. The maximum semi-fluidization velocity is the fluid velocity at which the entire bed of solid particles is transferred to the top packed bed. Theoretically, this velocity corresponds to the terminal or free-fall velocity of the particles. From Figure 2.8b it is evident that for the minimum bed expansion ratio, the H_{Pa}/Hs ratio is more. In other words, H_{Pa}/Hs ratio increases with an increase in static bed height for constant total bed height. From figure 2.8a, the maximum semifluidization velocity was obtained for particle sizes of 7.8 mm, 6.0mm and 3.86 mm are 0.084 m/s, 0.077m/s, and 0.072 m/s, respectively.



Figure 2.8: Variation of packed bed to static bed ratio H_{Pa}/Hs with superficial liquid velocity $U_{SL}(m/s)$ (a) for different particle sizes, at Hs = 25 cm, (b) for different bed expansion ratio (R) at particle size d_p 3.86 mm.

This bed behaviour is a little different compared to the two-phase system (gassolid/liquid-solid) reported in the literature (Jena et al. 2009; D. K. Samal, Mohanty, and Roy 2013). The graphical representation is different due to the significant effect of the gaseous phase used as the secondary fluid in the present study.

2.3.4 Bed pressure drop

Pressure drop variation through the bed with different operating parameters is a very important characteristic of a semifluidized bed reactor. In this present study, a manometer has been employed to measure the pressure drop across the bed. Figure 2.9a shows the bed pressure drop (ΔP) behaviour of a three-phase semifluidized bed reactor with superficial liquid velocity, U_{SL} . It was found that pressure drop first increases till the fluidization occurs and gets constant for a while, and again starts to increase when packed bed formation starts across the top restraint. The minimum semifluidization velocity (U_{sfm}) or onset liquid semifluidization velocity (U_{osfm}) was also obtained from the Fig 2.9a.

Figure 2.9b and 2.9c show the pressure drop $\Delta P(kPa)$ variation with superficial liquid velocity $U_{SL}(m/s)$ for different static bed height H_S and particle size d_p at a constant superficial gas velocity U_q .

Figure 2.9b shows that the pressure drop across bed increases with static bed height, and Figure 2.9c shows how the increase of pressure drop is affected by the particle sizes while all other parameters remain constant. Higher pressure drop (ΔP) was obtained for smaller particle size compared to larger particle size. This phenomenon occurs as the particle size reduces (where the other parameters are kept constant) the tendency of packed bed formation is more and also void volume decreases, hence, produces more resistance across the top portion of the reactor. As a result, the pressure drop across the system increases significantly for the smaller particles.

Gas velocity also plays a significant role in system pressure drop. Figure 2.9d illustrates the dependency of gas velocity on bed pressure drop. It is clear from Figure 2.9d that the gas velocity higher the bed pressure drop. The introduction of gas flow into the system enhances the packed bed formation, with the increase of the pressure drop which may be disadvantageous for semifluidized bed operation.



Figure 2.9: Variation of Pressure drop $\Delta P(kPa)$ with superficial liquid velocity $U_{SL}(m/s)$ (a) at static bed height $H_s = 25$ cm, $d_p = 3.86$ mm and $U_g = 0.004246 m/s$, (b) for different static bed height H_s at $d_p = 3.86$ mm $U_g = 0.004246m/s$, (c) for different particle sizes d_p , static bed height H_s 25 cm, (d) for different superficial gas velocity U_g , particle size $d_p = 3.86$, static bed height $H_s = 25$ cm.

This obtained results on (ΔP) are comparatively low concerning other reported studies (Jena et al. 2009; D. K. Samal et al. 2013). This reduction of pressure drop is because of low solid-liquid density. This is a very important finding of this current work for the development of such a reactor as an industrial reactor where the density of the solid phase

is relatively less (biomass, immobilized cells, etc.). This is also advantageous for industrial point of bed operation.

2.4 Development of various bed characteristics correlations

The various hydrodynamic and bed characteristics correlations for the three-phase semifluidized bed system have been developed based on experimental data. The obtained correlations are solved through MATLAB 2016 and compared the results with experimental values.

2.4.1 Minimum fluidization velocity (U_{lmf})

The developed correlation for liquid minimum fluidization velocity (U_{lmf}) is

$$U_{lmf} = 0.097 \left(\frac{d_p}{D_c}\right)^{1.22} \left(U_g\right)^{-0.3012}$$
(2.22)

The correlation in equation (2.22) indicates how liquid minimum fluidization velocity (U_{lmf}) depends on various operating parameters such as d_p , U_g , etc, which are confirmed by experimental analysis.

Graphical representation of experimental vs calculated values for minimum fluidization velocity is shown in Fig 2.10. The calculated values are well in line with the experimental results with a high R^2 value of > 0.95. At a confidence level of 95%, the confidence interval for the value obtained from the correlation is 0.0122 ± 0.00242 .



Figure 2.10: Experimental vs Calculated values for minimum fluidization velocity.

2.4.2 Minimum semifluidization velocity (U_{Sfm})

The predicted correlation for minimum semifluidization velocity U_{Sfm} from the experimental analysis has been developed as

$$U_{Sfm} = 0.69 \left(U_g \right)^{-0.577} \left(\frac{H_s}{D_c} \right)^{-0.812} \left(\frac{d_p}{D_c} \right)^{1.695}$$
(2.23)

Minimum liquid semifluidization velocity $U_{Sf}(min)$ is a significant function of initial static bed height (H_s) , particle size (d_p) and superficial gas velocity (U_g) .

Graphical representation of experimental vs calculated values for minimum semifluidization velocity is shown in Fig 2.11. The calculated values are agreed with the experimental results with a high R^2 value of >0.95. The confidence interval for the values obtained from the correlation is 0.022 ± 0.00452 at a 95% level of confidence.



Figure 2.11: Experimental vs calculated values for minimum semifluidization velocity.

2.4.3 Top packed zone formation (H_{pa})

From the experimental results, it is evident that the formation of the top packed bed is a strong function of initial static bed height (H_s) , particle size (d_p) , superficial liquid velocity (U_{SL}) superficial gas velocity (U_g) . The dimensionless correlation developed based on experimental data is given below,

$$\left(\frac{H_{pa}}{H_s}\right) = 0.512 \left(\frac{H_s}{D_c}\right)^{0.91} \left(\frac{d_p}{D_c}\right)^{0.317} \left(\frac{U_{SL}}{U_{lmf}}\right)^{2.31} \left(\frac{U_g}{U_{lmf}}\right)^{0.3875}$$
(2.24)

Graphical representation of experimental vs calculated values for top packed zone formation is shown in Fig 2.12. The calculated values are well fit with the experimental results with a high correlation coefficient. The values obtained from the correlation having a confidence interval of 0.425 ± 0.1074 at a 95% confidence level.



Figure 2.12: Experimental vs calculated values for top packed zone formation.

2.4.4 Pressure drop of semifluidized bed $(\frac{\Delta P_{sf}}{\Delta P_{mf}})$

The dimensionless correlation for the pressure drop across the semifluidized bed $(\frac{\Delta P_{sf}}{\Delta P_{mf}})$ is,

$$\left(\frac{\Delta P_{sf}}{\Delta P_{mf}}\right) = 3.42 \left(\frac{H_s}{D_c}\right)^{0.4049} \left(\frac{d_p}{D_c}\right)^{0.0743} \left(\frac{U_{SL}}{U_{lmf}}\right)^{0.2254} \left(\frac{U_g}{U_{lmf}}\right)^{0.01239}$$
(2.25)

The correlation is given in equation (2.25) shows how the dimensionless pressure drop across the system is related to various operating parameters like initial static bed height (H_s) , particle size (d_p) , superficial liquid velocity (U_{SL}) superficial gas velocity (U_g) .

Graphical representation of experimental vs calculated values for a pressure drop of Semifluidized bed is depicted in Fig 2.13. The software predicted results are well in line with the experimental data and the correlation coefficient is >95. The confidence level assumed here is 95% and the confidence interval is 5.92 ± 0.2656 .



Figure 2.13. Experimental vs calculated values for a pressure drop of semifluidized bed

Table 2.2:	A comparative study	of other reported	results of hydro	dynamic paramet	ters of
the semiflui	idized bed system.				

System	Minimum fluidization velocity (m/s)	Minimum semifluidization velocity (m/s)	Maximum system pressure drop (kPa)	Reference
Liquid-solid		0.0983-0.1214	22	(Jena et al. 2009) (Shrivastava,
Gas-liquid-solid			18	Soni, and Kumar 2013) (Ho, Yau, and
Gas-solid	0.1008-0.4813	0.3-1.21	7.8	Hopper 1987)
Liquid-solid			7.19	(Roy and Sarma 1978)
Gas-liquid –solid (alumina)			11.8	(Samal et al. 2015)
(alumina beads 2-6 mm)			10-19	(D K Sanial, Mishra, et al. 2014)
Gas-liquid-solid	0.004 -0.0108	0.006 - 0.032	5.6	Present study

A comparative study of other reported results of hydrodynamic parameters of a semifluidized bed system of gas-liquid-solid / gas-solid/liquid-solid has been tabulated in Table 2.2. This comparison also indicates the low power consumption of the proposed system which can be an economic one in the industrial application.

At the same time, few reported correlations for three-phase semifluidized bed system has been tried to fit with the present experimental condition. There is a large deviation between the experimental data and model predicted values from the reported correlations. This difference between the experimental and model-predicted values is obtained due to the extensive difference in various operational conditions used by the researchers. From Figure 2.14, we can see the actual versus model predicted values of the dimensionless form of packed bed height formation and Figure 2.15 depicts the same for dimensionless semifluidized bed pressure drop.



Figure 2.14: Experimental vs predicted values for dimensionless top packed zone formation



Figure 2.15: Experimental vs predicted values for a dimensionless pressure drop of semifluidized bed

Hence, the correlations developed from this current study will be helpful to predict the hydrodynamic parameters for a system like this. Particularly for industrial applications where low-density solids are used such as biomass, polymer-supported biofilm polymer-coated or entrapped adsorbent, etc.

2.5 Conclusions

The hydrodynamic and bed characteristics study of a multi-phase semifluidized bed system illustrates that the minimum fluidization velocity (U_{lmf}) significantly depends on operating parameters such as superficial gas velocity (U_g) and particle sizes (d_p) , but independent of initial static bed height (H_s) . Minimum semifluidization and maximum semifluidization velocities decreased with the rise in static bed height (H_s) . Top packed zone formation and bed pressure drop across the bed also strongly depended on particle diameter (d_p) , superficial gas (U_g) , liquid velocity (U_{SL}) and initial static bed height (H_s) . The introduction of the dispersed gaseous phase as a secondary fluidizing agent plays a significant role by reducing minimum fluidization and semifluidization velocities and also enhanced the packed bed formation at lower liquid velocity. The significant outcomes of this study are reduced minimum fluidization velocity ranging from 0.004 - 0.01 m/s, and minimum semifluidization velocity of 0.032 - 0.006 m/s compared to reported high values. In this present study, the pressure drop generated in the system was fairly low due to low solid-fluid relative density. As a top packed bed is formed in such a bioreactor, the reactor pressure drop is slightly high. This shows that a semifluidized bed reactor is operated under little higher-pressure condition than a simple fluidized bed reactor but lower than that of a normally packed bed reactor. The maximum bed pressure drop was found to be 5-6 kPa. Empirical mathematical correlations for bed hydrodynamic characteristics have been developed for this particular system for a better understanding of such a reactor system with multi-phase. These correlations will be applied for calculating various hydrodynamic parameters for dynamic model development of semifluidized bed system. The hydrodynamic and bed characteristic study results confirm that this proposed reactor can be handled at lower fluid pumping cost and low bed pressure drop which will be very economical for commercial large scale operations. Effect of different liquid properties such as liquid density, viscosity, surface tension and solid properties like density, porosity can be studied in the future to understand the fundamental and phenomenological behaviours of a semifluidized bed system in case of three-phase operation.

Chapter 3

Synthesis and Characterization of Composite Adsorbent from Biochar as The Solid Phase of The Semifluidized Bed Reactor

Chapter 3²

Synthesis and Characterization of Composite Adsorbent from Biochar as the Solid Phase of the Semifluidized Bed Reactor

3.0 Introduction

In the era of industrialization and modern civilization, the globe is enriched with technical knowhow and scientific information and continuously striving to improve the lifestyle of mankind in every aspect. Industrialization is such a process that causes huge costs on the world environment. But, the industrialization and sustainability should go hand in hand to keep the planate greener and safe for all the living species (Basu, Guha, and Ray 2019). Among all the damages caused by several human activities, pollution of water are the most serious issue and the threat to mankind and other living organisms. This severe water pollution caused mainly by the industrial discharging toxic inorganic, organic pollutant laden effluent into water bodies. Various traditional treatment technologies which are used for the removal of such hazardous metals such as chemical precipitation, electrocoagulation, electro precipitation, reverse osmosis, membrane filtration and adsorption (Azouaou et al. 2010; Hanra and Ramachandhran 1996; Sabry et al. 2007; Sreejalekshmi, Krishnan, and Anirudhan 2009). However, adsorption has become one of the most attractive among all due to some disadvantages of those conventional methods like the high cost of operation and maintenance, more power consumption, etc. The widely used commercial activated carbon adsorbent also facilitate the researchers to find

¹ This chapter work has been published **Subrata Biswas**, Tushar Sen, Anteneh Mesfin Yeneneh ,Bhim Charan Meikap, *Synthesis and characterization of a novel Ca-alginate-biochar composite as efficient zinc* (Zn^{2+}) adsorbent: Thermodynamics, process design, mass transfer and isotherm modeling, Separation Science and Technology, 2019, 54(7),.

Subrata Biswas, Manisha Bal, Sushanta K Behera, Tushar Sen,Bhim Charan Meikap, Process Optimization Study of Zn^{2+} Adsorption on Biochar-Alginate Composite Adsorbent by Response Surface Methodology (RSM), Water, 2019, 11(2):325.

alternative cost-effective adsorbents because of its high cost and difficult to regenerate. Hence research focus has been moved to find some low-cost bio adsorbent from waste biomass. Biochar produced by pyrolysis from waste biomass was found a widespread application in wastewater treatment. Biochar is very effective in removing hydrocarbon and inorganic heavy metals from industrial wastewater (Mohan et al. 2014).

Along with biochar, the use of algae in living and non -living form is also a very effective and innovative alternative in heavy metal ion uptake (Lamai et al. 2005). Over the last few decades, environmentalists are working on algae to find out the potentiality and valuable role in the remediation of heavy metal ions from process effluent (Oswald 2003). Non-living algae, on the other hand, were found to be more effective for heavy metal removal because of its polymeric structure like cellulose glycoproteins, etc. (Volesky 2007). Non-living algae in the form of alginic acids or salt of such acids are effective to metal ion adsorption because of the presence of different functional groups like OH⁻, COO^{-} etc. These functional groups are responsible for the metal uptake capacities by binding positive metal ions with the group to form surface complex or by enhancing the electrostatic charge separation (Kaplan 2013). Therefore, the objectives of this work are to synthesize and characterize a novel Ca-alginate -biochar adsorbent and tested its effectiveness in the removal of aqueous phase Zn^{2+} under various physiochemical process conditions. In this work algae in the form of Ca-alginate and biochar obtained from pine, cone biomass has been used in the synthesis of Ca-alginate biochar composite (CABC). Alginate is well known for its adsorption property (Soares et al. 2004) and pinecone char is also used as an adsorbent for dye and heavy metal removal (Dawood, Sen, and Phan 2017). The use of a composite of Ca-alginate -biochar is an innovative method for their synergistic effect in the sorption of heavy metals from aqueous solution due to its low cost and availability.

3.1 Materials and method

3.1.1 Synthesis of bed materials

Two waste agricultural waste biomass has been used as a biochar precursor for this research work. The initial portion was done at Curtin University, Australia. Dried pine cones which are very abundant waste material were collected from Curtin University campus, Bentley, Western Australia. After collection, the pine cones were washed carefully with distilled water to remove unnecessary dust and other impurities. Then the washed pine cone is dried at 75^o C for 24 hours. Char was prepared by slow pyrolysis in a muffle furnace in the presence of N₂ gas at a rate of 10^o C/min up to 500^o C for 150 minutes as per method Dawood et al., (2017). Once the pyrolysis process finished, the biochar was cooled gradually and ground to fine particles required for the composite adsorbent preparation. Biochar from sugarcane bagasse was prepared in the same way which was collected from the local market of the IIT Kharagpur campus.

3.1.2 Ca-alginate -biochar composite preparation

Low viscosity and high viscosity sodium alginate powder purchased from Sigma Aldrich Co. was used to prepare the composite. The powder Na –alginate 4g (1:3) (w/v%) was dissolved in ultrapure water using a constant temperature magnetic stirrer to obtain a viscous polymeric solution. The synthesized pinecone-based biochar/ sugarcane bagassebased biochar of 1g then mixed with 100 ml of Na –alginate solution and again mixed properly with a magnetic stirrer and sonicated the solution to remove air bubbles formed during mixing. Then this mixture solution was added drop by drop in chilled CaCl₂ solution and spherical Ca-alginate biochar beads were formed by phase inversion method (Kim et al. 2008). The freshly prepared composites as shown in Figure 3.1b were kept in the CaCl₂ solution for one hour for hardening and then it was washed several times to remove excess salt and were preserved in distilled water for future use.



Figure 3.1: (a) Preparation of Alginate biochar composite beads, (b) composite adsorbent in distilled water.

3.2 Adsorbent characterization

3.2.1 Physicochemical characterization

Various physicochemical properties of the synthesized adsorbent are very important to determine its effectiveness in the removal of inorganics/organics from the aqueous phase. Table 3.1 shows various physicochemical properties of synthesizing composite adsorbent. To study the properties of any carbonaceous material like cellulose/lignocellulose etc. proximate and ultimate analysis is very crucial. These analyses are done to determine the coal or any carbonaceous materials energy value and other valuable information regarding the material's chemical composition. The proximate analysis determines sulphur, ash, volatile matter and fixed carbon content. The ultimate analysis is further compressive. It is a quantitive analysis of various elements like C (carbon), N (nitrogen), S (sulphur), O (oxygen), H (hydrogen), the content of the sample.



Figure 3.2: Dry adsorbent bead under the scan electron microscope.

Table 3.1: Proximate analysis data for the adsorbents.

Parameters	Value (%)				
	PC	CAPC	SB	CASB	
Moisture	8.9	10.2	1.08	9.87	
Ash	0.8	0.6	1.32	1.48	
Fixed Carbon	22.9	12.3	17.28	29.78	
Volatile matter	68.4	77	68.45	59.14	

Ultimate analysis data for all the adsorbent materials are listed in Table 3.2.

Table 3.2: Ultimate analysis data for all the adsorbent materials

		Material type		
Composition (%)	PC	CAPC	SB	CASB
С	73.27	61.87	84.42	77.27
Н	2.92	2.46	2.28	2.82
Ν	1.00	1.41	0.93	1.16
S	0	0	0	0
\mathbf{O}^{**}	48.11	44.26	35.06	22.63

** calculated by subtraction

To understand the surface properties like specific surface area, pore-volume, pore size, nature of pores BET and BJH isotherm models have been used in this present study. All the samples were tested in the Autosorb iQ BET analyzer through nitrogen adsorption-desorption isotherm at 77K temperature. Before that, all the samples were degassed at 300^oC to remove all impurities. The BET analyser for the analysis has been shown in Figure 3.3.



Figure 3.3: Autosorb iQ BET analyser.

According to BET theory, the rate of N_2 adsorption is equal to desorption at equilibrium. The isotherm equation mathematically expressed as(Avnir and Jaroniec 1989):

$$1/[\nu\{(p_0/p)-1\}] = \left(\frac{c-1}{c\nu_m}\right)\left(\frac{p}{p_0}\right) + \left(\frac{1}{c\nu_m}\right)$$
(3.1)

where, v is the amount of gas adsorbed m³, p and p_0 are equilibrium and saturation pressure in the atmosphere, C is BET constant.

$$C = e\left(\frac{E_1 - E_L}{RT}\right) \tag{3.2}$$

where, E_1 and E_L are the heat of adsorption of the first layer and second layer which is equivalent to heat of liquefication or vaporization.

Also, the rate of adsorption at ith layer must be proportional to the number of sites in the adjacent lower layer and, desorption rate from ith is proportional to the number of sites occupied by the ith layer but, not occupied by molecules of the higher layer (Biswas, Siddiqi, et al. 2020). Using all this assumption and applying the BET isotherm equation, the surface of all the three types of carbon materials were calculated and data are listed in Table 3.3. Pore volume, pore diameter, and pore nature were determined from BJH and t-plot. From this analysis, the porosity type of the surface can be identified either microporous, mesoporous or macroporous. The size of Micropore is < 2 nm, mesopore 2-50 nm and macropore >50 nm. The bulk density of adsorbent material is also very important to determine. The bulk density of the adsorbent plays a significant role in designing of industrial adsorption column. It affects the performance of the adsorption. As per the American Water Work Association, adsorbents bulk density should be greater than 0.25 g/cm³ for real field applications.

Properties		value		
	PC	CAPC	SB	CASB
BET surface area (m ² /g)	144.94	163.28	391.42	200.14
Bulk density (g/ cm ³)	0.31	0.41	0.29	0.39
Pore volume (cm^3/g)	0.289	0.3608	0.232	0.24
Average pore size (nm)	0.79	1.4	1.18	1.41

Table 3.3: Physical properties of the adsorbent materials

In this work, all the adsorbent materials were tested and the adsorption-desorption isotherm plot which has been presented in Figure 3.4a-3.4d. The figures indicate a significant change in surface characteristics and surface area. Figure 3.4a and 3.4c follow Langmuir II type of nature which postulate macroporous adsorbent. This type of isotherm indicates unrestricted monolayer-multilayer adsorption. The central linear section in the

curve indicates the relative pressure where monolayer coverage is complete. Figure 3.4b and 3.4d following type I isotherm. Type I isotherm exhibited by mainly microporous solids having a relatively low external surface area. Therefore, PC or the pine cone biochar has less surface area than the composite with alginate namely CAPC.



Figure 3.4: BET isotherm plot for a) Scot pine cone biochar (PC) b) pinecone alginate composite (CAPC) (c) sugarcane bagasse biochar (SB) (d) Ca Alginate sugarcane bagasse biochar composite (CASB).

3.2.2 FTIR analysis

FTIR (Fourier transform infrared) spectroscopy is a powerful tool for the characterization of any material as it signifies the comprehensive view about the functional groups of the material. Infrared transmission percentage signals at different wavelengths are mapped. From the nature of signal and wavelengths at which signals are obtained functional groups are identified. The apparatus used for the spectra analysis has been shown in Figure 3.5.



Figure 3.5: Perkin Elmer Spectra 100 FT IR

For four different types of adsorbent materials, different types of signals have been obtained as shown in Figure 3.6a and 3.6b. Pinecone biochar and its composite (as shown in figure 3.6a) week peak obtain in 3650-3748 cm⁻¹ indicates O-H stretching group but the same is absent for CAPC, a medium peak at wavelength 2850-2924 signify that there is C-H stretching and N-H stretching. The weak peak at 2300 for O=C=O and a group of the medium peak in the range 1000-1744 is an indication of the presence of C=C, N-H, and C-O stretching groups. And few weak peaks at 600-750 is for C-H bending. The biochar made from sugarcane bagasse and its alginate composite has shown in Figure 3.6b. Significant changes have been observed in the peaks. Several weeks and medium

peaks are also found in this figure. The weak peak at 3446 cm⁻¹ indicates the presence of the N-H stretching group, the medium peak from 2854-2925 cm⁻¹ for C-H and N-H group and some weak peaks from 996-1631 cm⁻¹ are for C=C and C-H groups. In the case of SB biochar and its composite, many small peaks are observed from 500-759 cm⁻¹ represent the presence of C=C bending.



Figure 3.6: FTIR spectrum for a) Pinecone biochar and CAPC composite b) Sugarcane bagasse biochar and CASB composite.

3.2.3 XRD analysis

The crystallinity of the pine cone biomass and carbon derived from it were evaluated by X-Ray Diffraction. The instrument was operated with Cu K α radiation, at 45.0 kV of voltage and 40 mA of electric current. A continuous scan from 10.0 to 80.0 degrees was applied for all the materials in this analysis at a 2 θ angle. This analysis allowed the detection of the amorphous part of the lignocellulosic biomass, as well as the modification of the crystalline structure of the cellulose. Some distinct peaks ware observed at $2\theta = 22^{0}$, $32-36^{0}$ for pine cone biochar (PC). After encapsulation in alginate beads, some distinct peaks are observed between $20^{0}-25^{0}$. For sugarcane bagasse biochar SB has peaks at 25^{0} , 34^{0} , $42-45^{0}$, 55^{0} 75-80⁰, From observation, it has been found that the amount of intensity has changed significantly for SB which signifies that PC and SB have a significantly different crystal structure (as shown in Figure 3.7a &b).

This analysis allowed the finding of the crystal structure of the biochar and the composite adsorbent. The crystallinity index (CI) was found to be 21.62% from the ratio of the maximum peak intensity 002 (I_{002} , $2\theta = 22.5$) and minimal depression ($I_{am} 2\theta = 18.5$) between peaks 001 and 002.

$$CI(\%) = \frac{(I_{002} - I_{am})}{I_{am}} \times 100$$
(3.1)

Where I_{002} is the maximum intensity of the 002 peaks and I_{am} the minimal depression of the amorphous structure. Thus, the adsorbent structure was found to be largely amorphous.



Figure 3.7: XRD spectrum for a) Pinecone biochar b) CAPC composite c) Sugarcane bagasse biochar d) CASB composite.

3.2.4 Surface morphology Analysis by FESEM Imaging

In this study, the surface morphology of the biochar and biochar alginate composite has been investigated in JEOL -JSM-7610F FESEM. The instrument has been showing in Figure 3.8.



Figure 3.8: JEOL -JSM-7610F FESEM for Surface morphology analysis.

Figure 3.9a -3.9d presents the surface morphology of pine cone biochar, CAPC, sugarcane bagasse biochar, and CASB respectively. All the images have been taken at identical resolution and scale. But there is a difference in working distance and applied voltage due to get clarity of the images. From the analysis, it has been observed that the pine cone biochar (PC) has some small micropores of nano-scale and rough surface, but when encapsulated in alginate the surface roughness has been increased significantly. The alginate creates a net-like boundary outside the carbon particles. However, some distinct difference has been noticed in case of pine cone biochar and sugarcane bagasse biochar. The sugarcane bagasse biochar has a more porous surface than a pine cone. The same has been found in the BET isotherm analysis also. Therefore, sugarcane bagasse biochar and its composite have more surface area than the pinecone one.



Figure 3.9: FESEM images for a) Pine cone biochar b) CAPC composite c) Sugarcane bagasse biochar d) CASB composite.

3.2.5 Effect of pH and temperature on the stability of composite adsorbent

The novel composite adsorbents have been synthesized from agricultural solid wastebased biochar and alginate composite which will apply for waste effluent. The effluent may have various solution pH and temperature. Therefore, the stability of the composite adsorbent at very low and high pH and low and high temperatures has been investigated in this study. It has been found that at very low pH (pH below 2) the adsorbent beads are very unstable and melted as the cross-linking between Ca²⁺ and alginate is broken at low pH. For temperature, in this study, up to 333 K, there is no significant change has been observed for the adsorbent beads. The very high temperature was not investigated as an adsorption-based process is not performed at very high temperature and in case of largescale application also operating a process at very high temperature is not feasible.

3.3 Conclusions

In this chapter, two different types of biochar were synthesized from two different biomass precursor one is pine cone and another is sugarcane bagasse. Both are very cheap and no cost and naturally available in many countries. Later, both of them are immobilized in alginate beads. Both the synthesized adsorbents exhibit excellent properties like surface area pore volume, availability of functional groups, rough and porous surface, and various physicochemical parameters. When the properties of both the material compared, it has been found that, sugarcane bagasse and its composite exhibited better properties. It has a higher fraction of carbon and high surface area with more micropores. Surface area for the sugarcane bagasse and the composite was found 391.2 and 200.14 m²/g and for pinecone based biochar and composite has a surface area of 144.94 and 163.28 m²/g. surface morphology also exhibited that, SB and CASB have more micropores it is more crystalline which has been confirmed from XRD. Moreover, the composite adsorbents are very lightweight and density very close to water. The adsorbent prepare from sugarcane bagasse has better properties compared to the pine cone. And, it is very commonly available in many countries as a waste by-product of the sugar factory. Therefore, the performance of the composite adsorbent need to be analysed elaborately to ensure its efficiency for removal of heavy metals and organic pollutants. So that such novel, low cost and lightweight adsorbent can easily be used as a bed material of packed, fluidized and semifluidized bed reactors.

Chapter 4

Batch Adsorption Studies for Removal of Heavy Metals, MB Dye and Phenol from Wastewater by the Synthesized Composite Adsorbents
Chapter 4³

Batch Adsorption Studies for Removal of Heavy Metals, MB Dye and Phenol from Wastewater by the Synthesized Composite Adsorbents

4.0 Introduction

Contamination of water bodies by the presence of various heavy metals and organic pollutants is an alarming threat to the global environment. Generally, the metal ions bearing atomic mass over 60 are classified as heavy metals (Kara, Yilmazer, and Akar 2017). Among all Zinc (Zn²⁺), Copper (Cu²⁺) and Nickel (Ni²⁺), Lead (Pb²⁺) Cadmium (Cd²⁺) laden effluents are generated from industries such as electroplating, galvanizing, paints, steel plant by-products, metallurgical industries, mining operations etc. (Aydin et al. 2008; Mobasherpour et al. 2011; Randhawa et al. 2015, 2014). Along with these heavy metals, Phenol is also recognised as a priority pollutant for water bodies which is released from various industries like cosmetics, pharmaceuticals, pulp and paper mill, steel plant etc. (Ahmaruzzaman 2008; Kumar and Pal 2012). However, many of these metal ions are also important and regarded as an important micronutrient for the living organism but their presence above threshold limit is very dangerous and cause severe health issues. According to the United State Environment Protection Agency the permissible limit for Zinc, Copper, Nickel, Lead, Cadmium in discharged water are 0.8 mg/L, 0.25 mg/L (Prasad and Freitas 2000) and 0.2 mg/L, 0.006 and 0.01 mg/L (Mobasherpour et al. 2011)

³This chapter work has been published, **Subrata Biswas**, Bhim Charan Meikap, Tushar Sen, "Adsorptive removal of aqueous phase copper (Cu2+) and nickel (Ni2+) metal ions by synthesize Biochar-biopolymeric hybrid adsorbents and process optimization by response surface methodology (RSM)", Water, Air, & Soil Pollution, 2019, 230, 197.

Subrata Biswas, Tushar Sen, Anteneh Mesfin Yeneneh ,Bhim Charan Meikap, Synthesis and characterization of a novel Ca-alginate-biochar composite as efficient zinc (Zn²⁺) adsorbent: Thermodynamics, process design, mass transfer and isotherm modeling, Separation Science and Technology, 2019, 54(7), 2019,

respectively. Therefore, it has become an issue with high priority to treat all such metal ions and organic pollutants containing wastewater before discharging into water bodies. Over the last few decades, several treatment methods are already in practices. Few commonly used techniques are ion exchange (Dabrowski et al. 2004), chemical precipitation (Charerntanyarak 1999), coagulation, filtration, membrane etc.(Qdais and Moussa 2004). However, these conventional methods face a lot of drawbacks such as high operational cost, difficulties in operation, a lot of chemical by-products discharge etc.(Kurniawan et al. 2006). Hence researchers have focused on biochar based adsorbent synthesis from various agricultural biomass which is cost-effective and also alternative adsorbents to CAC(Sen 2018) and also valorise of those large amount of solid agricultural wastes. Biochar is prepared from various waste biomass by slow pyrolysis and may researchers have already reported the use of various biochar obtained from rice husk, cellulosic materials, fly ash, sawdust, pine bark, tea industry waste, bagasse, cone biomass and many more for removal of Zn^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} various dyes, Phenol (Aydin et al. 2008).

Along with this low cost and potential biochar, algae in both living and nonliving form also become an attractive alternative for biosorption of heavy metals. The non-living algae have a polymeric structure like cellulose, glycoproteins etc. and some active functional groups like COO⁻, NH⁻, C=H, OH⁻. These functional groups uptake heavy metals by forming a surface complex or sometimes enhancing the electrostatic charge separation (Kaplan 2013).

Therefore, in this present study, we have synthesized and characterised hybrid adsorbents with agricultural biomass-based biochar and alginate biopolymer and tested its effectiveness in the removal of aqueous phase inorganic metal ions such as Zn^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} and organic pollutants like MB dye and phenol by batch adsorption

study. Mechanism of adsorption and optimization of various process parameters are also analysed here experimentally and theoretically.

4.1 Materials and method

4.1.1 Adsorbate and other chemicals

The aqueous solution of Zn^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} MB dye and Phenol was prepared by dissolving a calculated amount of $Zn(NO_3)_2$. $6H_2O$, $Cu(NO_3)$. $6H_2O$, $Ni(NO_3)_2$. $6H_2O$, $Pb(NO_3)_2$. $6H_2O$, $3Cd(SO_4)_3$.7 H_2O , Laboratory grade MB dye ($C_{16}H_{18}N_3SCl.3H_2O$) with a molecular weight of 319.86 g/mole and 99.5% Phenol respectively in double-distilled water. The stock solutions were prepared for 1000 mg/L. The working solutions of various concentration were prepared by series dilution method. The pH of the working solution was adjusted by 0.1 M HNO_3 and 0.1M NaOH using a pre-calibrated digital pH meter. Similarly, 1000 mg/L of stock solution of some other metal salts like NaCl, FeCl₃ solution were also prepared.

4.1.2 Synthesis of composite hybrid adsorbents and its characterization

The adsorbent materials were prepared from two different precursors one is pine cone and another is sugarcane bagasse. First biochar was prepared and later the biochar alginate was prepared by phase inversion in the presence of calcium chloride (CaCl₂. 2H₂O). Later, the synthesized adsorbents were characterized by its composition, surface area, crystallinity, presence of functional groups, surface morphology etc. Details synthesis and various characterizations have been discussed in earlier chapter-3

4.1.3 Batch adsorption experiments

The kinetics and equilibrium adsorption studies of Zn^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} MB dye and Phenol using synthesized CAPC/CASB composite adsorbents was conducted in a batch experimental mode. Removal of Zn^{2+} , Cu^{2+} , Ni^{2+} by adsorption experiments was performed at Curtin University Perth Australia and Pb²⁺, Cd²⁺, MB Dye and Phenol adsorption experiments were conducted at IIT Kharagpur, India. A known amount of CAPC/CASB adsorbent was mixed with 50 mL of aqueous adsorbate solution of known concentration and optimum solution pH in a series of 125ml plastic bottles as per method used by Afroze et al., 2016b. The adsorbent-adsorbate mixture was shaken in a constant temperature shaker at 130 rpm for 180 minutes. Liquid samples were filtered and collected at predetermined time intervals to measure the amount of adsorbate uptake by the CAPC/CASB. The residual metal ion concentration was measured by Perkin Elmer Optima 8300 ICP-OES (Inductive coupled Plasma Optical Emission Spectrometer) (at Curtin University), Perkin Elmer AAS, Perkin Elmer UV-Vis and Perkin Elmer HPLC (IIT Kharagpur). The initial concentration was varied between 25 – 100 mg/L for metal ions, 5-200 m/L for Phenol and 20-50 mg/L MB dye. The adsorbent dose was 0.04 -0.2 gm and the temperature were constant for this experiment.

For kinetic studies a known amount of hybrid adsorbent was mixed with 50 mL of metal ions of various concentration in a series of plastic bottles placed in a constant temperature shaker. The solution pH was controlled at 5.5 ± 0.1 (for metal ion and MB dye) and 6.9 ± 0.2 (for phenol) throughout the experiment. The adsorbent –metal ion solution was shaken in a constant temperature shaker at 130 rpm for 180 minutes to achieve the equilibrium condition. Samples were collected at a predetermined time interval (10,15,30,45,60,90,120, 150 Minutes) and filtered through a 45-micron syringe filter to avoid any adsorbent present in the sample solution. The residual metal ions MB dye and phenol concentration was quantified by the analytical instruments mentioned above. All the experiments were conducted in triplicate to get the accurate results and less than 5% error was obtained. For isotherm studies, the samples were not collected at different time intervals. Samples collected after 240 Minutes so that the adsorbent-adsorbate system get sufficient time to reach equilibrium.

For the thermodynamic study, the above procedure was repeated at different temperatures from 298-318 K and 303-333 K for MB dye removal study keeping other parameters constant. All experiments were done in triplicates for better accuracy.

Amount of solute adsorbed per gram of composite adsorbent $q_t(mg/g)$ was calculated as per the following equation

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{4.1}$$

Where, q_t is the amount of solute adsorbed, (mg/g), C_0 and C_t are the initial concentration and concentration at any time (t), (mg/L), V is working solution volume (L), m mass of adsorbent, (gm).

The removal efficiency was calculated by the following equation:

Removal (%) =
$$\frac{(c_0 - c_t)}{c_0} \times 100$$
 (4.2)

Where C_0 and C_t are the initial concentration and concentration at any time, mg/L

4.2 Theory of adsorption

4.2.1 Kinetics studies of adsorption

Kinetic study of adsorption is very important to understand the mechanism of adsorption and to determine various kinetic parameters which are essentials for the design of an adsorption column in real field application. In this present study, the two main kinetic model, Lagrangian Pseudo-first- order kinetic, pseudo-second-order kinetic model and Intra-Particle Diffusion Model or Webber –Morris model(Weber and Morris 1963) were applied to kinetic experimental data.

The generalized integral form of the pseudo-first-order kinetic model can be expressed as (Lagergren 1898), in nonlinear form as,

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4.3}$$

By integrating the above differential equation at B.C t = 0, q_t = 0 and at t = t (>0), $q_t = q_t$ the linear form was obtained:

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{4.4}$$

Where q_t and q_e are amount of solute adsorbed (mg/g) at any time (t) and amount adsorbed at equilibrium time respectively, k_1 represents the first-order rate constant (min⁻¹), t contact time (min). The plot of $ln(q_e - q_t)$ versus t gives a slope and intercept from which rate constant k_1 and theoretical value of q_e can be determined.

Pseudo-second -order kinetic can be represented as,

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{4.5}$$

By integrating the above equation, at same boundary condition the linearized form obtained as,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(4.6)

A plot between $\frac{t}{q_t}$ against t gives the slope of $\frac{1}{q_e}$ and intercept of $\frac{1}{k_2 q_e^2}$. From the slope

and intercept, the theoretical value of q_e (mg/g) and second-order rate constant k_2 (g/mg.m) was calculated. Equation 4.7 also gives the value of the initial sorption (*h*) rate at $t \rightarrow 0$.

$$h = k_2 q_e^2 \tag{4.7}$$

For validation of the models with the experimental data an error function (χ) was determined as per below,

$$\chi^2 = \sum \frac{(q_e(\exp) - q_e(cal))^2}{q_e(cal)}$$
(4.8)

The intraparticle diffusion model was proposed by Webber and Morris (Weber and Morris 1963) was used to determine the rate-limiting steps or mechanism of the adsorption process. According to this model, if any adsorption process is followed only intraparticle diffusion, the plot of q_t against $t^{1/2}$ yield a straight line with slope and intercept. But when the adsorption process is controlled by multiple steps mechanism or it has more than one rate limiting steps the plot gives multiple straight lines with different slope and intercept. The initial portion of the straight line stands for the surface diffusion or macro pore –mesopore diffusion and another portion signifies the micro pore or intraparticle diffusion (Fierro et al. 2008). The mathematical form of the model is as reproduced below,

$$q_t = k_{id} t^{1/2} + I \tag{4.9}$$

Where q_t amount of solute adsorbed at any time (mg/g), $t^{1/2}$ is the square root of time (min^{0.5}) and k_{id} is intraparticle diffusion coefficient (mg/g.min^{0.5}) respectively.

4.2.2 Equilibrium isotherm

The isotherm study is important to optimize the adsorption system and to estimate the maximum adsorption capacity of the adsorbent. In this study, Freundlich and Langmuir's isotherms have been investigated.

According to the Freundlich isotherm model (Freundlich 1906), the adsorption phenomenon occurs on the heterogeneous surface of the adsorbent and multilayer adsorption takes place. The nonlinearized isotherm equation can be written as,

$$q_e = K_f C_e^{1/n} \tag{4.10}$$

The linear form of the equation obtained as,

$$lnq_e = \frac{1}{n}lnC_e + lnK_f \tag{4.11}$$

where, q_e amount of solute adsorbed at equilibrium (mg/g), C_e is the concentration of metal ion at equilibrium (mg/L), K_f and n are Freundlich constant. The plot of lnq_e against lnC_e produces a straight line with a slope of $\frac{1}{n}$ and intercept K_f . Where n is the value of system heterogeneity and K_f is the adsorption capacity of the system. The value of n should be higher than 1 for favourable adsorption.

On the other hand, Langmuir isotherm (Langmuir 1918) explain the adsorption phenomenon on the homogeneous surface and monolayer adsorption takes place. This particular isotherm predicts the maximum adsorption capacity of an adsorbent for a range of initial concentration at a particular condition. The nonlinearized form has been used in this study which is as below,

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4.12}$$

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m}$$
(4.13)

Where, K_L is the energy of adsorption (L/mg), q_m is the maximum adsorption capacity of the adsorbent (mg/g). The plot of $\frac{1}{q_e}$ vs $\frac{1}{c_e}$ produces a straight line with slope $\frac{1}{q_m}$ and intercept of $\frac{1}{K_L q_m}$. The dimensionless separation factor (R_L) also determined from this isotherm which signifies the feasibility of adsorption process for a different initial solute concentration. The dimensionless parameter, also called separation factor can be calculated as,

$$R_L = \frac{1}{1 + K_L C_0} \tag{4.14}$$

Where, C_0 is the initial metal ion concentration (mg/L). The condition for favourable adsorption is $0 < R_L < 1$.

4.2.3 Thermodynamics studies of adsorption

Thermodynamic properties like Gibbs free energy change ΔG (kJ/mole), enthalpy change (ΔH^0) (kJ/mol) and entropy change ΔS^0 (J/mol.K) plays a significant role in adsorption to

determine the feasibility of exothermic/endothermic nature of the process. The equations for determination of various thermodynamic parameters are as follows,

$$\log\left(1000 \times \frac{q_e}{c_e}\right) = \frac{\Delta S^0}{2.303R} + \frac{-\Delta H^0}{2.303RT}$$
(4.15)

$$\Delta G = \Delta H^0 - T \Delta S^0 \tag{4.16}$$

Where, q_e is the solid –phase concentration at equilibrium (mg/L), C_e is the equilibrium concentration of the solution (mg/L), T is the temperature in K and R is the universal gas constant (8.314 J/mol.K). The plot between $log\left(1000 \times \frac{q_e}{c_e}\right)$ versus $\frac{1}{T}$ gives a straight line having a negative slope gives the value of enthalpy change ΔH^0 and intercept yield entropy change ΔS^0 .

From those values obtained from the linearized Van't Hoff plot can substitute in Equation 4.16 to compute the value of Gibb's free energy of the system at different temperature.

4.3 Results and discussion

4.3.1 Effect of solution pH on metal ion and organic compound adsorption

Solution pH plays a significant role in metal ion adsorption. The surface charge of the adsorbent depends upon the pH of the working solution. Here in this present study, we have studied the effect of pH for Zn²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Cd²⁺, MB dye and phenol removal over a pH range of 3 to 10. An example of adsorption capacity against solution pH has been presented in Figure 4.1. The experimental results reveal that most of the metal ions exhibit an increasing trend upto pH 5-6 and after pH 7 it is decreasing. Most of the metal ions are present in the aqueous solution in the ionic form upto pH 6-6.5 (Randhawa et al. 2014) in M^{+/2+} or M(OH)⁺. Above this solution pH of 6.5 -7 most of the adsorption operation below pH 7 to avoid any kind of metal ion precipitation. At very low pH the concentration of H₃O⁺ ions are very high and exceed the concentration of metal ions. Hence excess H₃O⁺ ions occupied the active sites of the adsorbent and keep the metal ions free in the solution. This results in a competition between the adsorbate metal

ion and the excess H_3O^+ ions at very low pH. With an increase in solution pH the competition decreases and positively charged metal ions adhered free binding sites of the adsorbent. Moreover, the pH_{PZC} is another important factor which plays a significant role for higher adsorption capacity at high solution pH. The pH_{PZC} of this hybrid adsorbent was quantified as 5.4 for CAPC and 5.3 for CASB and therefore any solution pH below 5.4/5.3 the surface becomes positively charged and above 5.4/5.3 the surface becomes negatively charged in nature. Hence, any solution pH value above 5.4 metal ions adsorption due to the electrostatic force of attraction to form a surface complex with the adsorbent and enhance removal efficiency. The solid phase metal ion surface complexation takes place formed as per the following ionic equation

$$-MOH+OH^{-} = -MO^{-} + H_{2}O$$
(4.17)

$$-MO^{-} + /Cu^{2+} /Ni^{2+} = -M - O^{-} - - - Cu^{2+} /Ni^{2+} -$$
(4.18)

Therefore, in this study, we conducted all the experiments at a pH range of $5.9-6.3 \pm 0.2$ to obtain the maximum uptake of the metal ions.

Unlike heavy metals Phenol removal mechanism is complicated. There are many reported possible mechanisms are involved in Phenol adsorption. The most common mechanism is H₂ bonding with the carboxylic group and the carbonyl group(Franz, Arafat, and Pinto 2000). Other two-parallel mechanisms involve are electrostatic force and π - π dispersion force. The π - π force arises due to the interaction between the delocalized electron present in the basal plane of the adsorbent surface and the aromatic ring of the phenol molecule. (Radovic et al. 1997; Yang et al. 2014). Phenol is a weak acid and partially ionized in aqueous solution to form phenolate ion which is negatively charged. Therefore, Phenol will be adsorbed less at high pH due to surface deprotonation(Mukherjee et al. 2007). Moreover, some studies reported that low phenol concentration pH effect is not highly

significant, but adsorption reduces high pH above 9-10 due to exceeding the kPa value (9.6) of Phenol (Halhouli, Darwish, and Al-Dhoon 1995). In this study, also it has been observed that maximum adsorption capacity reaches from pH 5.5-7, above pH 7.5 adsorption capacity reduces significantly.

The main component of the adsorbent is carbon and alginate and they contain polar functional groups that can be involved in chemical bonding. These functional groups are actively responsible for cationic dye adsorption. The possible reactions occur for MB dye removal on CASB adsorbents are (WANG and ZHU 2007):

$$-CO^{-} + NC^{+}(Dye^{+}) \rightarrow -CO - Dye \tag{4.19}$$

$$-C00^{-} + NCH^{+}(Dye^{+}) \rightarrow -C00 - Dye \tag{4.20}$$

Variation of pH from 3 to 10 adsorption capacity increases from 3.24 mg/g to 9.34 mg/g and percentage MB dye removal was from 17.23% to 90.7%. At higher solution pH the adsorbent surface becomes negatively charged due to deprotonation, which enhances electrostatic force for attraction between the positively charged dye molecules and the adsorbent surface and hence the amount of dye adsorption and percentage MB removal was increased. This phenomenon also supported by point of zero surface charge, pH_{zpc} of the adsorbent. Any pH above the pH_{PZC} surface is positive and below pH_{PZC} surface is negative. It has been reported that adsorption of cation favours the solution pH higher than pH_{pzc} (Dawood et al. 2017).



Figure 4.1: Effect of pH on adsorption of heavy metals and Phenol

4.3.2 Effect of time and initial adsorbate concentration on adsorption kinetics

An initial metal dose of 25, 50, 75 and 100 mg/L respectively were used for all the metal ions for the present experiment MB dye concentration range varied from20-50 mg/L and for Phenol the concentration was upto 200 mg/L. For Zn²⁺, Cu²⁺and Ni²⁺ CAPC adsorbents were used (experimental work is done at Curtin University) and Pb²⁺, Cd²⁺ MB dye and Phenol CASB adsorbent was used (Experiments were conducted at IIT Kharagpur). An example of the time versus adsorption capacity profile at various concentration has given in Figure 4.2. It is evident from Figure 4.2 that the amount of adsorption increases with an increase in the initial metal ion concentration. For Cu²⁺ the amount of adsorption (q_t) increases from 21 mg/g to 68.6 mg/g for an initial metal ion concentration increases from 25 mg/L to 100 mg/L and , for Zn²⁺ capacity increases from 10.51 to 39.7 mg/g. Whereas, for Ni²⁺ ions, the amount of adsorption (q_t) increases from 15.82 mg/g to 41 mg/g on the same initial metal dose increment at a constant adsorbent dose of 1 g/L, solution pH of 5.6±0.2 and system temperature of 298 K. For Pb^{2+} , Cd^{2+} initial adsorbent dose was used 2 g/L and keep all other parameters same. Experimental results indicate that for Pb²⁺ adsorption capacity increases from 11.25 to 39 mg/g and Cd^{2+} it increased from 10.6 to 38 mg/g. Higher initial metal ion concentration increases the concentration gradient and reduces the mass transfer resistance which enhances the adsorption (Wang et al. 2015) but reduces the removal efficiency. Higher metal ion concentration increases the competition due to the presence of excess ions in the system to adhere with an adsorbent surface which reduces the overall removal efficiency of the system for the metal ions. Removal efficiency reduces from 62% to 38% for Zn^{2+} , 80% to 66% for Cu^{2+} and 65% to 43% for Ni²⁺ when initial metal ion concentration increases from 25 mg/L to 100 mg/L. For Pb²⁺ and Cd²⁺ the percentage of removal was decreased from 86% to 76% and 83 to 70% respectively. For phenol, initial concentration was varied from 25 to 200 mg/L. Form experimental analysis it was evident that adsorption capacity was increased from 10.11 to 15.97 mg/g and percentage removal was reduced from 42%-7%. Dye removal studies showed that the removal efficiency was 91.15% when the initial MB concentration was 20 ppm and it decreased to 42.96% at 50 mg/L concentration and the adsorption capacity q_e (mg/g) increased from 17.07 to 23.38 for the same range of MB concentration for the CASB adsorbent (graphical representation is not given for MB dye), From Figure 4.2, it was also evident that adsorption takes place rapidly for both the metal ion within the initial 30-45 minutes and reaches equilibrium with 120 minutes of operation. These types of fast kinetic are very significant for designing any continuous adsorption column using this novel hybrid adsorbent. From Figure 4.2, it was noticed that the adsorption of metal ions and organic pollutants like MB dye and Phenol on hybrid adsorbents was more or less 3 steps process where a very rapid metal ions adsorption occurred at the initial stage followed by slow intra-particle diffusion adsorption through the interior surface of solid adsorbent.



Figure 4.2: Effect of time and initial adsorbate concentration on adsorption

4.3.3 Effect of adsorbent dose on adsorption of metal ions, MB dye and Phenol

The role of adsorbent dose on the removal of all the pollutants been studied by varying adsorbent dose 1 g/L to 3 g/L. For phenol removal experiments adsorbent dose were varied from 1 g/L to 5 g/L at a constant initial metal concentration of 50 mg/L and temperature of 298 K. Typical representations for heavy metal ions adsorption with varying adsorbent doses are presented in Figure 4.3. Based on the adsorption capacity of an adsorbent, design and other optimization can be done for development a large- scale adsorption column. It is evident from the Figure 4.3 that amount of adsorption for Zn^{2+} 29.87 to 15.1 mg/g, Cu²⁺ reduces from 37 mg/g to 14 mg/g, for Ni²⁺ capacity drop down from 27 mg/g to 13 mg/g. Pb²⁺ was reduced from 31.2 to 14 3 mg/g, Cd²⁺ adsorption capacity decreases from 38.7 to 14.7 mg/g and for Phenol respectively when adsorbent dose increases from 1 g/L to 5 g/L capacity reduced from 21.1 mg/g to 9 mg/g. The number of available adsorbent sites per unit mass of total adsorbent in the total system is fixed. Hence, increasing overall adsorbent mass is likely to reduce active sites per unit mass of adsorbent and reduce adsorption capacity. Moreover, high adsorbent dose reduces net mass flux or a concentration gradient of the solute molecules between the bulk phase and surface of the adsorbent. On the other hand, studies are also reported that the adsorbent particles interact between themselves and any system containing a large number of solids sometimes block some of the active sites which leads to lower adsorption capacity. But increased adsorbent dose increases the percentage of metal ions removal significantly. For Zn²⁺ metal ion percentage removal increased from 42% to 90%, percentage removal of Cu²⁺ increased from 31% to 84%, for Ni²⁺ from 45% to 81%, for Pb²⁺ percentage removal increased from 62.2% to 84%, for Cd²⁺ ion it is 72.4 to 89%, percent removal of MB dye increased from 78.35% to 95.44% for the increase of CASB adsorbent dose from 0.05 to 0.25 g and for Phenol 42-95% respectively. Higher the

adsorbent dose, higher the active sites and hence percentage removal rate is not a function of active sites per unit mass of adsorbent. Therefore, higher adsorbent dose, the amount of metal ion adsorption increases the removal efficiency of the system.



Figure 4.3: Effect of adsorbent dose on the adsorption process

4.3.4 Effect of system temperature on adsorption kinetics

Metal ions perform differently with the change of temperature with the different adsorbent. Many researchers reported in their studies that metal ions removal efficiency increases with system temperature due to the increment of activities of various functional groups of the adsorbent. This enhanced activity of functional groups enhances the metals/organic substances removal capacity. Many studies also reported that higher system temperature reduces the mass transfer resistance. On the other hand, researchers

also reported that temperature affects adversely on metal ion removal efficiency (Gupta, Rastogi, and Nayak 2010; Tuzen et al. 2009) whereas some researchers found temperature has very less or no significant effect on system temperature. Here in this present study, the removal of all the metal ions and MB dye increased with system temperature which indicates that the system is endothermic but Phenol exhibits different behaviour with temperature changes. Adsorption capacity and percentage removal both increase with temperature change from 298 K to 308K, but both reduces when system temperature rises to 318 K (as shown in Figure 4.4). This observation indicates that removal of phenol is not favoured at high temperature. Same nature of Phenol adsorption behaviour has been reported earlier also. The examples of effect of system temperature on adsorption is shown in Figure 4.4. It was found from Figure 4.4 that the amount of Zn^{2+} adsorption capacity on CAPC increased from 28 mg/g to 34 mg/g, Cu²⁺ ion adsorption has increased from 31 mg/g to 39 mg/g and for Ni^{2+} it increases from 27 mg/g to 38 mg/g respectively for the same temperature range of 298 K to 318 K. The experimental results showed that for Pb²⁺ percentage removal increases from 70% to 74.8% (adsorption capacity increased from 35 mg/g to 37.5mg/g) which not very much. Similarly, for Cd²⁺ percentage removal changes from 68.3% to 73% (adsorption capacity rises from 34 to 36.5 mg/g) for the same temperature range with CASB adsorbent. For phenol adsorption capacity increased from 12.45 mg/g to 13.87 mg/g when temperature rises from 298 K to 308 K but further increase in temperature to 318 K adsorption capacity reduced to 10.02 mg/g. The percentage removal increased from 88% to 92% with the temperature rise from 303 K to 333 K and 20 ppm initial MB dye concentration and 3g/L adsorbent dose. Therefore, it can be concluded from the experimental observation that this hybrid adsorbent can be applied in large scale operation at room temperature and get a high percentage of metal and organic pollutants removal by adsorption.



Figure 4.4: Effect of system temperature on adsorption

4.3.5 Effect of the presence of salts/ electrolytes on adsorption

Actual process effluent contains various monovalent, divalent and trivalent salts. Therefore, to use the hybrid adsorbent for treatment of any real industrial wastewater it is important to know its adsorption performance in the presence of such salts. To ensure the superior applicability, we have tested the performance of the hybrid adsorbent in the presence of NaCl, CaCl₂, and FeCl₃ at different concentration. It has been observed from the experimental studies that for the high concentration of those salts (100 mg/L of other salt and 50 mg/L of Cu²⁺ and Ni²⁺) the percentage removal for Cu²⁺ was drop down from 74% to 59% and for Ni²⁺ percentage removal decreased from 58 % to 49% respectively. Therefore, it is clear that presence of other monovalent, divalent or trivalent salts decreased the amount of adsorption and percentage removal by attributing competition

with the heavy metal ion to adhere with the available active sites on the adsorbent surface. This ionic strength also changes the equilibrium constant among the bulk liquid and adsorbent interface which plays a significant role in the overall adsorption process. Moreover, size, atomic radius and molecular weight of the entire metal ion effect significantly on the adsorption behaviour. It has been reported that divalent and trivalent ions affect more compared to monovalent ions and being a transition metal Fe³⁺ has more electrons at outer orbit which causes helps to make a surface complex with an adsorbent surface more than the earth metal Ca²⁺. Hydration diameter has also significant contribution on metal ion adsorption. A metal ion having a smaller hydration diameter will adsorb fast. As hydration diameter of Cu²⁺ and Ni²⁺ is less than Fe³⁺ those metals adsorbed faster than Fe³⁺ ion. However, the reduction of metal removal in the presence of other salts is not very high, therefore, this hybrid adsorbent can be used for large scale application in the presence of other salts also. Similar effects have been found for other pollutants also, just difference in values of adsorption capacity or percentage removal for different adsorbate.

4.3.6 Adsorption kinetics and mechanism of adsorption

4.3.6.1 Pseudo first order and pseudo-second-order kinetic models

Pseudo-first-order and pseudo-second-order kinetic models were applied to the batch experimental data to study the kinetic behaviour and understand the mechanism of Zn^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} , MB dye and phenol adsorption on the hybrid adsorbents. The suitability of the kinetic model over a large number of experimental data set was examined form the linear regression coefficient (R^2) and the error function (χ^2). The error function was quantified from the $q_e(cal)$ verses $q_e(exp)$ as per equation (8). Here the experimental data were fitted with the pseudo-first-order model as described in equation

(3) with very poor linear regression coefficients values (\mathbb{R}^2) of 0.75 to 0.82, for which plots are not presented here. Therefore, this low value of linear regression coefficient (\mathbb{R}^2) suggested that this model is not applicable for the current adsorption system on the hybrid adsorbent (both CAPC and CASB) and also this model predicts very low values of q_e (cal). The second-order kinetic model both nonlinear and linear Eqn. 4.5 & 4.6, on the other hand, fitted very well with the experimental data at various physio-chemical conditions with high values of the linear regression coefficient (R^2 >0.98). Typical graphical pseudo-second-order fitted plots of linear and non-linear models are presented in Figure 4.5. The graphical representation is almost the same for other metal ions MB dye and Phenol only the different slope and intercept, which are not presented here. The error function or chi-square test was also proved the suitability of the pseudo-secondorder kinetic model by providing a low magnitude of the error function. The suitability of PSO model also indicates the electron sharing between solute and adsorbent. From the pseudo-second-order kinetic model, the initial sorption rate was also determined and it was found that the initial sorption capacity increases with system temperature. With an increase in temperature, the affinity of active sites increases and attracts the aqueous phase metal ion faster. Also increased temperature reduces the thickness of the diffusion boundary layer to enhance the sorption rate. It has been observed that initial sorption for Cu²⁺ increases from 1.03 to 1.53 and Ni²⁺ from 0.68 to 1.49 when system temperature increases from 298 K to 318 K. for rest of systems also the initial sorption rate increases except phenol. At 318K the sorption rate reduces as adsorption capacity reduces at this temperature.



Figure 4.5: Typical Pseudo-second –order kinetic model for a) Liner fit model b) non-linear fit model

Various fitted kinetic parameters obtained over the different initial solute concentration are tabulated in Table 4.1. From the Table-4.1, it is clear that the amount of adsorption increases with initial metal ion concentration and system temperature (the values are not presented here) for both the metal ions and organic pollutants. At the lower initial concentration, there is less competition between metal ions and adsorption site hence, there is a reduction in second-order kinetic constant K₂ was observed. Many studies on removal of heavy metals like Zinc (Zn²⁺) (Subrata Biswas, Bal, et al. 2019; Subrata Biswas, Sen, et al. 2019), Copper (Cu²⁺) and Nickel (Ni²⁺) (Randhawa et al. 2015, 2014) have been reported that their system also followed the Pseudo-Second –order kinetics. This also indicates that the adsorption is not only governed by only one step mechanism but also follow more than one steps to get adsorbed on the hybrid adsorbent for both the metal ions (Fierro et al. 2008; Sen and Gomez 2011).

Adsorbate	\mathbf{K}_2	\mathbf{K}_2	q _e (mg/g)	q _e (mg/g)	q _e (mg/g)	h	R ²	χ^2
	(g/mg.min)	(g/mg.min)	(calculated)	(calculated)	(experimental)	(mg/g.min)		
	Liner	Nonliner	Liner	Nonliner				
	model	model	model	model				
	0.0104	0.0124	10.81	10.53	10.51	1.29	0.99	0.031
$7n^{2+}$	0.0071	0.0077	20.8	20.32	20.21	3.1	0.99	0.0163
Zn	0.0053	0.0061	29.83	29.31	29.3	4.76	0.99	0.094
	0.0015	0.0022	40.1	38.5	38.21	2.32	0.99	0.086
	4.03×10 ⁻⁴	4.13×10 ⁻⁴	20	21.14	21.5	0.435	0.99	0.029
Cu^{2+}	3.71×10 ⁻⁴	3.91×10 ⁻⁴	37.21	3867	38.63	1.03	0.99	0.00161
Cu	8.43×10 ⁻⁴	8.61×10 ⁻⁴	53.3	54.85	54.9	3.04	0.99	0.0094
	4.79×10 ⁻⁴	5.01×10 ⁻⁴	67.21	69	68.6	3.13	0.99	0.0086
	1.66×10 ⁻⁴	1.87×10 ⁻⁴	16.2	15.9	15.82	1.44	0.99	0.0021
Ni ²⁺	3.79×10 ⁻⁴	4.01×10 ⁻⁴	27.6	29.68	29.63	3.04	0.99	0.026
111	3.53×10 ⁻⁴	3.84×10 ⁻⁴	32.1	32.71	32.6	3.31	0.99	0.024
	3.63×10 ⁻⁴	3.92×10 ⁻⁴	40.6	41.23	41.1	3.4	0.99	0.0065
	1.59×10 ⁻³	1.88×10 ⁻³	11.25	12.02	11.95	0.297	0.99	0.0435
Dh ²⁺	1.43×10 ⁻³	1.78×10 ⁻³	23.60	22.24	22.16	0.865	0.99	0.0936
ro	1.37×10 ⁻³	1.21×10 ⁻³	32.1	31.04	30.9	1.5	0.99	0.039
	5.54×10 ⁻⁴	5.74×10 ⁻⁴	39.02	38.5	38.42	1.72	0.99	0.61
	6.65×10 ⁻³	6.31×10 ⁻³	10.45	10.65	10.6	0.752	0.99	0.303
$\mathbf{C}\mathbf{d}^{2+}$	4.09×10 ⁻³	4.17×10 ⁻³	20.75	21.11	21.06	1.91	0.99	0.035
Cu	1.37×10 ⁻³	1.59×10 ⁻³	29.35	31.33	31.2	2.73	0.99	0.117
	1.71×10 ⁻³	1.48×10 ⁻³	38.2	37.9	38	2.79	0.99	0.022
	0.0018	0.0022	9.91	9.11	9.05	0.182	0.97	0.0085
	0.00171	0.00165	14.45	13.15	12.9	0.285	0.98	0.045
Phenol	0.00122	0.00131	23.53	22.23	22.4	0.647	0.967	0.0067
	0.00108	0.00114	32.57	31.48	31.57	1.12	0.96	0.0022
	0.00161	0.00153	51.33	49.63	49.55	3.76	0.95	0.0027
	2.42×10-3	2.27×10^{-3}	44.84	43.78	43.97	4.86	0.99	0.009
MD	5.3×10 ⁻³	4.79×10 ⁻³	65.36	59.43	59.16	2.22	0.98	0.031
MD	6.3×10 ⁻³	6.35×10 ⁻³	86.28	82.2	81.9	4.69	0.99	0.0023
uye	1.93×10 ⁻³	2.06×10-3	114.94	94.03	93.16	2.57	0.99	0.43

Table 4.1: Pseudo-Second-order kinetic parameters at different initial adsorbate concentration, temperature 308 K, adsorbent dose 1g/L.

4.3.6.2 Intra-particle diffusion model and mechanism of adsorption

Webber-Morris model is also known as the intraparticle diffusion model is very significant to understand the mechanism in any adsorption process (Subrata Biswas, Sen, et al. 2019). For control and process design of any large -scale adsorption system, it is very important to understand the mechanism of adsorption and it is underlying in the

apparent dynamic behaviour of the system. From the experiment it has been observed that adsorption of both metal ions is very fast at the initial stage then it became slow down. So, from the observation, it can be stated that the adsorption mechanism follows the following steps

- (1) Transport of metal ion from the bulk solution to the adsorbent surface
- (2) Diffusion through the boundary layer of the adsorbent surface
- (3) Adsorption on to the active site of the adsorbent surface
- (4) Intraparticle diffusion into the pores of the adsorbent

The overall adsorption rate will be controlled by the slowest steps, it may be external film diffusion or pore diffusion. Even the rate-controlling step may be distributed among two steps. In both cases, external film diffusion will be involved significantly in the overall adsorption process.

Webber-Morris model is commonly used to predict the rate-limiting step for adsorption system with porous materials. According to this model, a system is completely governed by intraparticle diffusion if the plot between q_t and $t^{0.5}$ produces a straight line passing through the origin. In this present study, the plot did not produce any single straight line. It produces multiple straight lines which indicate that the system is not only governed by intraparticle diffusion but a combination of multiple steps. The adsorption of heavy metals as well as organic pollutants may be controlled by external film diffusion or bulk diffusion at the initial stage of operation, and once the adsorbent surfaces are coated with solute molecules the adsorption may be controlled by the intraparticle diffusion. Example of this model has been given in Figure 4.6. From Figure 4.6, it is clear that all the adsorbate-adsorbent systems have three distinct sections. The straight lines are deviated from the origin at the initial stage due to the difference in the mass transfer rate between the final and initial stage of adsorption. The very initial section is fast with high slope indicates the bulk or surface diffusion. Next step is slower one and indication of pore diffusion-controlled zone and the last section is nothing but the equilibrium section with almost no slope. The slope of the second section obtained from the plot gives the values of the intraparticle diffusion coefficient and intercepts give the magnitude of the boundary layer of the particular system. All the fitted calculated kinetic parameters values at various operating conditions (various solute concentration has been presented here) are represented in a tabulated form in Table 4.2.

Adsorbate	K _{id} (IPD)(mg/g.min ^{0.5})	I (IPD)	
	0.907	8.1	
$7n^{2+}$	1.193	16.21	
LII	1.126	25.25	
	1.132	27	
	2.24	3.02	
Cu^{2+}	3.98	6.7	
Cu	4.25	26.5	
	5.96	29.3	
	1.44	4.48	
Ni ²⁺	3.04	4.8	
	3.31	7.5	
	3.40	12.6	
	0.561	4.42	
Pb^{2+}	1.18	6.72	
	1.917	14.77	
	2.12	17.08	
	1.25	1.84	
Cd^{2+}	1.71	3.62	
	2.23	5.86	
	3.44	/.45	
	0.854	1.21	
D1 1	0.976	1.89	
Phenoi	1.25	2.08	
	2.35 4.53	4.55	
	1.06	0.70	
	1.00	20 30.8	
MB Dye	3.14 3.48	30.0 34 2	
wid Dyc	3.40	30	
	5.70	57	

Table 4.2: Intra-particle diffusion model parameters

Some recent studies on removal of heavy metal ions (Afroze, Sen, and Ha Ming Ang 2016; Subrata Biswas, Sen, et al. 2019) and organic dye by using various adsorbent(Afroze, Sen, Ang, et al. 2016; Dawood and Sen 2012) have been used this model to understand the inside mechanism of the adsorption process.

4.3.7 Pore diffusion model

Like intraparticle diffusion, pore diffusion and pore diffusion coefficients are very significant for adsorption study. It has been reported that the pore diffusion coefficient is influenced by the surface property of the adsorbent. In this present study, the diffusion coefficients on the composite adsorbent were calculated from the equation given below:

$$t^{0.5} = \frac{0.03r_0^2}{D_p} \tag{4.21}$$

$$t^{0.5} = 1/K_2 q_e \tag{4.22}$$

where, $t^{0.5}$ is the half-life for adsorption, min, D_p is the pore diffusion coefficient, m^2/s , r_0 is the average radius of the adsorbent particles, m.

The experimental values of temperature-dependent pore diffusion coefficients for Zn^{2+} obtained in the range of 2.53×10^{-11} to 8.57×10^{-11} m/s² for Cu²⁺ were obtained as 7.08×10^{-10} , 9.15×10^{-10} , and 1.94×10^{-9} m²/s for 298K, 308K and 318K. On the other hand, for Ni²⁺ the values were 5.72×10^{-10} , 1.09×10^{-9} , 1.24×10^{-9} m²/s for the same operating temperature on CAPC adsorbent. Similarly, for Pb²⁺ the magnitude ranges from 8.31×10^{-10} to 1.49×10^{-9} m²/s, for Cd²⁺ 5.56×10^{-9} to 2.29×10^{-9} m²/s, phenol has the values 7.19×10^{-10} to 1.10×10^{-9} m²/s and MB dye the values are 1.97×10^{-8} to 8.53×10^{-9} m²/s. We have also found that some published studies for various heavy metal removal (Sen and Gomez 2011) also reported the same trend for the diffusion coefficient values with different magnitude.



Figure 4.6: Intra-particle diffusion model and the mechanism of adsorption

From the pore diffusion analysis this is evident that, phenol has the lowest diffusion coefficient. Which may reduce the overall mass transfer rate compared to the metal ions.

4.3.8 Activation energy of heavy metal adsorption and concept of the adsorption mechanism

To understand the adsorption type, further studies have been done based on the Arrhenius equation for all the adsorbates. Like the present study, kinetic data fit the pseudo-second-order model the Arrhenius model was fitted using the second-order rate constant to evaluate the rate parameters as per the following equation,

$$k_2 = k e^{\frac{-E_a}{RT}}$$
(4.23)

where, *K* is the temperature-independent constant (g/mg.h), E_a is the activation energy for the metal ion adsorption on the hybrid adsorbent (kJ/mol), R is the universal gas constant (8.314 J.K/mol), and T is the system temperature (K). A plot between lnk₂ versus 1/T produced a straight line, with a slope of $\frac{-E_a}{R}$ for both the metal ions at different operating conditions the activation energy required for the adsorption generally indicates the adsorption type physical or chemical. For complete physical adsorption, the activation energy value ranges from 5-40 kJ/mole, which indicates that the system is rapid, reversible and attain equilibrium fast. For chemical adsorption, larger activation energy is required (40-800 kJ/mole) as it requires higher forces. Here in this present case, the activation energy for Zn²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Cd²⁺ were found as 48.05, 19.94, 21.9, 26.32, and 10.63 kJ/mol respectively. From this activation energy data, it is clear that the system is dominated by physical adsorption but there is some ion-exchange mechanism is there (Randhawa et al. 2014). For organic pollutants, MB dye the value found was, 23.6 kJ/mole and for phenol the value was 28.4 kJ/mole for the present experimental conitions.

4.3.9 Adsorption isotherm studies

In this present investigation, the equilibrium data for both the metal ions and phenol were fitted with the linearized form of well-known Langmuir and Freundlich isotherm as described in Eqn. (4.10) and (4.13). The isotherm study gives the idea of maximum adsorption capacity of any adsorbent over a range of operating condition. Also, these isotherms give an idea regarding the heat of adsorption with surface area coverage. According to Langmuir isotherms assumption, there is no decrease with surface coverage, and Freundlich assumes that there is a logarithmic decrease (Fierro et al. 2008).

The Langmuir plot of C_e vs C_e/q_e and Freundlich plot lnq_e vs lnC_e both produce a straight line. From the plot, it has been observed that the Langmuir model fitted better (R²>0.95) than the Freundlich model(R²<0.9). An example of both linear and non-linear fitted model for Langmuir isotherm is presented in Figure 4.7. The Langmuir isotherm model assumes the existence of maximum limiting uptake corresponding to a saturated monolayer of adsorbate molecules on the adsorbent surface. According to this model, all the active sites have the same adsorption activation energy, no interaction with the exist adsorbed molecules and the limiting reaction step the surface reaction like heterogeneous catalytic reaction (Subrata Biswas, Meikap, and Sen 2019).

All the fitted parameters of this isotherm model were calculated from the experimental data for all the metal ions and phenols which are tabulated form in Table 4.3. To ensure whether the adsorption process is favourable or not we have quantified dimensionless separation factor R_L . If $R_L > 1$ system is unfavourable, $R_L=1$ system is linear, $0 < R_L < 1$ system is favourable and for $R_L = 0$ system is irreversible. The value of R_L was calculated as Eqn no (4.14). In this present investigation, the separation constants were found in the desirable range for all the adsorbate adsorbent system. For the isotherm studies, both the

non-linear and non-linear model were fitted. It was found that the values obtained were more accurate in the non-liner model fit as there is no modification done over the proposed isotherms.

In contrast, the Freundlich isotherm model assumes that the adsorption occurs on the heterogeneous surface of the adsorbent through the multilayer adsorption mechanism. It also describes that adsorbed amount increases with the initial concentration of the adsorbate (according to the Eqn. 4.10 & 4.11). The graphical representation for this isotherm has not to be given here as it produces a comparatively low regression coefficient. Table 4.4 shows all the calculated parameters for the Freundlich isotherm along with the correlation coefficient. The adsorption process is considered to be satisfactory if the Freundlich constant value takes the range from 1-10. From the experimental data analysis over a long range of experimental conditions, the Freundlich constants obtained for all the adsorbent on the hybrid adsorbent are in the satisfactory range. Therefore, it can be concluded that hybrid adsorbent is highly suitable for heavy metal adsorption as well as for the organic pollutants like phenol and MB dye.



Figure 4.7: Example of Linear fit and non-linear fit of isotherm models

Adsorbate	q_m (mg/g)	K_L (L/mg)	<i>R</i> ²
Zn ²⁺	89	0.028	0.975
	112	0.043	0.968
	120	0.075	0.986
Cu ²⁺	83.3	0.065	0.98
	96	0.074	0.978
	105	0.048	0.98
Ni ²⁺	78.3	0.029	0.974
	110	0.034	0.98
	129	0.047	0.980
Pb ²⁺	78	0.0186	0.97
	84	0.0193	0.98
	89	0.0198	0.97
Cd^{2+}	68	0.043	0.97
	71	0.0463	0.98
	79	0.0468	0.98
Phenol	20.20	0.0246	0.95
	23.51	0.035	0.96
	21.22	0.031	0.94
MB Dye	68.39	0,045	0.96
	69.11	0.0463	0.97
	71.21	0.0468	0.97

Table 4.3: Langmuir isotherm model parameters

Table 4.4: Freundlich isotherm model parameters

Adsorbate	n	K_f (L/g)	<i>R</i> ²
Zn ²⁺	1.25	3.27	0.91
	1.44	5.75	0.89
	1.49	6.73	0.9
Cu ²⁺	1.36	2.12	0.9
	1.60	2.22	0.87
	1.76	2.41	0.89
Ni ²⁺	1.79	4.57	0.86
	1.52	4.81	0.9
	1.86	4.93	0.88

Pb ²⁺	1.48	4.05	0.91
	1.51	4.48	0.9
	1.56	5.09	0.91
Cd^{2+}	1.39	2.43	0.91
	1.41	3.02	0.88
	1.45	3.73	0.89
Phenol	4.61	5.20	0.90
	5.33	5.68	0.87
	5.14	5.32	0.91
MB Dye	1.22	1.29	0.91
	1.42	1.38	0.88
	1.61	1.49	0.87

4.3.10 Adsorption thermodynamics and nature of adsorption

To know the nature of any kind of adsorption system whether it is endothermic or exothermic chemical or physical adsorption study and quantification of various thermodynamic parameters are very important. Here in this present study, various thermodynamic parameters like Gibes free energy change (ΔG^0), entropy change of the system (ΔS^0) and enthalpy change of the system (ΔH^0) were calculated. All the calculated parameters are given in Table 4.5.

 Table 4.5:
 Thermodynamic parameters for all the adsorbate at various system

 temperature

Adsorbate	Temperature (K)	$\Delta G^0(KJ/mole)$	$\Delta H^0(KJ/mole)$	∆S ⁰ (J/moleK)
Zn^{2+}	298 308 318	-18.64 -20.16 -21.68	26.655	152
Cu ²⁺	298 308 318	-19.48 -20.72 -21.96	17.47	124
Ni ²⁺	298 308 318	-17.36 -18.73 -20.103	23.463	137

Pb ²⁺	298 308 318	-17.50 -18.41 -19.31	9.52	90.7
Cd ²⁺	298 308 318	-17.294 -18.264 -19.234	11.62	97
Phenol	298 308 318	-14.535 -14.66 -14.78	-10.81	10.50
MB Dye	303 318 333	-5.21 -6.47 -7.62	19.12	80.28

From the Vant Hoff's equation as given in Eqn. no (4.12) a plot between $\log \left(1000 \times \frac{q_e}{C_e}\right)$ versus $\frac{1}{T}$ produces a straight line, having a negative slope with the value of $\frac{\Delta H^0}{R}$ and intercept yield $\frac{\Delta S^0}{R}$, where R is the universal gas constant (8.314 J/mol.K).

From the slope and intercept entropy change of the system (ΔS^0) and enthalpy change of the system (ΔH^0) were calculated for both the metal ions. From Eqn. 4.16 Gibes free energy change (ΔG^0) was calculated. The thermodynamic parameters proved that the system is endothermic, spontaneous and physical adsorption in nature.

4.4 A comparative study for both the adsorbents

It has been mentioned earlier section that some part of the present works were performed at Curtin University Perth Australia and rest were done at IIT Kharagpur India. Depending upon the availability two different types of precursors have been used as waste biomass. Pinecone biochar used at Curtin university and Sugarcane bagasse biochar. Therefore, a study is required to perform for both adsorbents to find its adsorption capacity under identical operation so that a clear conclusion can be done on the performance of the developed adsorbent. Hence, both the adsorbents are used for removal of Ni^{2+} , Zn^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Phenol and MB Dye.

The surface morphology along with EDS analysis for all the adsorbent and adsorbate are presented in Figure 4.8 and 4.9 and 4.10. The adsorption capacities of both of them are found from the Langmuir monolayer model and have been produced in Table 4.6.

Adsorbate	Adsorption capacity (mg/g)		
	CAPC	CASB	
Zn^{2+}	95.86	75.18	
Cu^{2+}	89.09	88	
Ni ²⁺	110.84	144.29	
Pb^{2+}	78.4	86	
Cd^{2+}	71.22	72	
Phenol	16.33	20.20	
MB Dye	70.66	68.4	

Table 4.6: The adsorption capacities of both the adsorbents at identical experimental conditions at initial adsorbate Volume 50 mL, adsorbent dose 1g/L, temperature 308 K



Figure 4.8: Surface morphology changed for CASB after interaction with adsorbent a) Zn^{2+} b) Cu^{2+} c) Ni^{2+} d) Cd^{2+} e) Pb^{2+} f) Phenol




Figure 4.10: Surface morphology changed for (a) CASB and (b) CAPC after interaction with MB dye

4.5 Recycling of the adsorbent

Various methods and materials are reported for adsorbent regeneration (Park et al. 2007). Here in this study eluent HNO₃ of 0.05M was used to desorb both Zn^{2+} and Pb^{2+} . As alginate material is weak Alginic acid regeneration can be possible by using an acid like HNO₃ or H₂SO₄ (Park et al. 2007).

It can be observed from Table 4.7 that the percentage regeneration capacity in the first cycle is above 85% for both the cases and the percentage regeneration in the second cycle dropped down below 80% and the regeneration in the third and fourth cycle decreased significantly below 40%. The reduction in recyclability is believed to be due to permanent or semi-permanent complex formation which makes desorption difficult. The usability of the adsorbent for a few cycles provides the opportunity for this novel adsorbent to be used for the large-scale operation. Besides its low cost, easily decomposable nature makes is competitive.

Cycle No	%Adsorption (Zn ²⁺)	Mode Section (Zn ²⁺)	%Adsorption (Pb ²⁺)	%Desorption (Pb ²⁺)
1	78	85	81	88
2	52	73	62	76
3	41	35	45	59
4	34	29	33	38

Table 4.7: Adsorption desorption study for Zn^{2+} (CAPC adsorbent) and Pb²⁺(CASB adsorbent)

4.6 Conclusion

In this chapter, detailed studies have been conducted to evaluate the performance of both types of adsorbents namely CAPC and CASB for removal of a group of heavy metals and organic pollutants Phenol and MB Dye. All the targeted material used in this study are regarded as highly hazardous and carcinogenic. For the CAPC adsorbent the capacity of adsorption is like Ni>Zn>Cu>Pb>Cd>MB Dye>Phenol (capacities are 110.84, 95.86, 89.09, 78.4, 71.22, 70.66 and 16.33 mg/g respectively) on the other hand, CASB adsorbent has the adsorption capacity order like, Ni>Cu>Pb>Zn>Cd>MB Dye>Phenol (capacities are 144,29, 88, 86, 75.18, 72, 68.4 and 20.20 mg/g respectively). The Pseudo-second-order kinetic model fits well with the experimental data. Both the liner form and nonlinear form have been analysed and it has found that the predicted values are much closer with the non-linear solution in MATLAB. From the kinetic studies, it was found that the process is quite fast and reached equilibrium within 90 minutes for all the heavy metals, but adsorption of phenol is slower. It was also found that the adsorption process involves multiple steps including, fast bulk or surface diffusion for first 15-30 minutes, next it is intraparticle or pore diffusion and last the equilibrium condition. The isotherm

model also studied for both linear and non-linear form. The difference between the obtained parameters is very close in both the form and the adsorption process is mainly followed by Langmuir monolayer isotherm. Other isotherm parameters confirm that the adsorption of all the components is favourable. The thermodynamic behaviours are very similar for all the heavy metals as well as MB dye are endothermic process and adsorption capacity increases with temperature. But Phenol exhibited some difference as adsorption capacity reduces at a temperature above 313 K. which indicates that, the system is exothermic after a certain range of temperature and it has also found from the enthalpy values. However, the overall process is spontaneous and favourable. The activation energy of the process also confirms the nature of adsorption. The process is mainly governed by physical adsorption but, there is some portion where some chemical interaction, ion exchanges are involved. Therefore, from the elaborate investigation in a batch study, it can be concluded that the synthesized material is very promising as an alternative low-cost adsorbent compared to others reported adsorbent and some Commercial activated Carbon. Hence the low cost and lightweight adsorbent materials can be recommended to be used as a bed material for a Semifluidized bed reactor.

Chapter 5

Performance Analysis of Semifluidized Bed Reactor for Heavy Metals, Phenol and Steel Plant Effluent treatment

Chapter 5⁴

Performance Analysis of Semifluidized Bed Reactor for Heavy Metal, Phenol and Steel Plant Effluent Treatment

5.0 Introduction

The concept of semifluidization was first introduced in the late fifties by Fan and co-workers(L. . Fan and Wen 1961). Later many studies reported its specific advantages over other conventional Liquid-solid or Gas-liquid-solid systems. Still, there is very limited application of such a novel reactor in wastewater treatment research area. Few theoretical studies and model-based studies have been reported(Alade et al. 2011; De, Sikder, and Narayanan 2017; Meikap and Roy 1997; Narayanan and Biswas 2016) so far which is very less compared to other reactors like packed bed and fluidized bed system. The packed and fluidized bed systems are well established and use in many fields of industrial applications including water treatment purpose(Aksu, E, and Kutsal 1998; Andalib et al. 2014; Banat et al. 2007; Dineshkumar, Sivalingam, and Thirumarimurugan 2015).

A semifluidized bed reactor system comprising two classical reactors, packed bed section followed by a fluidized section in series of a single column has been developed (Fan and Hsu 1981; L. . Fan and Wen 1961; Fan, Yang, and Wen 1960) in this research and applied in the removal of various heavy metals such as Zn^{2+,} Cu²⁺, Ni²⁺, Pb²⁺, Cd²⁺ and organic pollutant like Phenol with a semi-continuous mode of operation. It has several advantages like continuous reaction at high liquid flow rate without particle washout, easy separation, and high mass transfer separation, etc. (Meikap and Roy 1995, 1997;

⁴This chapter work has been published in "**Subrata Biswas**, Shubham Sharma, Subhrajit Mukherjee, Bhim Charan Meikap, Tushar Sen, *Process modelling and optimization of a novel Semifluidized bed adsorption column operation for divalent heavy metal removal*, Journal of Water Process Engg. 2020 (in Press)"

Narayanan 2019; Narayanan and Biswas 2016) which gives a feasible option for real industrial wastewater treatment situation. The hindrances of fluidized beds, such as solid back-mixing, particle attrition, and surfaces erosion, and those of packed beds, like, non-uniform bed temperatures, solid's segregation and channelling (González et al. 2001; Sokol 2003), can be partially taken care of in a semi-fluidized bed reactor. So, a combination of two such ideal reactors must give a synergistic effect and can be a benefitted one. Therefore, the present study is an attempt to analyse the performance of such a rector for the removal of various synthetic wastewater and real industrial wastewater. As per our knowledge, to date, no such study has been reported for the removal of such pollutants in a semifluidized bed reactor using the alginate biochar composite adsorbent as bed material.

Therefore, the present study aimed to investigate various heavy metals and organic pollutants removal efficiency using cost-effective sustainable solid biomass sugarcane bagasse based composite (CASB) adsorbent bed materials through close circuit semifluidized bed operation under various operating process conditions. Further, the performance of the system has been analysed with actual steel plant effluent to ensure the SFBR's suitability in real industrial application.

5.1 Materials and method

The aqueous solution of Zn^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} , and Phenol was prepared by dissolving the calculated amount of $Zn(NO_3)_2$. $6H_2O$, $Cu(NO_3)$. $6H_2O$, $Ni(NO_3)_2$. $6H_2O$, $Pb(NO_3)_2$. $6H_2O$, $3Cd(SO_4)_3$.7 H_2O and 99.5% Phenol respectively in double-distilled water. All the chemicals used were of laboratory reagent grade and procured from Sigma Aldrich Pvt. Ltd. The stock solution was prepared for 1000 mg/L. The working solutions of various concentrations were prepared by series dilution method. The pH of the working

solution was adjusted by 0.1 M HNO₃ and 0.1M NaOH using a pre-calibrated digital pH meter.

A semifluidized bed adsorption column has been used here to evaluate its performance for the removal of Zn²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Cd²⁺ and Phenol from its aqueous solution in a closed-circuit mode. The experimental setup is a Perspex tube of inner diameter 5 cm and height 25 cm. A gas-liquid distributor has been placed at the bottom of the column and a top restraint is there to restrict the solid phase at a certain fluid velocity to create a packed zone across the top restraint. The detailed experimental set-up has been discussed in Chapter-2. A weighted amount of hybrid adsorbent beads was loaded in the column to obtain a certain bed height. In this investigation, bed heights were taken 5, 10 and 15 cm. The feed flow rate was controlled by a single-phase mono-block centrifugal pump at a variable flow rate (2-6 LPM) by a pre-calibrated rotameter. A constant airflow rate was maintained at 0.5 LPM from an air pump. Feed concentration for all the metal ions was varied from 10-30 mg/L (for Cd²⁺ concentration range was 5-20mg/L) and for Phenol the inlet concentration range varied from 25- 100 mg/L. The concentration range was selected based on the permissible limit of such dangerous pollutant in the surface water. The above concentration range is also very high and industries release wastewater having less concentration than the chosen one for the present investigation. Moreover, high concentration metal ion or Phenolic solution in the laboratory is also a very risky job. Keeping in mind all the safety precaution the above concentration has been used for the experimental work.

A sampling point is there in the setup to collect the effluent sample after a specific time interval. Residual concentration for all the metal ions was measured by AAS and Phenol concentration was measured in HPLC by the C18 column at 270 nm wavelength. All the experiments were conducted at room temperature with an error between 5-6%.





Semifluidized bed under operation

Bed at Semifluidized condition

Figure 5.1: Pictorial view of Semifluidized bed under operation (a) complete experimental set up (b) semifluidized bed only reacting section

The range of various operating conditions for the experimental run are given in Table 5.1

Operating Parameters	Values
Initial adsorbent bed height	5-15 cm
	10-30 mg/L
Initial solute concentration	5-20 mg/L (for Cd ²⁺)
	25-100 mg/L (for Phenol)
Liquid flow rate	2-4 LPM
Airflow rate	0.5 LPM

Table 5.1: Range of the operating parameters for the semifluidized bed operation

5.2 Results and discussion

The synthesized composite bio adsorbents exhibit very good adsorption capacity for both the heavy metals and phenol which has been presented in the previous chapter. Therefore, this material has been used as the solid phase of an SFBR system. The system is called a closed-loop because the effluent is recirculated over the period. The reason behind such type operation is because the system needs a minimum fluid velocity to make the bed fluidized and some higher to obtain the semifluidized condition and by recirculation, the adsorbent –adsorbate interaction will be more and maximum utilization will be achieved. For this present investigation, three parameters were varied to find out the performance of the bed. The initial concentration of both metal ions solutions, initial bed height (dose of adsorbent) and the liquid flow rate. The system was operated at room temperature and pH was maintained at the optimum value obtained from the batch study. There are few assumptions have been taken care of for the experimental investigation. The assumptions are:

- > The composite adsorbents are uniform in size
- > There is no wall effect and column to particle diameter ratio was constant (25)
- There is no radial concentration gradient for both the liquid and solid phase in the column
- Adsorption rate is determined from the linear driving force model based on batch kinetics data
- > Equilibrium is represented by the Langmuir equation
- There is no dispersion of adsorbate in the solid phase
- > The solid adsorbent is uniformly distributed in the fluidized section
- > The liquid phase is described by the axial dispersion model
- Each section will behave like individual PFDR reactors in series- a packed section followed by the fluidized section(De et al. 2017; Narayanan and Biswas 2016).

The adsorption capacity of the bed has been calculated from the following equation (Afroze, Sen, and H. M. Ang 2016)

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ad} dt$$
(5.1)

Here, q_{total} is the total amount of dye adsorbed throughout the operation, Q is the feed flow rate (L/min), C_{ad} amount of dye adsorbed on the adsorbent surface (mg).

5.2.1 Effect of initial metal ion and phenol concentration on SFBR performance

Effect of metal ion concentration or adsorbate loading on the performance of any adsorption-based reactor is very important. The bed performance also depends upon this parameter. In this present investigation, the initial concentration for Zn^{2+} , Cu^{2+} , Ni^{2+} , Pb²⁺ was selected as 10, 20 and 30 mg/L, for Cd²⁺ was 5, 10 and 20 mg/L and for Phenol initial concentration was 25, 50, 100 mg/L. Various reports showed that for these pollutants this concentration is significantly higher. Therefore, this value was chosen for the operation. Disposing of a high amount of water containing such heavy metal after the operation (if all the metal does not uptake by adsorbent) is also very harmful. The performance curve for both metals and phenol showed that for higher concentration it takes a long time to reach the equilibrium. At this low bed volume, the retention time or contact time is also comparatively lower. Therefore, for high metal contain solution required enough time to get adsorb on the adsorbent surface and with the increasing metal dose equilibrium time was also increased. For low concentration range of 10-20 mg/L, Zn²⁺ reached equilibrium at around 120 minutes, but for a high concentration of 30 mg/L 240 to 300 minutes are required to reach equilibrium. For 10 mg/L initial concentration, maximum percentage removal was 82% and for 20 and 30 mg/L, percentage removal reduced to 72.36 and 69.83%. For, Cu^{2+} metal ion the equilibrium time is comparatively faster for all the concentration. When the initial concentration 10 mg/L equilibrium time was 60-90 minutes and for 20 and 30 mg/L 360 minutes was required. It has also been observed that Ni²⁺ needs more time to reach equilibrium even at the lowest concentration. Almost 180 minutes were required when initial solute concentration was 10 mg/L and more than 360 minutes were required for the metal ion concentration of 20 and 30 mg/L. From the experimental data, it was also found that percentage removal for Ni²⁺ was reduced from 72 % to 70.43% over the concentration range.

For Pb^{2+} treatment, when the initial metal dose was 10 -20 mg/L within 100 minutes the system almost reached the equilibrium. For 30 mg/L initial concentration the system takes almost 240 minutes to achieve the equilibrium. The same scenario was also observed for Cd^{2+} metal ion adsorption. For 10 mg/L solution, equilibrium reached within 240 minutes with maximum percentage removal of 96% for Pb^{2+} and higher concentration of 20 and 30 mg/L Pb^{2+} has removal efficiency 92% and 87% respectively.

For Cd^{2+} the lowest concentration was used 5 mg/L and bed efficiency was found 97.38%. At a higher initial metal concentration of 10 and 20 mg/L, the bed efficiency or percentage removal was found 84.3% and 80.3 % respectively.

In Phenol removal study removal rate is less and the equilibrium time is higher compared to the metal ions. The lowest initial concentration was 25 mg/L and it took almost 300 min to reach equilibrium with 62% removal. When initial concentration increased to 50 and 100 mg/L 360 to 400 minutes were required for the system to reach the equilibrium with a removal efficiency of 56.2% and 53.4%.



Figure 5.2: Effect of initial metal ion concentration on performance of Semifluidized bed reactor (a) Cu^{2+} (b) Ni^{2+} (c) Pb^{2+} and (d) Cd^{2+} at initial adsorbent bed height 10 cm, Feed flow rate 2 LPM

5.2.2 Effect of initial bed height or adsorbent dose on SFBR performance

Initial concentration, initial static bed height or initial solid loading is also a very important parameter for determination of bed performance. In this present study, three different bed heights were taken as 5, 10 and 15 cm. Total bed height was 25 cm. every 5 cm bed height was equivalent to 75 gm of weight adsorbent. So, for higher bed height adsorbent amount is more. From the experimental analysis, performance behaviour has been presented in Figure 5.3. It has been evident that for higher bed height lower the time

taken to reach the equilibrium. When the adsorbent amount is higher, the adsorbate molecules getting more available active surface area to interact with. Therefore, for a particular amount of metal ions, it adsorbs faster due to less competition for the adsorbent site. With an increase in bed height, packed bed formation tendency increases in a semifluidized bed, which reduces the axial dispersion coefficient and enhance the diffusion of adsorbate in the adsorbent. At initial bed height of 5 cm and initial metal ion concentration of 20 mg/L removal efficiency of Zn²⁺ is 64.36%, Cu²⁺ is 74.45%, Ni²⁺ is 77.9%, Pb²⁺ removed upto 86% and Cd²⁺upto 78.6 %. When bed height increased from 5 to 15 cm percentage removal increased to 77.5%, 82.75%, 81.75%, 98.56% and 90.55 for Zn²⁺, Cu²⁺, Ni²⁺, Pb²⁺ and Cd²⁺ respectively. At the same bed height change, phenol removal increases from 47% to 58% for an initial concentration of 50 mg/L. At the same amount of adsorbent and solute concentration different removal efficiency achieved because of difference in solute to adsorbent surface affinity or mass transfer coefficient. This phenomenon is later evident from the mass transfer coefficient analysis from the dynamic model of the individual solute-adsorbent system.



Figure 5.3: Effect of initial adsorbent loading on performance of Semifluidized bed reactor (a) Zn^{2+} (b) Cu^{2+} (c) Ni^{2+} and (d) Pb^{2+} at initial concentration 20 mg/L, Feed flow rate 2 LPM

5.2.3 Effect of liquid flow rate on SFBR performance

The liquid feed flow rate is another important variable to determine the performance of the novel reactor. The hydraulic retention time or the residence time of the solute inside the reactor column depends upon the feed flow rate. The residence time of the system can be evaluated from the equation given below:

$$\tau = \frac{\varepsilon.V}{Q} = \frac{\varepsilon}{Q_{rel}}$$
(5.2)

$$\varepsilon = \frac{V_b - V_p}{V_b} \tag{5.3}$$

Where, τ is the residence time, (h), V is the void volume of the bed (m³), Q_{rel} the relative volumetric flow rate of the liquid (m³/h), ε is the porosity of the bed, V_b and V_P are total bed volume and total particle volume respectively, (m³).

Another important parameter associated with the residence time is hydraulic loading, solid loading and no off passes. The hydraulic loading and solid loading of the system have been expressed as,

$$H.L(Hydraulic Loading) = \frac{Q}{M} = \frac{Q}{V.\rho_b} = \frac{1}{\tau.\rho_b}$$
(5.4)

$$S.L (Solid loading) = \frac{V.\rho_b}{V_{tot}}$$
(5.5)

$$R (No of cycle) = \frac{Q.t}{V_{tot}}$$
(5.6)

Where, Q volumetric flow rate (m³/h), V_{tot} is the total effluent treated (m³), t is total treatment time (h)

In a fixed bed system generally, very low flow rates have been maintained to ensure the maximum possible contact between the adsorbate and the adsorbent. But in case of the reactor of this particular investigation is very different from normal fixed bed operation as it requires a minimum flow rate to create a packed zone at top of the reactor. Therefore, the flow here is quite high, which is good for a large-scale reactor to treat a huge volume of effluent. However, to ensure maximum contact between adsorbate and the adsorbent the system is run as a closed-loop form. From Figure 5.4, it has been evident that for all the treated pollutants the characteristic curves are similar in trend. It is also clear, that

when the flow rate is 2 LPM, equilibrium reached quickly for both the heavy metals and phenol. It took 100 min to reach the equilibrium and after that, there is no significant reduction of the outlet concentration. But for a higher flow rate, the outlet concentration is much higher for the same time of operation. This indicates that at higher liquid flow rate the retention time or the contact time between the solute and the adsorbent is less hence, less conversion has been achieved over the same time of operation. At flow rate 2 LPM percentage removals were 75%, 78.4,72.6% %, 95.5, 81.5% and 56% for Zn^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} and Phenol. At high liquid flow rate of 6 LPM bed efficiency drop down to 62.5%, 52%, 62.3%, 62.7 %, 65.75% and 44% respectively. Therefore, a very high flow rate is not recommendable for such types of reactors in large scale operation also.



Figure 5.4: Effect of Liquid flow rate on performance of Semifluidized bed reactor (a) Zn^{2+} (b) Ni^{2+} (c) Pb^{2+} and (d) Cd^{2+} at initial concentration 20 mg/L, initial adsorbent bed height.

5.2.4 Performance analysis of the semifluidized bed reactor for real industrial effluent

To establish a novel reactor like this the reactor performance must be analysed with real effluent. In synthetic effluent, only one pollutant component is there but in real industrial effluent there are many pollutants are present. Therefore it will be a real challenge to establish a system for industrial purposes. In this present investigation, raw steel plants liquid effluents were collected from Durgapur steel plants (DSP), Durgapur, Burdwan,

India and is characterised. After collecting the sample was kept in an airtight container and bring to IIT Kharagpur campus and stored in Refrigerator for analysis and experiments. The characteristic of the raw and treated effluents are summarised in Table 5.2

Parameters	Value before treatment	Value after treatment	
pH	7.9-8.2	7.1-7.3	
TDS (mg/L)	4.82×10^{3}	1.12×10^{3}	
COD (mg/L)	6200-6400	<1000	
BOD (mg/L)	355	85	
Phenol (mg/L)	203	64.3	
Ni ²⁺ (mg/L)	2.08	< 0.002	
Cu^{2+} (mg/L)	1.18	< 0.001	
$Zn^{2+}(mg/L)$	ND	ND	
Pb ²⁺ (mg/L)	ND	ND	
Cd ²⁺ (mg/L)	ND	ND	

Table 5.2: Characterisation of Steel Plant wastewater before and after treatment.

Our prime target was to analyse the removal of BOD, COD, Phenol and Heavy metals from the untreated steel plant effluent. The untreated effluent's pH was adjusted to 7, the total bed height of the bed was 15 cm and the flow rate was maintained and the experiment was run for 540 minutes to ensure the system reaches equilibrium by that time. Samples were collected at a specific time analysed as per the method mentioned earlier. From the analysis, it has been evident that phenol removal was achieved up to 68% and Ni²⁺ and Cu²⁺ were almost eliminated. BOD reduced from 355 mg/L to 85 mg/L and COD reduced from 6400 to <1000 mg/L. Therefore, from the above analysis, it can be concluded that this developed Semifluidized bed adsorption column with the composite hybrid adsorbent solid material are useful industrial effluent treatment operation



Figure 5.5: Effect of a) initial adsorbent bed height b) initial phenol concentration c) Liquid flow rate on the performance of Semifluidized bed reactor, d) Performance of SFBR on the removal of phenol from steel plant effluent

5.2.5 Effect of Airflow rate on the performance of SFBR

The overall study has been conducted at a constant airflow of 0.5 LPM. Therefore, to ensure the effect of air on the performance of a semifluidized bed reactor one set of experiments were carried out without air flow rate. The experimental conditions are initial adsorbent bed height 10 cm, initial Pb^{2+} ion concentration 20 mg/L, liquid feed flow rate of 2 LPM. From the analysis, it has been found that when there is no airflow the

percentage removal for Pb^{2+} reduced from 96% to 88%. This indicates that airflow has a significant contribution to the performance of the Semifluidized bed reactor. Air enhances the mixing of the liquid-solid system to enhance the removal rate and gas-liquid-solid semifluidization may be simultaneously removed of gaseous pollutants also, but it must be reminded that at a very high airflow rate there will be the formation of large bubbles which will reduce the mass transfer between the bulk phase and the surface of the adsorbent.

5.2.6 Comparison of performance of SFBR with fixed/packed bed and fluidized bed adsorption column

Some literature-based investigation has been done in this study to find out the superior performance of a Semifluidized bed adsorption column over normal packed bed/fixed bed and fluidized bed adsorption column at very similar experimental conditions. The performance has been analysed based on operation time, the total volume of effluent treated, initial concentration and percentage removal. It has been found that most of the packed bed reactors required very long operational time and less amount of water treated, on the other hand, very few reported studied were found for the fluidized bed adsorption column. However, the studies reported that in fluidized bed percent removal is less though the operation time is also high.

Few reported results have been represented in Table 5.3.

142

Type of bed	adsorbate	Flow rate mL/min	Volume treated	Operation time (min)	Reference	
			Litre			
	Cu(II) (maximum metal conc. 55 ppm)	5-30	15	1580	(Amirnia, Ray, and Margaritis 2016)	
	Zn(II)/Cu(II) maximum conc for Zn(II) was 0.15 and Cu(II) 0.12 ppm)	5	0.4	80	(Tsibranska and Hristova 2010)	
	Zn(II)/Cu(II)/Ni(II)	3	2.4	800	(Suzaki et al.	
Packed bed	(maximum metal conc 0.2 ppm)				2017)	
	Pb(II)/Cd(II)	10-25	8	800	(Zulfadhly, Mashitah, and Bhatia 2001)	
	Cd(II)	2-9	2.16	1080	(Muhamad, Doan, and Lohi 2010)	
	Pb(II)/Cd(II)	10-20	12	1400	(Lim and Aris 2014)	
	Zn(II)/Cu(II)/Ni(II)		10	4day	(Zhou et al.	
	(maximum metal conc 20 ppm)		(70-75% removal)		1999)	
Fluidized bed	Zn(II) (maximum conc	68.9	10	480	(Stylianou,	
	10 ppm)		(68% removal)		Inglezakis, and Loizidou 2015)	
	Pb(II)/Cd(II)	0.015 m/s	10	70	(Tsibranska	
		(velocity)	(30-35% removal)		and Hristova 2010)	
	Pb(II)	300 (flow	15	4000	(Corrêa et al. 2007)	
		velocity)	(88% removal)			

Table 5.3:	Performance	of	packed/fixed	bed	and	fluidized	bed	adsorption	column	for
heavy meta	ıl removal									

5.3 Conclusion

The performance of the developed semifluidized bed has been analysed for the removal of aqueous phase Zn^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , and Cd^{2+} ions, and Phenol and the study were extended for the raw steel plant effluent treatment operation. The used hybrid adsorbent bed materials were synthesized from waste biomass-based biochar and an alginate-based The semifluidized bed also performed well for the removal of such biopolymer. hazardous heavy metal ions from aqueous phase up to 98%. But, the bed performance varies with the nature of the pollutants and it's properties like the degree of hydration, mass transfer coefficient, surface complex formation tendency etc. The equilibrium time for the system was 240-300 minutes which is satisfactorily lower compared to individual packed bed or fluidized bed. In this investigation, a real-time dynamic model for the novel system can be developed based on Langmuir kinetics of adsorption and dispersion flow principle. Axial dispersion coefficients for both the sections as well as mass transfer coefficients for both metal ions can be estimated from the model. The bed being a closedloop has an advantage of more contact time compared to open-loop systems. Thus, it ensures maximum liquid-solid contact and the highest removal efficiency. Moreover, the introduction of gas-phase forms higher packed section at lower fluid velocity and increase the retention time of solute inside the reacting system. Maximum capacity for Zn²⁺, Cu²⁺, Ni^{2+} , Pb^{2+} , Cd^{2+} and Phenol for the bed operation were found 42.4, 43.27, 46.12 54.4, 36.8 and 89.35 mg/g respectively. The actual effluent collected from the steel plant also tested in the bed and found satisfactory results for the removal of Phenol, COD, BOD and some heavy metals. Also, some comparative studies exhibit that, the Semifluidized bed reactor has the synergistic effect of both the packed and fluidized bed and can remove many organic and inorganic pollutants simultaneously.

Chapter 6 Mass Transfer Dynamic Modelling and Process Optimization of SFBR Performance

Chapter 6⁵

Mass Transfer Dynamic Modelling and Process Optimization of SFBR Performance

6.0 Introduction

In recent years several statistical design and process optimization techniques are successfully adopted in the various industrial unit operations such as optimizing the process variables of leaching and beneficiation of coal, condition optimization for preparation of activated carbon and many more (Aghaie et al. 2009; Behera et al. 2018; Das and Meikap 2017; Gratuito et al. 2008; Panda et al. 2014; Tripathy, Biswal, and Meikap 2016). Optimization of process variables for adsorptive removal of heavy metal or other organic pollutants is also reported (Niad, Zaree, and Tahanzadeh 2016; Saranya et al. 2017; Sarkar and Majumdar 2011). But, the optimization of various operating parameters on novel composite adsorbent's synthesis and its application in water treatment through the SFBR process has not been reported yet.

6.1 Theory of Response Surface Methodology (RSM) optimization technique

Response Surface Methodology (RSM) can be defined as a set of mathematical and statistical tool or technique to build some empirical models. The objective of the optimization tool is to define a regression-based model and optimize an output variable (called the response) which is governed by several independent input variables. Set of experiments were performed by changing all the input variables to identify the reason for

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output or response variable change. The RSM tool is employed in design optimization to minimize or reduce the cost of expensive analysis (e.g. finite element method or CFD analysis) and the numerical noise associated with the analysis.

Here, an attempt has been made to analyse the effect of operating parameters for various heavy metals and Phenol removal by Alginate biochar composite adsorbent in a novel Semifluidized bed adsorption column with the response surface methodology (RSM) system by central composite design (CCD) technique. For a quadratic surface fitting, this method is very suitable and it optimizes the independent system variables with less number of experimental data set. Moreover, this method is efficient to find the interacting effects of the operating parameters.

The pictorial view of the CCD technique has been represented in Figure 6.1. From the Figure, it is understandable that in this method there are 2^n factorial runs (n is the no of independent variables) improved with 2n axial runs and n_c is the central runs to estimate the experimental errors. As this is a three-factor experiment the experiment is designed and coded as (± 1) notation and all the axial points are (± α ,0,0,0), (0,± α ,0,0), (0,0, ,± α ,0) (0,0, ,± α) respectively. All the Centre points are at (0,0,0,0) coordinate. This CCD model predicts the optimum condition more accurately over the normal factorial design because of axial points data and central point data. Also, this model is further improved with compared to Box-Behnken model due to more data points used for optimization calculation.

All the independent variables are examined at 2 (two) levels. According to the theory as the numbers of independent parameters (n) increase, total numbers of experimental runs increase rapidly for every full repetition of the design. It has been reported that discrete 2^{nd} Order effect cannot be projected distinctly by 2^{n} factorial design only. Hence, the CCD technique was adopted for investigating the quadratic effect and develops the model equation for the removal of aqueous phase Zn^{2+} ion by the composite adsorbent.



Figure 6.1. A pictorial view of CCD design

The output or response (removal efficiency) with conforming independent system variables was modelled to optimize the system variables for the preferred response using the statistical analysis. ANOVA was used to compute all the statistical constraints with the benefit of a response surface technique.

There are three major steps involved in the process optimization by RSM technique. The steps are, statistical design of experiments, estimation of coefficients in the mathematical model and prediction of the response and check the accuracy within the range of experimental variables. In the current research, three independent operating parameters were selected for the statistical analysis. The parameters are, initial metal ion dose (X_1 , mg/L), adsorbent dose (X_2 , mg) and system temperature (X_3 , K). The level and range of the factor change consequently with the experimental design. All the independent parameters for efficient

metal ions or organic pollutant removal from wastewater in an SFBR on the composite adsorbent. Therefore, the response is represented as a function of all independent variables.

$$Y = f(X_1, X_2, X_3 \dots \dots X_n)$$
(6.1)

Where Y is the response or output variables and $X_1, X_2, X_3 \dots \dots X_n$ are independent variables. An empirical model equation has been developed which correlate the response, removal efficiency with process variables by a second-degree polynomial equation and reproduced below in Equation (6.2)

$$Y = A_0 + \sum_{i=1}^n A_i X_i + \sum_{i=1}^n A_{ii} X_i^2 + \sum_{i=1}^n \sum_{j=i+1}^n A_{ij} X_i X_j$$
(6.2)

Where, Y is the predicted response, A_0 , A_i , A_{ii} , A_{ij} are constant, linear, quadratic, and interaction coefficient respectively. X_i , X_i^2 , X_j are level of independent variables.

Several tests (N) can be performed by considering the typical 2^n a factorial design consisting origin at the centre as mentioned earlier. The quadratic term was generated by the axial fixing of the 2n points at the distance α from the centre. Independent variable was defined as (n). In a CCD design for three independent variables in these present experiments, there are 8 factorial points, 6 axial points, and 6 replicate at the central points. Hence, the total number of tests (N) necessary for 3 independent process variables can be estimated from the equation given below (6.3)

$$N = 2^{n} + 2n + n_{c} = 2^{3} + (3 \times 2) + 6 = 20$$
(6.3)

6.2 Development of an unsteady-state mass transfer adsorptive model for the closed-circuit Semifluidized bed reactor

Performance curves are the representations of saturation of a given amount of adsorbent loaded in the reactor column with a certain amount of adsorbate passes through the bed at a fixed flow rate at a constant temperature. Though the performance curves are empirical and depend upon all the process parameters it has few purposes:

- Whether the adsorbent is efficient for the successful separation of target solute
- To find out the saturation point based on some criteria

The dynamic model for the system can be developed based on mass balance for the adsorbate over a fixed volume of adsorbent which is continuously percolated by the adsorbate containing liquid. In this investigation, the system is a recycling type to ensure maximum utilization of the adsorbent. The prime hypothesis followed during the model development are:

- The system is assumed to be isothermal throughout the operation. The heat of adsorption is also neglected.
- The feed flow rate or the liquid velocity for a particular set of the experiment will remain constant
- The velocity profile of the liquid as a dispersed plug flow for the fluidized bed regime dispersion is more compared to the packed zone. Hence the reactor is termed as PFDR (Plug flow dispersion Reactor) different dispersion coefficient is there for the different section
- There is no chemical reaction occurs between the adsorbate and the adsorbent.
- Eddy mixing is neglected

Bed porosity is uniform for both the section respectively. Under the above conditions, the solute or the adsorbate mass conservation of the process can be written as per the following equation,

$$D_Z \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} = \frac{\partial C}{\partial t} + \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial C_a}{\partial t}$$
(6.4)

Where, D_Z is the axial dispersion coefficient, this value has found different for a different section, fluidized has a higher dispersion, and the packed bed has very low dispersion value, t is operation time, ε is the bed porosity, and C_a is the adsorbate concentration on adsorbate.

Equation (6.4) can be rewritten as

$$D_Z \varepsilon \frac{\partial^2 c}{\partial z^2} - u \varepsilon \frac{\partial c}{\partial z} = \varepsilon \frac{\partial c}{\partial t} + \rho_a (1 - \varepsilon) \frac{\partial q}{\partial t}$$
(6.5)

where ρ_a is the density of the adsorbent material and q, defined previously, is the actual concentration of adsorbate in the adsorbent.

As a matter of fact $\rho_a(1-\varepsilon)$ is the density of the adsorbent bed, symbolized simply by ρ . Thus equation (6.5) becomes

$$D_{Z}\varepsilon\frac{\partial^{2}c}{\partial z^{2}} - u\varepsilon\frac{\partial c}{\partial z} = \varepsilon\frac{\partial c}{\partial t} + \rho\frac{\partial q}{\partial t}$$
(6.6)

Since diffusion is generally a slow process compared to the bulk flow present in fixed-bed adsorption systems, the first term in equation (6.4) can be neglected giving:

$$u\varepsilon\frac{\partial c}{\partial z} + \varepsilon\frac{\partial c}{\partial t} + \rho\frac{\partial q}{\partial t} = 0$$
(6.7)

The initial and boundary conditions associated with equation (6.7) are

$$t=0$$
, $C=C_0$ $(0 \le z \le H_{sf})$ (6.8)

$$t > 0, C = C_F$$
 ($z = 0$) and $\frac{\partial C}{\partial z} = 0$ ($z = Hsf$) (6.9)

where H_{sf} is the height of the semifluidized bed and C_F is the concentration of adsorbate in the liquid in the bed feed stream. The total bed height can be expressed as

$$H_{sf} = H_p + H_f \tag{6.10}$$

where H_p and H_f are the height of the packed and fluidized section respectively. This height can be obtained from experimental data at different operating conditions.

An additional simplification regards the third term in equation (6.5), the adsorption rate of the adsorbate. It can be expressed in terms of an overall liquid phase mass transfer coefficient, K_l ; the interfacial mass transfer area per unit volume of bed, a; and the deviation from equilibrium concentration in the fluid, as follows:

$$\rho \frac{\partial q}{\partial t} = \varepsilon K_l \alpha (C - C^*) \tag{6.11}$$

By substituting equation (6.11) in equation (6.6), we obtain –

$$D_{z}\varepsilon\frac{\partial^{2}c}{\partial z^{2}} - u\varepsilon\frac{\partial c}{\partial z} = \varepsilon\frac{\partial c}{\partial t} + \varepsilon K_{L}a(C - C^{*})$$
(6.12)

Equation (6.12) is a linear second-order Partial differential equation, which can be solved with given initial and boundary condition to obtain the concentration profile. Equation 6.12 will be solved individually for both the packed and fluidized sections. The final boundary condition for the fluidized section will be the initial boundary condition for the packed section (Equation 6.9)

6.3 Solution for the developed model

The partial differential equation (Eqn. 6.12) was solved in MATLAB 2019 simulation tool by using PDPE function. The unknown parameters like axial dispersion coefficient D_z for both packed and fluidized section and mass transfer coefficient K_L were obtained from the optimization route. Initially, the values were assumed and it was changed until the calculated value of concentration is much closer to the experimental values and the error was minimum between the experimental and model-predicted values.

6.4 Results and discussion

An elaborate column studies for all the targeted pollutant over a specific range of operating parameters. The bed experiments indicate that some parameters affect positively and some negatively. Among all three parameters, bed height, initial pollutant concentration and liquid flow rate. It has been found that with increasing be height removal increased for all the cases and increasing pollutant concentration and feed flow rate reduces the bed efficiency. But the percentage removal is different for the different solid-liquid system, which has been discussed in Chapter 5. To carry out this present investigation, as per the design method we have considered the data sets of all the highest and lowest point of all the parameters at the same time we have taken many data points in between. This makes the experimental results more reliable and software also able to provide a very accurate model for better understanding of the work. The proper design saves experimental time and experimental cost also.

The response surface method has been used to analyse the three-dimensional response plot produced from the effect of all the process variables on various heavy metals and Phenol removal in a novel Semifluidized bed reactor. It is evident from the ANOVA table that all the individual process variables are significant in increasing the performance of the Semifluidized bed reactor in terms of percentage removal (Y). In Figure 6.2 and Figure 6.3 examples of the combined effect of various parameters on percentage removal, normalized graph, actual vs predicted data are given for Zn^{2+} and Pb^{2+} . The combined effect of all three independent variables like the combined effect of initial adsorbent dose or bed height and initial concentration.

6.4.1 Individual and Combined effect of operating parameters on SFBR Performance

In this section of investigation, the effect of all operating parameters on bed performance has been conducted. The effects have been analysed on the individual as well as the combined basis. From ANOVA analysis (for which tables are not presented) the contour plot in 3D form have been obtained. Examples of such Figures have been given in Figure 6.2a-c and 6.3a-c for Zn^{2+} and Pb^{2+} adsorption is a semifluidized bed. As the trend of all the graphs is the same just different in their magnitude, therefore we have only represented these two sets of figures. The obtained results indicate that all the independent variables have a significant effect on removal of various heavy metals and Phenol in a novel Semifluidized bed adsorption column, but, the combined effect is less on the bed performance. In Figure 6.2d and 6.3d, the performance of bed in terms of percentage removal have been mapped with the variation of adsorbent bed height and initial feed solution concentration at the optimum flow rate. The red zone indicates the maximum value of percentage removal and blue zone indicates the lowest per cent removal at heights initial solution concentration. Figure 6.2a-c and 6.3a-c stand for the response (percentage removal) with the variation of all the parameters together. It has been found that bed height has the most strong effect when varying with other parameters.

6.4.2 Statistical Model development

The statistical parameters were assessed from the Analysis of Variance. In this optimization study by RSM, the ranges of independent experimental variables and coded variables are presented in Table 6.1, Table 6.2.

Table 6.1. The coded form and the actual level of the independent variables

Coded variables	Variables at its actual level
-α	X _{min}
-1	$[(X_{max}+X_{min})/2] - [(X_{max}-X_{min})/2\beta]$
0	$(X_{max}+X_{min})/2$
+1	$[(X_{max}+X_{min})/2] + [(X_{max}-X_{min})/2\beta]$
$+\alpha$	X_{max}

Here β is $2^{n/4}$, n is the number of independent variables for any particular experiment

Name	-1 Level	+1 Level	-α	+α
Initial bed height (X ₁)	7.03	12.97	5	15
Adsorbate conc. (X ₂)	14.05	25.95	10	30
For Cd^{2+} (X ₂)	8.1	16.9	5	20
for Phenol (X ₂)	40	85	25	100
Liquid flow rate (X ₃)	2.81	5.19	2	6

Table 6.2. Detail scope of experiments and range of the operating parameters

The effects of all model terms were evaluated. Statistical parameters like F-value, R^2 , adj R^2 , predicted R^2 and lack of fit was evaluated and compared with the experimental results for the reliability of the model. 95% confidence interval was taken into

consideration for finding the significance of factors and their interactions on the responses. Based on all the analysis a quadratic model equation has been developed.

In a model like this, lack of fit is undesirable. Lack of fit is a comparison between the residual error and the pure error (Ferreira et al. 2007). Hence, a small value of F and probability more than 0.1 are desired for the prediction of response.

In a model like this, lack of fit is undesirable. Lack of fit is a comparison between the residual error and the pure error (Ferreira et al. 2007). Hence, a small value of F and probability more than 0.1 are desired for the prediction of response.

In this present study, the F value of the model is obtained indicating that the model is significant. Besides, X_1 , X_2 , X_3 are also significant model terms with significant F-values. The ratio between signals to noise was quantified in term of adequacy precision, including the expected values at different design points and the average predicted errors. A desirable value of adequacy precision ratio is reported between 3-7 (Isar et al. 2006). The value obtained in the present study is much higher than the desired value. Therefore, the developed model is suitable for governing the design space. Also, this is the principal part of the predicted model to validate the present experimental data analysis. The normal probability versus studentized residual plot is presented in Figure 2e and 3e for $Zn^{2+}Pb^{2+}$ removal from wastewater in Semifluidized bed reactor. Figure 2e and 3e reveal that response alteration is not there and no major problem with the normality.

The actual vs model predicted percentage for Zn^{2+} and Pb^{2+} removal is presented in Figure 2f and 3f respectively. From Figures, it was found that the regression coefficient R^2 and adjusted R^2 were 93% and 91%, respectively. These values of R^2 illustrates till which extent model can perfectly estimate the experimental data and adjusted R^2 signifies the variation of mean described by the developed model. Also, the predicted R^2 value is close to R^2 value and therefore experimental data for Zn^{2+} and Pb^{2+} removal by novel composite adsorbent are well in line with the predicted values from the model equation.

The quadratic model equation developed from the Response surface Analysis for all the targeted pollutants have been presented below:

The percentage removal of Zn^{2+} in terms of coded variables:

$$Y(\%) = 71.65 + 5.65X_1 - 4.21X_2 - 2.70X_3 - 3.0X_1X_2 - 0.25X_1X_3 + 0.5X_2X_3 - 0.72X_1^2 + 0.87X_2^2 - 0.54X_3^2$$
(6.13)

Final Equation in Terms of Actual Factors:

Zn²⁺Removal(%)

= 40.26 + 7.21 Bed height - 0.278 Concentration +0.108 Flow rate - 0.1691 Bedheight × Concentration -0.070 Bed height × Flow rate + 0.07 Concentration × Flow rate -0.0816 Bed height² + 0.0245 Concentration² - 0.38 Flow rate² (6.14)

The percentage removal of Cu^{2+} in terms of coded variables:

$$Y(\%) = 66.41 + 5.66X_1 - 6.67X_2 - 4.66X_3 + 0.38X_1X_2 + 1.13X_1X_3 - 0.37X_2X_3$$
(6.15)
+ 1.77X_1^2 + 4.42X_2^2 + 1.24X_3^2

Final Equation in Terms of Actual Factors:

Cu²⁺Removal(%)

 $= 12.06 - 3.79Bed \ height - 6.21Concentration - 13.03 \ Flow \ rate \\+ 0.212 \ Bedheight \times Concentration \\+ 0.3182 \ Bed \ height \times Flow \ rate \\- 0.053Concentration \times Flow \ rate + 0.2008Bed \ height^2 \\+ 0.0245Concentration^2 - 0.38 \ Flow \ rate^2$ (6.16)

The percentage removal of Ni²⁺ in terms of coded variables:

$$Y(\%) = 71.29 + 4.88X_1 - 2.95X_2 - 1.24X_3 - 1.56X_1X_2 + 0.063X_1X_3 + 1.06X_2X_3$$
(6.17)
+ 1.56X_1^2 + 0.86X_2^2 - 1.03X_3^2

Final Equation in Terms of Actual Factors:
*Ni*²⁺Removal(%)

 $= 79.76 - 0.1956Bed \ height - 1.18Concentration \\+ 1.58 \ Flow \ rate - 0.088 \ Bedheight \times Concentration \\+ 0.0176 \ Bed \ height \times Flow \ rate$ (6.18)

+ 0.015*Concentration* \times *Flowrate*

The percentage removal of Pb^{2+} in terms of coded variables:

$$Y(\%) = 94.95 + 2.43X_1 - 0.89X_2 - 2.38X_3 + 0.75X_1X_2 + 0.25X_1X_3$$
(6.19)
- 0.25 X₂X₃ + 0.16X₁² + 0.46X₂² - 0.88X₃²

Final Equation in Terms of Actual Factors:

*Pb*²⁺Removal(%)

$$= 103.83 - 0.72Bed \ height - 0.984Concentration + 2.98 \ Flow \ rate + 0.0424 \ Bedheight \times Concentration + 0.0707 \ Bed \ height \times Flow \ rate - 0.035Concentration \times Flow \ rate - 0.0202Bed \ height^2 + 0.0138Concentration^2 - 0.62 \ Flow \ rate^2$$
(6.20)

The percentage removal of Cd^{2+} in terms of coded variables:

$$Y(\%) = 77.94 + 2.27X_1 - 1.20X_2 - 2.50X_3 - -0.25X_1X_2 - 0.25X_2X_3$$
(6.21)
+ 0.91X_1^2 + 0.20X_2^2 + 0.78X_3^2

Final Equation in Terms of Actual Factors:

$$Cd^{2+}Removal(\%)$$

$$= 97.93 + 1.0072Bed \ height - 0.147Concentration$$

$$- 5.53 \ Flow \ rate - 0.01414 \ Bed \ height \times Flow \ rate$$

$$- 0.035Concentration \times Flow rate - 0.102Bed \ height^{2}$$

$$+ 0.517 \ Flow \ rate^{2}$$

$$(6.22)$$

The percentage removal of Phenol in terms of coded variables:

$$Y(\%) = 77.94 + 2.27X_1 - 1.20X_2 - 2.50X_3 - -0.25X_1X_2 - 0.25X_2X_3$$
(6.23)
+ 0.91X_1^2 + 0.20X_2^2 + 0.78X_3^2

Final Equation in Terms of Actual Factors:

Phenol Removal(%)

$$= 14.26 + 10.84Bed height + 0.246Concentration + 4.49 Flow rate - 0.03 Bedheight × Concentration - 0.86 Bed height × Flow rate + 0.047Concentration × Flowrate - 0.27Bed height2 - 1.36 Flow rate2 (6.24)$$

Table 6.3: Response values Experimental and model predicted at optimized condition (SFBR operation)

Adsorbate	Adsorbent bed height (X1)	Adsorbate concentration (X2)	Liquid flow rate (X3)	Removal efficiency (%)	
				Experimental	Predicted
Zn^{2+}	12.97	14.05	2.81	86.31	87.56
Cu^{2+}	12.97	14.05	2.81	88.12	88.89
Ni ²⁺	12.97	14.05	2.81	83.45	84.31
Pb^{2+}	12.82	14.16	3.02	98.51	99.01
Cd^{2+}	12.38	9.05	2.81	86.08	85.76
Phenol	11.28	45.28	2.95	66.85	68.72

6.4.3 Process optimization for the batch experiments

The batch adsorption experiments conducted for various heavy metals removal which are discussed in Chapter 4 are also optimized by using the same method. The optimization was done for Zn^{2+} , Cu^{2+} , Ni^{2+} . The detailed scope of the experiments used for optimization are given in Table 6.4 and the optimum conditions with the response are represented in Table 6.5.

Table 6.4: Level of the experimental conditions for the optimization for the batch studies of heavy metals

Name	-1 Level	+1 Level	-α	$+\alpha$
Initial metal ion concentration (X_1)	40.17	84.8	25	100
Adsorbent dose (X ₂)	2.59	1.41	1	3
Adsorbent dose (X ₂) For Zn^{2+}	0.19	0.65	0.04	0.8
Temperature (X ₃)	302	323.95	298	318

Effects of all the model terms individually, as well as combined form, are evaluated by ANOVA analysis. Various significant parameters like R^2 , adj. R^2 , Predicted R^2 , statistical F value, Lack of fit were estimated and compared critically with the experimental data. Based on the statistical analysis individual quadratic models for metal adsorption capacity by the hybrid adsorbent have been developed for both Zn^{2+} , Cu^{2+} and Ni²⁺ and presented in Eqn. 6.25, 6.26, and 6.27 respectively.

Final Equation in Terms of Coded Factors:

$Zn^{2+} Removal (\%)$ $Y(\%) = 81.38 - 3.19X_1 + 2.89X_2 + 1.84X_3 + 0.13X_1X_2 + 0.38X_1X_3 + 0.13X_2X_3 + 0.46X_1^2 - 0.60X_2^2 - 0.78X_3^2$ (6.25) $Cu^{2+} Removal (\%)$

 $Y(\%) = 24.11 + 10.05X_1 - 4.89X_2 + 1.0X_3 - 1.31X_1X_2 - 0.075X_1X_3 + 0.075X_2X_3 + 3.01X_1^2 + 2.30X_2^2 + 0.72X_3^2$ (6.26)

Ni²⁺ Removal (%)

$$Y(\%) = 21.01 + 4.85X_1 - 3.73X_2 + 1.04X_3 - 1.09X_1X_2 + 0.088X_1X_3 + 0.16X_2X_3 - 0.54X_1^2 - 0.26X_2^2 - 0.029X_3^2$$
(6.27)

The F value of the model for Zn^{2+} , Cu^{2+} and Ni^{2+} are 30.13, 21.11 and 116 respectively which are also desirable and significant to describe the model. As per the theory and many published works, the statistical F value should be higher and probability >0.1 for any model to be significant. Along with F the lack of fit also significantly low which stand for the comparison between residual error and pure error of the data set. Form the ANOVA analysis it is also evident that the individual effect of X₁ (initial metal dose, mg/L) and X₂ (adsorbent dose, g) is also significant for both the cases. Another important statistical parameter required to estimate to justify the model validity is adequacy precision ratio. This parameter compares the predicted values at different design points and the average predicted error. Any developed model can be called a significant model if the adequacy precision more than 4. Here in this present case, this ration was estimated 16, 9 and 12 for $Zn^{2+} Cu^{2+}$ and Ni²⁺ respectively.

	Initial metal ion	Adsorbate	System	Removal efficiency (%)	
Adsorbate	concentration (mg/L) (X1)	concentration(g) (X2)	Temperature (K) (X3)	Experimental	Predicted
Zn^{2+}	43.18	0.62	313.15	86.05	85.02
Cu^{2+}	44.8	1.40	308.9	91.12	90.79
Ni ²⁺	43.8	1.48	313.2	93.45	94.11

Table 6.5: Response values Experimental and model predicted at optimized condition (batch operation)



Figure 6.2: (a) Interaction effect of Bed height (X_1) and Concentration (X_2) on Zn^{2+} removal (b) Interaction effect of Bed height (X_1) and flow rate (X_3) on Zn^{2+} removal (c) Interaction effect of Flow rate (X_3) and Concentration (X_2) on Zn^{2+} removal (d) Couture plot at optimum condition for Zn^{2+} removal (e) The normal probability vs studentized residual plot (f) Actual vs predicted Zn^{2+} removal



Figure 6.3: (a) Interaction effect of Bed height (X_1) and Concentration (X_2) on Pb^{2+} removal (b) Interaction effect of Bed height (X_1) and flow rate (X_3) on Pb^{2+} removal (c) Interaction effect of Flow rate (X_3) and Concentration (X_2) on Pb^{2+} removal (d) Couture plot at optimum condition for Pb^{2+} removal (e) The normal probability vs studentized residual plot (f) Actual vs predicted Pb^{2+} removal



Figure 6.4: Validation of dynamic model for the performance of Semifluidized bed reactor for Pb^{2+} (a-c)/Cd²⁺ (d-f) removal at various operating conditions.

6.5 Model validation and kinetic parameter estimation

Process models are mathematical tool to improve the understanding of the various effect of process parameters on the overall performance of any system. As it has been mentioned earlier that a Semifluidized bed reactor is a combination of a packed and a fluidized bed in the same column, therefore, its dynamic behaviour will also the combination of two individual reacting systems. But, the 75 -80% of the bed is fluidized and rest is packed so, the characteristic will be dominated mostly by a fluidized bed reactor. The empirical model developed for the unique semifluidized bed based on the solute phase mass balance. Dispersion flow, bulk movement all are considered in the development of the model. Various parameters like mass transfer co-efficient and axial dispersion co-efficient for the packed section and fluidized section have determined. The model has been fitted with the experimental data with minimum error. In figure 6.4a-c and 6.4d-f, the experimental data and the model predicted data are displayed for both the Pb²⁺ and Cd²⁺. In all the cases the model predicted values are well in line with the experimental data.

From the mathematical modelling and simulation, it can be confirmed that the developed model significantly described the semifluidized bed system and its performance. The correlation coefficient between the experimental values and model predicted values are satisfactorily higher which indicates the adequacy of the developed model. Various model parameters that obtained are given in Table 6.6.

Parameters	Values	
Mass transfer coefficient (K_L) for Pb ²⁺	1.39-1.51×10 ⁻⁴ m/s	
Mass transfer coefficient (K_L) for Cd^{2+}	1.3-1.48×10 ⁻⁴ m/s	
Mass transfer coefficient (K_L) for Zn^{2+}	1.09-1.18×10 ⁻⁴ m/s	
Mass transfer coefficient (K_L) for Cu^{2+}	1.31-1.37×10 ⁻⁴ m/s	
Mass transfer coefficient (K_L) for Ni ²⁺	1.21-1.30×10 ⁻⁴ m/s	
Mass transfer coefficient (K_L) for Phenol	4.39-4.8×10 ⁻⁵ m/s	
Axial dispersion Coefficient D_{axf} (fluidized section)	$4.80 \pm 0.3 \times 10^{-6} \text{ m}^2/\text{s}$	
Axial dispersion Coefficient D_{axp} (Packed section)	$5.10 \pm 0.3 \times 10^{-11} \text{ m}^2/\text{s}$	

Table 6.6: Parameters obtained from the model fitting

6.6 Scale-up calculation

Scale-up studies predict the amount of adsorbent required for a particular volume of liquid over a long period in a real-life application. In this investigation, scale-up has been done based on the developed model for the time vs concentration profile curve and solute phase mass balance as reported by Biswas et al. 2019 (S. Biswas et al. 2019). For Zn²⁺, Pb²⁺ metal 20, mg/L to 0.01 mg/L conversion amount of adsorbent required will be 251 and 194 tons for 100000 Litter of waste water respectively. For other adsorbents also scaleup can be done in the same process.

6.7 Spent adsorbent management

In every separation process, there is a huge amount of waste material generated after the operation. Therefore, it is a challenging task to find out some sustainable process for the disposal of such waste. In this research work, the adsorbent used was biochar and alginate both are biodegradable and eco-friendly. Therefore, it will not harm the environment even

if it through or dump directly after desorption of metal or other adsorbed material. However, we have tested the calorific value of the waste adsorbent to compare it with coking coal. It has been found that the C.V for CASB was 18.81 and for CAPC 16.63 MJ/kg. The Calorific value was measured in Bomb Calorimeter by using the following working formulae.

$$C.V = \frac{1}{m} \{ (W+E)C_p \times T - m_1(C.V)_{string} - m_2(C.V)_{wire} \}$$
(6.28)

Where,

W	Weight of water 1810 g		
Ε	Water equivalent calorific value 450		
$(CV)_{wire}$	335 cal/g		
(CV) _{string}	4000 cal/g		
C_p	Specific heat of water 1		
т	Mass of sample 1.12 g		
m_1	Mass of string 0.032 g		
m_2	Mass of wire 0.014 g		
Т	Temperature rise 1.70 ^o C		

The Calorific values obtained for both the waste adsorbents are quite high and close to mine based coal. Therefore, waste adsorbent can be easily used as an alternative source of carbon-based fuel materials.

6.8 Conclusion

In the present study, three variables central composite design-based Response surface method (RSM) has been employed to investigate the individual as well as the combined effect of independent variables on heavy metal and Phenol adsorption in a semifluidized bed column. This particular method has been chosen over other methods like the normal

factorial design or Box-Behnken method because of its improved computation incorporating axial data points and centre points. The study revealed that all the parameters, i.e initial adsorbent bed height, initial solute concentration and liquid flow rate individually affect the performance of Semifluidized bed significantly compared to the combined effect. The coefficients of the developed model were calculated for each response, and the high acceptability of the postulated model was proven by presenting the statistical specifications of them. The reliability of the developed model has been ensured from the high magnitude of the correlation coefficient between the experimental and model-predicted values. The optimum conditions found for this work found as, bed height 11-13 cm, initial solute concentration 12-14.5 mg/L for metals and 45 for Phenol and water flow rate 3 LPM. The real-time dynamic model involves the aspects of fluid transport and adsorption. The fluid transport was modelled by the Darcy-Brinkman equation while a convection-diffusion equation and adsorption-kinetic equation have been used to understand the fate of contaminant in the filter. The mass transfer coefficient for $Zn^{2+}, Cu^{2+}, Ni^{2+} Pb^{2+}, Cd^{2+}$ and Phenol was obtained $1.09-1.18 \times 10^{-4}, 1.31-1.371 \times 10^{-4},$ 1.21-1.3×10⁻⁴, 1.39-1.51×10⁻⁴, 1.3-1.48×10⁻⁴ and 4.39-4.81×10⁻⁵ m/s respectively. The magnitude of the axial dispersion coefficient was calculated $4.8\pm0.3\times10^{-6}$ and $5.1\pm$ 0.3×10^{-11} m²/s respectively for fluidized and packed section. Further, the scale-up of the system shows that the reactor can be run for a long time to treat the huge amount of pollutants below the threshold limit. The waste adsorbent can be used as an alternate source of carbon as a source of fuel as it's CV is quite significant and the value obtained for CASB was 18.81 and for CAPC 16.63 MJ/kg. The developed model shows a satisfactory agreement with the experimental data and can we conclude that the model is valid for performance analysis of such kind of reactor which can further used for the development of a large scale semifluidized bed reactor for industrial operation.

Chapter 7

Conclusion and Future Scope of Work

Chapter 7

Conclusion and Future Scope of Work

7.0 Introduction

A detailed study has been conducted to develop and evaluate the performance of a three phase Semifluidized bed reactor (SFBR) for removal of various heavy metals and Phenol with a wide range of operating parameters. Along with synthetic wastewater, actual wastewater also used for the analysis to establish the suitability of the system in a real-life scenario. A lab scale three phase semifluidized bed system has been developed. The hydrodynamic behaviour like minimum fluidization velocity, semifluidization velocity, packed bed zone formation with various liquid flow rate and bed pressure drop have been studied with low density polymeric beads. Various correlations for the system have been developed from the experimental data. Later the developed correlations have been used to develop the unsteady state dynamic model of the system as an adsorption column. Low-cost and low density (similar density of the solid used for hydrodynamic studies) adsorbent as the bed material has been synthesized and characterized to show the potentiality of the material to be an alternative to the coal-based activated carbon. Effect of various operating conditions like solution pH, initial adsorbate concentration, adsorbent concentration, system temperature, the effect of co-metal ions have been analysed over a wide range in a batch process to find out adsorption mechanism, nature of adsorption and various kinetic parameters for the adsorption of such materials in a labscale reactor. The column studies were conducted by varying the initial adsorbent loading, initial solute concentration and flow rate which is contact time or retention time of the adsorbent inside the reactor column. The system has been optimized by Response Surface Method and Central composite Design tool to find the optimum operating conditions at which maximum removal will achieve. A real-time dynamic model for the

semifluidized bed based on mass transfer has been developed and overall mass transfer coefficient for each component and axial dispersion coefficient of individual packed and fluidized zone of the system have been evaluated.

The overall chapter wise conclusions are given below:

7.1 Hydrodynamic and bed characteristic of multiphase Semifluidized bed system

The hydrodynamic and bed characteristics study in Chapter 2 of a multi-phase semifluidized bed system illustrates that the minimum fluidization velocity (U_{lmf}) is significantly depends on operating parameters such as superficial gas velocity (U_g) and particle sizes (d_p) , but independent of initial static bed height (H_s) . Minimum semifluidization and maximum semifluidization velocities decreased with the rise in static bed height (H_s) . Top packed zone formation and bed pressure drop across the bed also strongly depended on particle diameter (d_p) , superficial gas (U_g) , liquid velocity (U_{SL}) and initial static bed height (H_s) . Introduction of dispersed gaseous phase as a secondary fluidizing agent plays a significant role by reducing minimum fluidization and semifluidization velocities and also enhanced the packed bed formation at lower liquid velocity. The significant outcomes of this study are reduced minimum fluidization velocity ranging from 0.004 - 0.01 m/s, and minimum semifluidization velocity of 0.032 -0.006 m/s compared to reported high values. In this present study, the pressure drops generated in the system was fairly low due to low solid-fluid relative density. As a top packed bed is formed in such a bioreactor, the reactor pressure drop is slightly high. This shows that a semifluidized bed reactor is operated under little higher-pressure condition than simple fluidized bed reactor but lower than that of a normally packed bed reactor. Maximum bed pressure drop was found to be 5.6 kPa. Empirical mathematical correlations for bed hydrodynamic characteristics have been developing for this particular system for a better understanding of such a reactor system with multi-phase. The hydrodynamic and bed characteristic study results confirm that this proposed reactor can be handled at lower fluid pumping cost and low bed pressure drop which will be very economical for commercial large scale operations. Effect of different liquid properties such as liquid density, viscosity, surface tension and solid properties like density, porosity can be studied in future to understand the fundamental and phenomenological behaviours of a semifluidized bed system in case of three-phase operation.

7.2 Synthesis and characterization of novel composite adsorbent as the solid phase of the Semifluidized bed reactor column

In this chapter, two different types of biochar were synthesized from two different biomass precursor and later both of them are immobilized in alginate beads. From the proximate and ultimate analysis, it has been found that Carbon amount is high for Sugarcane bagasse and it's composite. Both the synthesized adsorbents exhibit excellent properties like surface area pore volume, availability of functional groups, rough and porous surface and various physical-chemical parameters. When we analyse BET surface area, the biochar obtained from sugarcane bagasse and its composite have surface area 391.42 and 200.14 m²/g and pine cone based biochar and composite have surface area 144.94 and 163.87 m²/g respectively. Sugarcane bagasse-based biochar has more micropores than pine cone therefore, it has more surface area which can capture more pollutant from aqueous solution. Moreover, the composite adsorbents are very lightweight and density very close to water. The adsorbent prepare from sugarcane bagasse has better properties compared to the pine cone. And, it is very commonly available in many countries as a waste by-product of the sugar factory. So, it can be concluded that such

novel low cost and lightweight adsorbent can easily be used as a bed material of packed, fluidized and semifluidized bed reactor.

7.3 Performance analysis of synthesized adsorbent for heavy metal and Phenol removal under various operation conditions

In this chapter, detailed studies in the batch experiment have been conducted to evaluate the performance of both type of adsorbents CAPC and CASB for removal of a group of heavy metals and organic pollutants MB dye and Phenol. All the targeted material used in this study are regarded as highly hazardous and carcinogenic. For the CAPC adsorbent the capacity of adsorption is like Ni>Zn>Cu>Pb>Cd>MB Dye>Phenol (capacities are 110.84, 95.86, 89.09, 78.4, 71.22, 70.66 and 16.33 mg/g respectively) on the other hand, CASB adsorbent has the adsorption capacity order like, Ni>Cu>Pb>Zn>Cd>MB Dye>Phenol (capacities are 144,29, 88, 86, 75.18, 72, 68.4 and 20.20 mg/g respectively). The Pseudo-second-order kinetic model fits well with the experimental data. Both the liner form and nonlinear form have been analysed and it has found that the predicted values are much closer with the non-linear solution in MATLAB. From the kinetic study, it was found that the process is quite fast and reached equilibrium within 90 minutes for all the heavy metals, but adsorption of phenol is slower. It was also found that the adsorption process involves multiple steps including, fast bulk or surface diffusion for first 15-30 minutes, next it is intraparticle or pore diffusion and last the equilibrium condition. The isotherm model also studied bot linear and non-linear form, but the difference between the obtained parameters are very close in both the form and the adsorption process is mainly followed by Langmuir monolayer isotherm other isotherm parameters confirms that the adsorption of all the components is favourable. The thermodynamic behaviours are very similar for all the heavy metals it is an endothermic

process and adsorption capacity increases with temperature. But Phenol exhibited some difference as adsorption capacity reduces at a temperature above 318 K. which indicates that, the system is exothermic after a certain range of temperature and it has also found from the enthalpy values. However, the overall process is spontaneous and favourable. The activation energy of the process also confirms the nature of adsorption. The process is mainly governed by physical adsorption but, there is some portion where some chemical interaction, ion exchange is involved. Therefore, from the elaborate investigation in a batch study, it can be concluded that the synthesized material is very promising as an alternative low-cost adsorbent compared to others reported adsorbent and some Commercial activated Carbon. Hence the low cost and lightweight adsorbent materials can be recommended to be used as a bed material for a Semifluidized bed reactor.

7.4 Performance analysis of Semifluidized bed reactor with synthetic and actual industrial effluent

In Chapter 5, a detailed study has been conducted for the performance analysis of a threephase semifluidized bed adsorption column for removal of various hazardous heavy metals and organic pollutants. Actual industrial wastewater also collected from steel plant treated in the novel reactor to ensure its performance in a real-life scenario. Operating parameters varied were initial adsorbent bed height, initial solute concentration and feed flow rate. All the parameters have a significant effect on bed performance. The equilibrium time for the system is 240-300 minutes which is satisfactorily lower with compared to other systems like the packed bed or fluidized bed. Maximum capacity for Zn^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Cd^{2+} and Phenol for the bed operation were found 42.4, 43.27, 46.12 54.4, 36.8 and 89.35 mg/g respectively. Percentage removal maximizes at high adsorbent bed height, low solute and low flow rate. But to make the bed semifluidized we need to maintain a minimum velocity. However, this reactor can handle more liquid compared to normal packed bed system. And there is less chance of back mixing, channelling etc.

7.5 Process optimization, dynamic model development system scale up and waste adsorbent management method

In the present study, three variables central composite design-based Response surface method (RSM) has been employed to investigate the individual as well as the combined effect of independent variables on heavy metal and Phenol adsorption in a semifluidized bed column. This particular method has been chosen over other methods like the normal factorial design or Box-Behnken method because of its improved computation incorporating axial data points and centre points. The study revealed that all the parameters, i.e initial adsorbent bed height, initial solute concentration and liquid flow rate individually affect the performance of Semifluidized bed significantly compared to the combined effect. The coefficients of the developed model were calculated for each response, and the high acceptability of the postulated model was proven by presenting the statistical specifications of them. The reliability of the developed model has been ensured from the high magnitude of the correlation coefficient between the experimental and model-predicted values. The optimum conditions found for this work found as, bed height 11-13 cm, initial solute concentration 12-14.5 mg/L for metals and 45 for Phenol and water flow rate 3 LPM. The real-time dynamic model involves the aspects of fluid transport and adsorption. The fluid transport was modelled by the Darcy-Brinkman equation while a convection-diffusion equation and adsorption-kinetic equation have been used to understand the fate of contaminant in the filter. The mass transfer coefficient for Zn^{2+} , Cu^{2+} , Ni^{2+} Pb²⁺, Cd^{2+} and Phenol was obtained 1.09-1.18×10⁻⁴, 1.31-1.371×10⁻⁴, 1.21-1.3×10⁻⁴, 1.39-1.51×10⁻⁴, 1.3-1.48×10⁻⁴ and 4.39-4.81×10⁻⁵ m/s respectively. The magnitude of the axial dispersion coefficient was calculated $4.8 \pm 0.3 \times 10^{-6}$ and $5.1 \pm 0.3 \times 10^{-11}$ m²/s respectively for fluidized and packed section. Further, the scale-up of the system shows that the reactor can be run for a long time to treat the huge amount of pollutants below the threshold limit. The waste adsorbent can be used as an alternate source of carbon as a source of fuel as it's CV is quite significant and the value obtained for CASB was 18.81 and for CAPC 16.63 MJ/kg. The developed model shows a satisfactory agreement with the experimental data and can we conclude that the model is valid for performance analysis of such kind of reactor which can further used for the development of a large scale semifluidized bed reactor for industrial operation.

7.6 Future scope of work

The conclusion is drawn from the overall work that the novel semifluidized bed in the field of wastewater treatment is a very advantageous one. It provides high conversion at significantly low operation time and low-pressure drop. Further, the operation is very easy and use of immobilized adsorbent make the system more convenient as there is no extra separator is required to separate the adsorbent from the solution. However, due to time-bound, some work cannot be completed which can be carry forward in future. The future scope of works are listed below:

- Study of the performance of the SFBR by activated biochar-alginate bed materials
- > Extend the operation in the multicomponent effluent system
- Study the mass transfer phenomenon of the novel system
- Heat transfer related application studies
- Effect of system pressure on the performance of the reactor
 - 177

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APENDIX 1

Co- Author's Declaration

"Synthesis and characterization of a novel Ca-alginate-biochar composite as efficient zinc (Zn 2+) adsorbent: Thermodynamics, process design, mass transfer and isotherm modeling", **Sep.** Sci. Technol. Vol 54 (2019), pages 1106–1124.

	Conception and Design	Acquisition of data & method	Data condition & manipulation	Analyses & statistical method	Interpretation & discussion	Final approval
Dr T. K Sen Co-author 1	X			X	X	X
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"Experimental hydrodynamic and bed characteristics of co-current gas-liquid-solid three phase semifluidization with liquid as the continuous phase", **Part. Sci. Technol**. Vol 38 (2019), pages 1–13.

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Dr. B. C. Meikap Co-author 2 I acknowledg Signed:	X e that these repre	esent my contrib	ution to the above	X research output	X	X

"Batch and continuous closed circuit semi-fluidized bed operation: Removal of MB dye using sugarcane bagasse biochar and alginate composite adsorbents", J. Environ. Chem. Eng. Vol 8 (2020), pages 103637

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"Preparation and Characterization of Raw and Inorganic Acid-Activated Pine Cone Biochar and Its Application in the Removal of Aqueous-Phase Pb2+ Metal Ions by Adsorption," **Water, Air, Soil Pollut**. Vol 231 (2020), pages 3.

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"Adsorptive Removal of Aqueous Phase Copper (Cu2+) and Nickel (Ni2+) Metal Ions by Synthesized Biochar–Biopolymeric Hybrid Adsorbents and Process Optimization by Response Surface Methodology (RSM)", **Water, Air, Soil Pollut**. Vol 230 (2019), page 197.

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"Process modelling and optimization of a novel Semifluidized bed adsorption column operation for aqueous phase divalent heavy metal ions removal", **J. Water Process Eng**. Vol 37 (2020) page 101406.

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"Process Optimization Study of Zn2+ Adsorption on Biochar-Alginate Composite Adsorbent by Response Surface Methodology (RSM)," Water. Vol 11 (2019), page 325.

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