Department of Chemical Engineering

Treatment of Oily and Dye Wastewater with Modified Barley Straw

Shariff Che Ibrahim

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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 master can tell you what he expects of you.
A teacher, though,
Awakens your own expectations"
~Patricia Neal

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When my life overwhelms and does me in,
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~Joanna Fuchs

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~Christy Rakoczy

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and the blind can see."

~Mark Twain

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~Walter Winchell

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in the biography of souls."

~David Thomas

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~Unknown

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When you look at your life, the greatest happiness's are family happiness's.

~Joyce Brothers

PUBLICATIONS

Refereed journal publications

Broto Chandra Oei**, Shariff Ibrahim**, Ha-Ming Ang, Shaobin Wang., 2009. Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution, *Bioresource Technology*, 100(18): p. 4292-4295.

Shariff Ibrahim, Ha-Ming Ang, Shaobin Wang., 2009. Removal of emulsified food and mineral oils from wastewater using surfactant modified barley straw, *Bioresource Technology*, 2009. 100(23): p. 5744-5749.

Shariff Ibrahim, Shaobin Wang, Ha-Ming Ang. Removal of emulsified oil from wastewater using agricultural waste barley straw, *Biochemical Engineering Journal*, 2010. 49(1): p. 78-83.

Shariff Ibrahim, Ha-Ming Ang, Shaobin Wang. Adsorptive Separation of emulsified oil in wastewater using biosorbents, *Asia Pacific Journal of Chemical Engineering*. (Accepted for publication*)*

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Peer reviewed Conference proceedings

Shariff Ibrahim, Ha-Ming Ang, Shaobin Wang. Utilisation of barley straw for removal of emulsified oil in wastewater. *12th Asia Pacific Confederation of Chemical Engineering Congress (APCChE 2008)*, 2008, Dalian, China. (Oral presentation and Conference Proceeding)

Shariff Ibrahim, Ha-Ming Ang, Shaobin Wang. Kinetics of emulsified oil removal in wastewater using barley straw. *CHEMECA 2008*, Newcastle City Hall, Newcastle, Australia. (Oral presentation and Conference Proceeding**)**

Shariff Ibrahim, Ha-Ming Ang, Shaobin Wang. Adsorption of reactive dye in solution using chemically modified barley straw. *CHEMECA 2009*, Perth, Western Australia, Australia. (Oral presentation and Conference Proceeding**)**

Shariff Ibrahim, Ha-Ming Ang, Shaobin Wang. Utilization of Barley Straw as a Biosorbent for Treatment of Emulsified Oily Wastewater. Sino-Australia Symposium of Biomass and Coal 2009, Wuhan, China. (Oral presentation and Conference Proceeding)

Shariff Ibrahim, Is Fatimah, Ha-Ming Ang, Shaobin Wang. Adsorption of anionic dyes in aqueous solution using chemically modified barley straw. Water 09, International Water Association (IWA), Palmerston North, New Zealand (Oral presentation and Conference Proceeding)

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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
^oC	Degree Celsius

p	Number of experimental data
ppm	Part per million
Q	Column volumetric flowrate
q_e	Adsorption capacity at equilibrium
$q_{e, calc}$	Adsorption capacity of calculated value
$q_{e, meas}$	Adsorption capacity of experimental value
Q_{max}	Langmuir maximum adsorption capacity
q_o	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 hydrolization 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.