

## **DEDICATION**

This dissertation is dedicated to my beloved parents, Mrs. Miskiah Abu Naim and Mr. Mohammad Hj. Seman, and special dedication to my beloved husband Mr. Asan Azhari bin Sahalan. Without their continual love and support, the completion of this dissertation would not have been possible.

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## **ABSTRACT**

In this work, the adsorption potential of physic seed hull (PSH), *Jantrophe curcas L.* as an adsorbent for the removal of metal ions ( $Zn^{2+}$  and  $Cd^{2+}$ ) and malachite green dye (MG) from aqueous solution has been investigated. The study also has been extended to investigate the effect of anionic surfactant (tetra sodium N-(1, 2dicarboxy ethyl)-Noctadecyl sulfosuccinamate), known as Aerosol 22, on these adsorption processes. The performance of the adsorbent PSH has also been compared with granular activated carbon (GAC) adsorbent. The adsorbent, PSH was thoroughly characterized by SEM-EDX, BET, CHNS, Zeta potential measurement and FTIR studies. It has been observed that the adsorption of metal ions and dye increased with the increase in initial metal ions/dye concentration, contact time of adsorbent and adsorbate, temperature of adsorption, dosage of adsorbent and pH of the solution in an acidic range, but decreased with the increase in the particle size of PSH. Both PSH and GAC adsorbent exhibited better adsorption ability towards  $Zn^{2+}$  than  $Cd^{2+}$  from aqueous solution. But the adsorption capacity of PSH was found to be higher than that of GAC for both the metal ions and MG dye. Aerosol 22 was used during the adsorption process to provide the anionic functional group on the surface of PSH for supplying further adsorption site for metal ions. Addition of Aerosol 22 improved the adsorbing capacity of PSH for both the metal ions, but the effect was observed to be more for  $Zn^{2+}$ . Again, it was further observed that at higher concentration of the surfactant there was a decrease in the adsorption of metal ions. It might be related to the formation of micelles that prevented the adsorption of metal ions. The adsorption process for both the metal ions and dye on PSH was found to be consists of three-staged process - a rapid initial adsorption of the metal ions initially, followed by a period of slower uptake of the metal ions and finally no significant uptake of the metal ions. The kinetics of metal ions adsorption process

was therefore described by a pseudo-second order model. The adsorption equilibrium data were fitted in the three adsorption isotherms, e.g. Freundlich isotherm, Langmuir isotherm and Dubinin-Radushkevich isotherm. The adsorption data fitted best to the Langmuir isotherm indicating the adsorption of metal ions and dye on PSH could be described as a monolayer chemisorption process. The activating energy for the adsorption of metal ions and dye as calculated using from D-R Isotherm was found to be more than 16kJ/mol which is particle diffusion. The adsorption capacity of PSH was found to be comparable to that for other available adsorbents as cited in literatures. From the study it is evident that as an adsorbent, PSH has significant potential for usage in the separation of metal ions and dye from waste water.

## **ABSTRAK**

Dalam kajian ini, potensi lapisan kulit luar biji buah jarak pagar (PSH), (*Jantropha curcas L.*) sebagai bahan penjerap untuk membuang sisa logam berat ( $Zn^{2+}$  dan  $Cd^{2+}$ ) dan pewarna (Malachite Green) dari larutan cecair telah dikaji. Kajian tambahan telah dijalankan dengan menambahkan bahan aktif permukaan bersifat anionik (tetra sodium N-(1,2dicarboxy ethyl)-Noctadecyl sulfosuccinamate) atau dikenali sebagai Aerosol 22 dalam process penjerapan ini. Kajian perbandingan juga telah dilakukan terhadap prestasi bahan penjerap PSH dengan menggunakan bahan penjerap karbon teraktif berbutir (GAC). Kajian pencirian juga telah dilakukan terhadap PSH dengan menggunakan teknik SEM-EDX, BET, CHNS, ukuran potensi Zeta dan kajian FTIR. Pemerhatian mendapati penjerapan ion-ion logam dan pewarna bertambah dengan setiap peningkatan kepekatan ion-ion logam/pewarna, masa interaksi bahan penjerap dengan zat terjerap, suhu penjerapan, dos bahan penjerap dan pH larutan dalam julat berasid, tetapi berkurangan apabila saiz butiran PSH bertambah. Kedua-dua bahan penjerap PSH dan GAC menunjukkan keupayaan penjerapan lebih baik ke atas  $Zn^{2+}$  daripada  $Cd^{2+}$  di dalam larutan cecair. Walaubagaimanapun keupayaan jerapan PSH didapati lebih tinggi daripada GAC bagi kedua-dua ion logam dan pewarna MG. Aerosol 22 telah digunakan dalam proses penjerapan bagi menyediakan kumpulan berfungsi beranion pada permukaan PSH sebagai tapak penjerapan tambahan bagi ion-ion logam. Aerosol 22 mampu memperbaiki keupayaan menjerap PSH bagi kedua-dua ion logam dan kesan lebih baik adalah pada ion  $Zn^{2+}$ . Kajian juga mendapati bahawa pada kepekatan bahan aktif permukaan yang lebih tinggi, penjerapan ion-ion logam adalah berkurangan. Ia mungkin berkait dgn pembentukan misel yang menghalang penjerapan ion-ion logam. Proses penjerapan untuk kedua-dua ion logam dan pewarna pada PSH melibatkan tiga peringkat proses - penjerapan pantas pada

peringkat awal, diikuti penjerapan perlahan dan akhirnya tiada penjerapan. Proses kinetik penjerapan ion-ion logam dan pewarna juga dapat diterangkan menggunakan model pseudo-peringkat kedua. Data keseimbangan penjerapan adalah bersesuaian dengan tiga isoterma penjerapan - isoterma Freundlich, isoterma Langmuir dan isoterma Dubinin-Radushkevich. Data penjerapan isoterma Langmuir merupakan isoterma yang terbaik digunakan bagi menunjukkan penjerapan ion-ion logam dan pewarna pada PSH merupakan proses selapis serapan kimia. Tenaga pengaktifan bagi penjerapan ion-ion logam dan pewarna yang dikira dengan menggunakan isoterma D-R didapati lebih daripada 16kJ/mol dan ini menunjukkan jerapan partikel. Keupayaan jerapan PSH didapati setanding dengan bahan penjerap lain seperti yang dinyatakan dalam imbasan rujukan. Kajian jelas menunjukkan bahawa bahan penjerap PSH mempunyai berpotensi tinggi dalam proses pengasingan ion logam dan pewarna daripada air buangan.

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## LIST OF ABBREVIATIONS

<b>A</b>	area, $m^2$
<b>AAS</b>	Atomic Absorption Spectrometer
<b>b</b>	Langmuir constant, $L/mg$
<b>BET</b>	Brunauer-Emmett-Teller
<b>C<sub>i</sub></b>	initial concentration, $mg/L$
<b>C<sub>e</sub></b>	equilibrium concentration, $mg/L$
<b>C<sub>t</sub></b>	concentration of the sorbate at time t, $mg/L$
<b>Cd<sup>2+</sup></b>	cadmium ion
<b>cec</b>	cation exchange capacity
<b>D-R</b>	Dubinin Radushkevich
<b>E</b>	mean free energy ( $\text{kJ mol}^{-1}$ )
<b>EPA</b>	Environmental Protection Agency.
<b>FDA</b>	United States Food and Drug Administration
<b>FTIR</b>	Fourier Transform Infrared
<b>G</b>	Gibbs free energy
<b>GAC</b>	granular activated carbon
<b>h</b>	initial sorption rate
<b>H</b>	standard enthalpy
<b>HM</b>	heavy metals.
<b>IUPAC</b>	International Union of Pure and Applied Chemistry.
<b>k<sub>i</sub></b>	intraparticle diffusion rate constant
<b>k<sub>1</sub></b>	rate constant for first-order model, $min^{-1}$
<b>KBr</b>	potassium bromide.
<b>k<sub>f</sub></b>	rate constant for Freundlich
<b>k<sub>2</sub></b>	rate constant for second-order model, $g /mg.h$ ,
<b>K<sub>L</sub></b>	rate constant for Langmuir, $mg/g$
<b>k<sub>a</sub></b>	adsorption equilibrium constant for thermodynamic
<b>L<sub>a</sub></b>	separation factor of Langmuir
<b>m</b>	mass of adsorbent , $mg$
<b>MG</b>	malachite green
<b>n</b>	adsorption intensity for Freundlich
<b>P<sub>c</sub></b>	critical pressure
<b>pH<sub>zpc</sub></b>	pH at zero point charge
<b>PSH</b>	physic seed hull

$q_e$	adsorbed amount at equilibrium, $mg/g$
$q_t$	adsorbed amount at $t$ time, $mg/g$
$q_m$	adsorbed amount at maximum monolayer, $mg/g$
$r$	radius
$R$	gas constant (8.314 J/molK)
$R^2$	regression correlation coefficient
$R_L$	separation factor
$r_{peak}$	peak radius
$S$	standard entropy
$S_{l/s}$	spreading coefficient
$SEM$	Scanning Electron Microscopy
$T$	absolute temperature (k)
$t$	time, minute
$t^{1/2}$	half-time for adsorption, $min$
$UV-VIS$	Ultraviolet-visible spectrophotometer
$V$	solution volume, $m^3$ @ $mL$
$V_{mes}$	mesopore volumes.
$X_m$	maximum adsorption capacity for D-R isotherm (mg/g)
$XRD$	X-ray diffraction.
$Zn^{2+}$	zinc ion
$Z$	charge
$Z^2/r$	ionic potential

### Greek letters

$\text{\AA}$	Angstrom
$\lambda_{max}$	maximum wavelength, nm
$\Delta$	change
$\varepsilon$	Polanyi potential
$\beta$	constant related to sorption energy ( $\text{mol}^2 \text{ kJ}^{-2}$ )
$\Phi_s$	sphericity
$\theta$	contact angle