

Department of Chemical Engineering

Treatment of Oily and Dye Wastewater with Modified Barley Straw

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**This thesis is presented for the Degree of
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of
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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:

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All praises and glories to Almighty Allah (SWT) who had bestowed me courage and
patience upholding this work.

Whenever I was down at the life wheel, this '**Don't Quit!**' poem always helped me
undulate even stronger

Don't Quit!

When things go wrong, as they sometimes will,
When the road you're trudging seems all uphill,
When the funds are low, and the debts are high,
And you want to smile, but you have to sigh,
When care is pressing you down a bit,
Rest if you must, but don't you quit.

Life is queer with its twists and turns,
As everyone of us sometimes learns,
And many a failure turns about,
when he might have won had he stuck it out;
Don't give up though the pace seems slow,
You may succeed with another blow.

Success is failure turned inside out,
The silver tint of the clouds of doubt,
And you never can tell how close you are,
It may be near when it seems so far;
So stick to the fight when you're hardest hit,
It's when things seem worse, that...

You Must Not Quit.

~C. W. Longenecker ~

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A teacher, though,

Awakens your own expectations"

~Patricia Neal

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~Joanna Fuchs

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~Walter Winchell

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~David Thomas

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~Joyce Brothers

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TABLE OF CONTENTS

DECLARATION	
ACKNOWLEDGEMENT	
DEDICATIONS	
PUBLICATIONS	viii
TABLE OF CONTENTS	x
LIST OF TABLES	xv
LIST OF FIGURES	xvii
NOTATIONS	xxi
ABSTRACT	xxiii

CHAPTER 1 BACKGROUND

1.1 Introduction	1
1.2 Research objectives	3

CHAPTER 2 REVIEW OF LITERATURE

2.1 Introduction	5
2.2 Oils	6
2.3 Oily Wastewater	6
2.4 Emulsified Oily Wastewater for Environmental Concern	8
2.5 Dyes	9
2.6 Dye Wastewater	12
2.7 Dye Wastewater for Environmental Concern	12
2.8 Remediation of Oily and Dyes Wastewater	16
2.8.1 Mechanical/physical separation	16
2.8.1.1 Air flotation	16
2.8.1.2 Filtration	18
2.8.1.3 Sorption	19
2.8.2 Chemical methods	20
2.8.2.1 Chemical coagulation	20
2.8.2.2 Ozonation	21
2.8.3 Biological methods	23

2.9	Adsorption	25
2.10	Agricultural Waste as an Adsorbents	26
2.11	Modification of Agricultural Waste	27
2.12	Chemistry of Cationic Surfactant	28
2.13	Modification of Solid Surface with Cationic Surfactant	31
2.13.1	Binding mechanism	31
2.14	Surfactant Modified Adsorbent for Environmental Concern	32
2.15	Cationic Surfactant Selection	36
2.15.1	Influence of surfactant chain length	36
2.15.2	Influence of polar head group	38
2.15.3	Influence of cationic surfactant concentration	39
2.16	Section Summary	40

CHAPTER 3 EXPERIMENTAL

3.1	Introduction	41
3.2	Adsorbent Preparation	42
3.2.1	Materials	42
3.2.2	Treatment with base solution	42
3.2.3	Modification with cationic surfactant	42
3.3	Characterization of Adsorbent	43
3.3.1	Carbon and Nitrogen percentage	43
3.3.2	Surface area	43
3.3.3	Microstructure and surface morphology	43
3.3.4	Water soluble minerals	44
3.3.5	Identification of functional group	44
3.3.6	Elemental analysis	44
3.3.7	Acidic and basic surface groups	44
3.3.8	Bulk density	44
3.3.9	Cellulose, hemicelluloses and lignin	45
3.4	Stability/Desorption of CPC	45
3.5	Experimental Studies of Emulsified Oil Removal	45
3.5.1	Batch adsorption studies	45
3.5.2	Batch kinetic studies	46

3.5.3	Batch isotherm studies	46
3.5.4	Batch equilibrium studies	46
3.5.5	Batch experimental operational parameters	46
3.5.6	Leaching/desorption experiments	47
3.5.7	Fixed bed column breakthrough studies	47
3.5.8	Preparation of emulsified oil solutions	48
3.5.9	Measurement of oil in water	48
3.6	Experimental Studies of Dyes Wastewater	49
3.6.1	Batch adsorption preliminary studies	49
3.6.2	Batch kinetic studies	49
3.6.3	Batch Isotherm studies	49
3.6.4	Batch equilibrium studies	50
3.6.5	Leaching/desorption experiments	50
3.6.6	Batch experimental operational parameters	50
3.6.7	Fixed bed column breakthrough studies	50
3.6.8	Preparation of dyes wastewater	51
3.6.9	Measurement of dyes in wastewater	51
3.7	Batch Experimental Model	51
3.7.1	Kinetic models	51
3.7.2	Kinetic diffusion models	52
3.7.3	Isotherm models	53
3.8	Fixed Bed Column Models	54
3.8.1	Thomas model	56
3.8.2	Yoon-Nelson model	56
3.9	Best Fitting Model Estimation	57
3.10	Standard Error of The Measurement	57

CHAPTER 4 MODIFICATION AND CHARACTERIZATION OF STRAW SURFACE

4.1	Introduction	58
4.2	Treatment with Base Solution	59
4.3	Modification with Cationic Surfactant	60
4.4	Physicochemical Characteristics of Raw and Modified Barley	64

Straw	
4.5 Morphology of Raw and Modified Barley Straw	68
4.6 Spectroscopy Study of The Raw and Modified Straw	71
4.7 Desorption of Cationic Surfactant	73
4.8 Section Summary	75

CHAPTER 5 REMOVAL OF EMULSIFIED OILS

5.1 Introduction	77
5.2 Preliminary Experiments	78
5.3 Dynamics Adsorption of Oils	81
5.3.1 Kinetic models	83
5.3.2 Kinetic diffusion models	87
5.4 Isotherm Models	90
5.5 Comparison with other Adsorbents	93
5.6 Effect of Oil Solution Temperature	95
5.7 Effect of Initial pH of Oil Solution	96
5.8 Effect of Adsorbent Size	98
5.9 Desorption	99
5.10 Column Breakthrough Studies	101
5.11 Modelling of Fixed Bed Column Breakthrough	105
5.11.1 Thomas model	105
5.11.2 Yoon-Nelson model	107
5.12 Section Summary	109

CHAPTER 6 REMOVAL OF ANIONIC DYES

6.1 Introduction	111
6.2 Preliminary Experiments	112
6.3 Dynamic Adsorption	116
6.3.1 Kinetic models	118
6.3.2 Kinetic diffusion models	123
6.4 Isotherm Models	127
6.5 Comparison with other Adsorbents	131
6.6 Effect of Dye Solution pH	133

6.7	Effect of Dye Solution Experimental Temperature	135
6.8	Dye Desorption	137
6.9	Column Breakthrough Studies	138
6.10	Modelling of Fixed Bed Column Breakthrough	141
6.10.1	Thomas model	142
6.10.2	Yoon-Nelson model	144
6.11	Section Summary	146

CHAPTER 7 CONCLUSIONS AND FUTURE DIRECTIONS

7.1	Introduction	148
7.2	Conclusion	149
7.3	Future Directions	156

REFERENCES	158
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APPENDICES

LIST OF TABLES

Table 2.1	Concentration of oil in different sources	7
Table 2.2	Classification dyes according to the chemical structure	10
Table 2.3	Application classes of dyes and their chemical types	11
Table 2.4	Estimated degree of fixation for different dyes	12
Table 2.5	Some of the information of the dyes used in this work	15
Table 2.6	Typical characteristics of membrane processes	18
Table 2.7	Characteristic of some cationic surfactant	30
Table 2.8	Sorption capacity for some of the surfactant modified adsorbent for low polarity compounds	34
Table 2.9	Sorption capacity for some of the surfactant modified adsorbent for anionic dyes	35
Table 4.1	Characteristics of raw and modified straw	65
Table 5.1	Kinetics models constants and error analysis for adsorption of oil on SMBS and BMBS	86
Table 5.2	Effective diffusion constants (D_i) for adsorption of oil on SMBS and BMBS	90
Table 5.3	Freundlich and Langmuir isotherm constants and error analysis for adsorption of oil on SMBS and BMBS	92
Table 5.4	Oil sorption capacities of some sorbents reported in literature	94
Table 5.5	Adsorption breakthrough data for column experiments for the adsorption of CO and SMO on SMBS and BMBS	104
Table 5.6	Thomas model parameters for fixed-bed adsorption of CO and SMO	107
Table 5.7	Yoon-Nelsons model parameters for fixed-bed adsorption of CO and SMO	109
Table 6.1	Kinetics models constants and error analysis for adsorption of anionic dyes on SMBS and BMBS.	122
Table 6.2	Effective diffusion constants (D_i) for adsorption of anionic dyes on SMBS and BMBS	127
Table 6.3	Freundlich and Langmuir isotherm constants and error analysis for adsorption of anionic dyes on SMBS and BMBS	130

Table 6.4	Anionic dyes sorption capacities of some sorbents reported in literature	132
Table 6.5	Adsorption breakthrough data for column experiments for the adsorption of AB40 and RB5 on SMBS and BMBS	141
Table 6.6	Thomas model parameters for fixed-bed adsorption of AB40 and RB5	144
Table 6.7	Yoon-Nelsons model parameters for fixed-bed adsorption of AB40 and RB5	146

LIST OF FIGURES

Figure 2.1	Schematic illustration of a surfactant monomer and a micelle structure in aqueous solution	29
Figure 2.2	Adsorption of cationic surfactants onto perlite samples: (a) at low surface coverage, (b) of the point of zeta potential reversal, (c) at monolayer coverage, (d) at high surface concentration	32
Figure 2.3	Effect of the surfactants (1.0 CEC used for each of the different surfactant types) on adsorption capacity of surfactant-modified MMT for CR.	37
Figure 3.1.	Schematic diagram of fixed bed column study	48
Figure 3.2.	Examples of breakthrough curves: (a) poor adsorption (b) normal adsorption and (c) strong adsorption	55
Figure 4.1	Effectiveness of NaOH treated raw barley straw for methylene blue 1 removal	60
Figure 4.2	Sorption of CPC on RBS and RBS-N surface	61
Figure 4.3a	Log - log scale SMBS	62
Figure 4.3b	Log - log scale BMBS	62
Figure 4.4a	Schematic illustration of ion exchange mechanism of the cationic surfactants at straw water interface	63
Figure 4.4b	Incomplete bilayer formation of CPC onto straw surface	63
Figure 4.4c	Complete bilayer formation of CPC onto straw surface	64
Figure 4.5	SEM micrograph of (a) RBS (b) RBS-N (c) SMBS and (d) BMBS showing the irregular shape	69
Figure 4.6	SEM micrograph showing the fiber like structure	69
Figure 4.7	SEM micrograph of BMBS indicate (a) removal a thin wax layer (b) creating a perforation	70
Figure 4.8	SEM micrograph of straw indicating the deposition of organic molecules (a) before CPC treatment (b) after CPC treatment	70
Figure 4.9	FT-IR spectra of RBS, RBS-N, SMBS, BMBS and CPC	72
Figure 4.10a	Desorption of CPC from SMBS in various liquid media	73
Figure 4.10b	Desorption of CPC from BMBS in various liquid media	74
Figure 5.1	Adsorption of CO and SMO using unmodified and surfactant modified straw	78
Figure 5.2a	FT-IR spectra of SMBS and oil loaded SMBS	79
Figure 5.2b	FT-IR spectra of BMBS and oil loaded BMBS	80

Figure 5.3	Schematic diagram showing adsolubilization/partitioning of oils (represented by black round dots) in surfactant modified straw	80
Figure 5.4a	Effect of contact time on adsorption of CO onto SMBS and BMBS	82
Figure 5.4b	Effect of contact time on adsorption of SMO onto SMBS and BMBS	82
Figure 5.5a	Nonlinear kinetic models for adsorption of CO onto SMBS	83
Figure 5.5b	Nonlinear kinetic models for adsorption of CO onto BMBS	84
Figure 5.5c	Nonlinear kinetic models for adsorption of SMO onto SMBS	84
Figure 5.5d	Nonlinear kinetic models for adsorption of SMO onto BMBS	85
Figure 5.6a	Boyd plot for the sorption of CO onto SMBS	87
Figure 5.6b	Boyd plot for the sorption of CO onto BMBS	88
Figure 5.7a	Boyd plot for the sorption of SMO onto SMBS	88
Figure 5.7b	Boyd plot for the sorption of SMO onto BMBS	89
Figure 5.8a	Nonlinear adsorption isotherms for adsorption of CO onto SMBS and BMBS	91
Figure 5.8b	Nonlinear adsorption isotherms for adsorption of SMO onto SMBS and BMBS	91
Figure 5.9a	Effect of temperature on adsorption of CO and SMO onto SMBS	95
Figure 5.9b	Effect of temperature on adsorption of CO and SMO onto BMBS	96
Figure 5.10a	Effect of solution pH on adsorption of CO and SMO onto SMBS	97
Figure 5.10b	Effect of solution pH on adsorption of CO and SMO onto BMBS	97
Figure 5.11a	Effect of adsorbent size on adsorption of CO and SMO onto SMBS	98
Figure 5.11b	Effect of adsorbent size on adsorption of CO and SMO onto BMBS	99
Figure 5.12a	Desorption of oil loaded SMBS in deionized water	100
Figure 5.12b	Desorption of oil loaded BMBS in deionized water	100
Figure 5.13a	Breakthrough plot of CO adsorption on RBS and RBS-N	101

Figure 5.13b	Breakthrough plot of SMO adsorption on RBS and RBS-N	102
Figure 5.13c	Breakthrough plot of CO adsorption on SMBS and BMBS	102
Figure 5.13d	Breakthrough plot of SMO adsorption on SMBS and BMBS	103
Figure 5.14a	Nonlinear Thomas plots for adsorption of CO onto SMBS and BMBS	106
Figure 5.14b	Nonlinear Thomas plots for adsorption of SMO onto SMBS and BMBS	106
Figure 5.15a	Non linear Yoon-Nelson plots for adsorption of CO onto SMBS and BMBS	108
Figure 5.15b	Non linear Yoon-Nelson plots for adsorption of SMO onto SMBS and BMBS	108
Figure 6.1	Adsorption of AB40, RB4 and RB5 using unmodified and surfactant modified straw	112
Figure 6.2a	FT-IR spectra of SMBS and dyes loaded SMBS	114
Figure 6.2b	FT-IR spectra of BMBS and dyes loaded BMBS	115
Figure 6.3	Schematic diagram showing anionic dyes (represented by black round dots) attracted onto opposite charge on modified straw	115
Figure 6.4a	Effect of contact time on adsorption of AB40 onto SMBS and BMBS	116
Figure 6.4b	Effect of contact time on adsorption of RB4 onto SMBS and BMBS	117
Figure 6.4c	Effect of contact time on adsorption of RB5 onto SMBS and BMBS	117
Figure 6.5a	Nonlinear kinetic models for adsorption of AB40 onto SMBS	119
Figure 6.5b	Nonlinear kinetic models for adsorption of AB40 onto BMBS	119
Figure 6.6a	Nonlinear kinetic models for adsorption of RB4 onto SMBS	120
Figure 6.6b	Nonlinear kinetic models for adsorption of RB4 onto BMBS	120
Figure 6.7a	Nonlinear kinetic models for adsorption of RB5 onto SMBS	121
Figure 6.7b	Nonlinear kinetic models for adsorption of RB5 onto BMBS	121
Figure 6.8a	Boyd plot for the sorption of AB40 onto SMBS	124
Figure 6.8b	Boyd plot for the sorption of AB40 onto BMBS	124
Figure 6.9a	Boyd plot for the sorption of RB4 onto SMBS	125

Figure 6.9b	Boyd plot for the sorption of RB4 onto BMBS	125
Figure 6.10a	Boyd plot for the sorption of RB5 onto SMBS	126
Figure 6.10b	Boyd plot for the sorption of RB5 onto BMBS	126
Figure 6.11a	Nonlinear adsorption isotherms for adsorption of AB40 onto SMBS and BMBS.	128
Figure 6.11b	Nonlinear adsorption isotherms for adsorption of RB4 onto SMBS and BMBS	128
Figure 6.11c	Nonlinear adsorption isotherms for adsorption of RB5 onto SMBS and BMBS	129
Figure 6.12a	Effect of solution pH on adsorption of AB40, RB4 and RB5 onto SMBS	134
Figure 6.12b	Effect of solution pH on adsorption of AB40, RB4 and RB5 onto BMBS	134
Figure 6.13a	Effect temperature on adsorption of AB40, RB4 and RB5 onto SMBS	136
Figure 6.13b	Effect of temperature on adsorption of AB40, RB4 and RB5 onto BMBS	136
Figure 6.14a	Desorption of SMBS loaded AB40, RB4 and RB5 at different pH solution	137
Figure 6.14b	Desorption of BMBS loaded AB40, RB4 and RB5 at different pH solution	138
Figure 6.15a	Breakthrough plot of AB40 adsorption for RBS and RBS-N	139
Figure 6.15b	Breakthrough plot of RB5 adsorption for RBS and RBS-N	139
Figure 6.15c	Breakthrough plot of AB40 adsorption for SMBS and BMBS	140
Figure 6.15d	Breakthrough plot of RB5 adsorption for SMBS and BMBS	140
Figure 6.16a	Nonlinear Thomas plots for adsorption of AB40 onto SMBS and BMBS	142
Figure 6.16b	Nonlinear Thomas plots for adsorption of RB5 onto SMBS and BMBS	143
Figure 6.17a	Nonlinear Yoon-Nelson plots for adsorption of AB40 onto SMBS and BMBS	145
Figure 6.17b	Nonlinear Yoon-Nelson plots for adsorption of RB5 onto SMBS and BMBS	145

NOTATIONS

C_e	Concentration at equilibrium
C_{ex}	Column exhaustion concentration
C_i	Concentration at initial
cm	Centimeter
C_o	Concentration at time zero
C_t	Concentration at time t
CEC	Cation exchange capacity
D_i	Effective diffusion coefficient
F	Fraction of adsorbate adsorbed at time t
g	Gram
h	Hour
HRT	Hydraulic residence time
K_1	Rate constant pseudo-first-order
K_2	Rate constant pseudo-second-order
K_F	Freundlich equilibrium constant
kg	Kilogram
k_{TH}	Thomas rate constant
K_{YN}	Yoon-Nelson rate constant
L	Litre
M	Molar
m	Weight
mg	Milligram
Min.	Minute
mL	Milliliter
mm	Millimeter
mM	Millimolar
N	Normality
μm	Micrometer
nm	Nanometre
$^{\circ}\text{C}$	Degree Celsius

p	Number of experimental data
ppm	Part per million
Q	Column volumetric flowrate
q_e	Adsorption capacity at equilibrium
$q_{e, \text{calc}}$	Adsorption capacity of calculated value
$q_{e, \text{meas}}$	Adsorption capacity of experimental value
Q_{max}	Langmuir maximum adsorption capacity
q_0	Column adsorption capacity
q_t	Adsorption capacity at time t
q_{∞}	Adsorption capacity at infinite time
rpm	Revolutions per minute
s	Second
t	Time
t_b	Column breakthrough time
τ	Time at 50% column breakthrough
t_{exh}	Column exhaustion time
V	Volume
V_b	Column breakthrough volume
V_{exh}	Column exhaustion volume
σ_m	Standard error measurement

ABSTRACT

Barley straw, an agricultural byproduct, was identified as a potential adsorbent material for wastewater treatment as it offers various advantages such as abundant availability at no or very low cost, little processing cost and ability to biodegradation. The raw barley straw, however, needs to be modified as a preliminary study showed less favorability of the raw barley straw in removing oil and anionic dyes. Barley straw was chemically pretreated with sodium hydroxide and modified using a cationic surfactant, hexadecylpyridinium chloride monohydrate (CPC). Generally, the treatment with NaOH increases the negatively charged sites on straw surface and the cationic surfactant introduced forms a hydrophobic layer on the straw surface and changes the surface potential charge from negative to positive. From this exercise, four different adsorbents have been prepared, viz; raw barley straw (RBS), raw barley straw pretreated with sodium hydroxide (RBS-N), and the modification of RBS and RBS-N with the cationic surfactant CPC, which were labelled as surfactant modified barley straw (SMBS) and base pretreated surfactant modified barley straw (BMBS).

Several physical and chemical techniques were employed to characterize barley straw samples to understand the properties of raw and modified straws as well as to study the effects of modification on the textural and surface properties of the raw barley straw. Chemical compositional analyses showed that the amounts of potassium, sodium, arsenic and cadmium existing in RBS, RBS-N were generally low. The availability of cellulose, hemicellulose and lignin in RBS offers the great potential of using the barley straw as a biosorbent material. Surface group measurement by the Boehm titration showed higher acid groups in the base-treated straw (RBS-N) than raw straw due to the base hydrolyzation of lignocellulosic material, which is responsible for the increase in surface acidic sites such as carboxylic and hydroxyl groups. The percentages of carbon and nitrogen for SMBS and BMBS were greater compared to RBS and RBS-N, due to loading of CPC. Based on carbon and nitrogen values, the impregnated CPC on SMBS and BMBS was calculated as 0.086 and 0.109 mmol g⁻¹, respectively. For the surfactant modified straw, lower BET surface area was observed and could be explained by the attachment of the surfactant moieties to the

internal framework of raw adsorbents causing the constriction of pore channels. The electrical conductivity was found much lower in surfactant modified straw due to significant reduction in water soluble mineral after the surfactant modification. Higher bulk density of SMBS and BMBS was due to the addition of CPC onto the straw surface. SEM microphotos of all the prepared adsorbents showed the highly irregular shapes and sizes. The treatment with alkaline solution partly removed the protective thin wax on straw surface. The surfactant modified surface appeared to be rough, indicating that the surface had been covered with organic molecules. FT-IR spectra of RBS and RBS-N did not show any radical changes indicating that the treatment with mild base solution did not significantly alter the chemical properties of the straw. Two new bands lying at about 2920, 2850 cm^{-1} referred as asymmetric and symmetric stretching vibration of methylene (C-H) adsorption bands originated from the alkyl chain of CPC were observed on SMBS and BMBS, proving the existence of CPC on straw surface. Desorption of CPC from the surfactant modified straw was observed to increase with increasing acid solution concentration. The increasing desorption of CPC (with increased in acid solution) describes that ion exchange is the major binding mechanism. The sorption of CPC generally showed that the sorption capacity of CPC increases with increasing CPC equilibrium concentration for both RBS and RBS-N. The surfactant sorption was at the maximum when the equilibrium surfactant concentrations reached the critical micelle concentration, CMC.

Preliminary experiments found the effectiveness of the prepared adsorbents, namely; RBS, RBS-N, SMBS and BMBS in removing different types of emulsified oil from wastewater such as canola oil (CO) and standard mineral oil (SMO). Comparing to SMBS and BMBS, RBS and RBS-N showed low removal efficiency of the emulsified oil. This provided a sensible justification in using SMBS and BMBS as adsorbent materials. The adsorption tests were performed using SMBS and BMBS on CO and SMO by batch adsorption. For the sorption of CO and SMO on SMBS and BMBS, the adsorption was less favorable at high acidic condition and the maximum adsorption capacity was observed at about neutrality. Larger particle size would result in lower adsorption while adsorption temperature would not affect adsorption significantly. The kinetic study revealed that equilibrium time was short and pseudo first order model provided the best correlation for the kinetic adsorption data of CO

and SMO on both SMBS and BMBS. The film diffusion was observed as the rate limiting in the sorption of CO and SMO on SMBS and BMBS. The isotherm data for sorption of CO and SMO on SMBS and BMBS indicated that the adsorption was fitted well by the Langmuir model. The Langmuir adsorption capacities of CO and SMO on SMBS were 576.00 and 518.63 mg g⁻¹; and 613.29 and 584.22 mg g⁻¹ on BMBS, respectively. Desorption experiments also showed the stability of the oil loaded on straw. The adsorbent was later evaluated in a fixed bed column. The breakthrough curves indicated the favorable performance of SMBS and BMBS for both CO and SMO; however, less success was observed for RBS and RBS-N. The modeling of column tests showed a good agreement of experimental data of oil adsorption on SMBS and BMBS with the Thomas and Yoon-Nelson models. The column adsorption capacities from the Thomas model for SMBS and BMBS were 368.82 and 440.74 mg g⁻¹ for CO; and 310.16 and 336.31 mg g⁻¹ for SMO, respectively.

The applicability of the prepared adsorbents was also evaluated for treating dye containing wastewater. The adsorption tests were performed using SMBS and BMBS on anionic dyes of Acid Blue 40(AB40), Reactive Blue 4(RB4) and Reactive Black 5(RB5) as the preliminary batch adsorption experiments showed low removal percentage of dyes on RBS and RBS-N. The batch study also revealed that the adsorption was a function of dye concentration, pH and temperature. Adsorption capacity was found higher at pH about neutrality for AB40, and at acidic condition (pH 3) for the other dyes. Adsorption capacity of AB40 increased at increasing experimental temperature whereas no significant change was observed for RB4 and RB5. The kinetic experiment revealed that adsorption of dyes was rapid at initial stage followed by a slower phase where equilibrium uptake was achieved. Based on batch kinetic study of adsorption of AB40, RB4 and RB5 on SMBS and BMBS, the pseudo-second-order model fitted well with the kinetic data other than the pseudo first order model. The film diffusion was observed as the rate limiting in the sorption of AB40, RB4 and RB5 on SMBS and BMBS. The isotherm data of dye adsorption on SMBS and BMBS indicated that the adsorption was fitted well by the Langmuir model. The Langmuir adsorption capacities of AB40, RB4 and RB5 were 45.4, 29.16 and 24.92 mg g⁻¹ for SMBS and 51.95, 31.50 and 39.88 mg g⁻¹ for BMBS, respectively.

Desorption experiments also showed that the dye loaded straw was stable at acidic condition but desorption increased as the pH increased (i.e pH 11). The applicability of the adsorbents for AB40 and RB5 removal was also tested in a fixed bed column study. Similar to the column system for CO and SMO, the breakthrough curves on RBS and RBS-N was also poor, however, favorable column breakthrough performance was observed on SMBS and BMBS. The column breakthrough modeling showed the better fit of the experimental data of SMBS and BMBS with the Thomas and Yoon-Nelson breakthrough models. The adsorption capacities from the Thomas model for SMBS and BMBS were estimated as 53.39 and 77.29 mg g⁻¹ for AB40; and 24.57 and 33.46 mg g⁻¹ for RB5, respectively.