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Ion-exchange Adsorption of Reactive Dye Solution onto Quaternized Palm Kernel Shell

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Abstract: Quaternized palm kernel shell was successfully prepared by reacting with N-(3-chloro-2-hydroxypropyl)trimethylammonium chloride in basic condition. Adsorption experiments of Reactive Red E (RRE) dye were carried out in single batch system studied at various initial concentration, contact time and pH at 25°C. It was found that at pH 4 quaternized palm kernel shell showed the highest dye removal percentage of 99% at 100 mg L^{-1} initial dye concentration. The equilibrium data were analyzed by Langmuir, Freundlich and Redlich-Peterson models and Redlich-Peterson model was best fit to describe this adsorption. Contact time data were analyzed using pseudo-first-order and pseudo-second-order kinetic models and was found that the kinetics conformed pseudo-second-order kinetic model. The maximum adsorption capacity of RRE was 183 mg g^{-1} for single batch system.

Key words: Adsorption, reactive dyes, palm kernel shell, quaternization

INTRODUCTION

Synthetic dyes used in industry especially textile industry cause water pollution. Rinsing process in textile finishing industry is water demanding which produced about 100 to 500 L kg^{-1} product of strong colored effluent. Moreover, synthetic dye might contain aromatic amines and heavy metals which are genotoxic and hazardous (Pinheiro et al., 2004). Dye effluent needs treatment to meet the environment regulations. However, there is not much efficient and convention way to treat dyes wastewater because the xenobiotic and recalcitrant nature of dye molecules making it resists to aerobic digestion, light and oxidation agent especially reactive dyes (Robinson et al., 2002).

Adsorption is recognized as the best and widely used method for wastewater treatment because of simple equipment and process operation, no harmful by-product, efficient and low energy consumption (Dabrowski, 2001). Researches had studied the modified biomass as adsorbent in treating wastewater because it is cheap, feasible. Besides, it helps to manage the agro-waste (Bhatnagar and Sillanpaa, 2010). In Malaysia, the second world palm oil producers, 4.98 million hectares of area planted with oil palm which is 73% of agricultural land in year 2011 (MPOB, 2011). Malaysia produced 5.2 million tons of Palm Kernel Shell (PKS) in year 2010 (Ng et al., 2012). Research on modifying abundant biomass into reusable value added products is very encouraging. The large quantities of PKS is most suitable to be used as adsorbent because of its granular structure, insolubility in water, chemical stability and high mechanical strength (El-Sayed, 2011; Ofomaja, 2007; Jumasiah et al., 2005). However, thermal activation treatment on biomass to produce activated carbon is high in production cost.

Quaternization is a surface chemical treatment by adding positively charged surface functional group onto lignocellulosic fiber via epoxy substitution to increase affinity towards anionic substances by promote ion-exchange adsorption (Wartelle and Marshall, 2006; Orlando et al., 2002). N-(3-chloro-2-hydroxypropyl) trimethylammonium chloride (CHMAC) is a commonly used quaternization agent. Quaternized cellulose used as anion-exchange adsorbent was proven to be effective in removing various anionic dyes (Simkovic et al., 2009; Wartelle and Marshall, 2006). Research had done using quaternized flax shive (Wang and Li, 2013), Maize cobs (Elizalde-Gonzalez et al., 2008), rice husk (Low and Lee, 1997) and wheat straw (Xu et al., 2010) to remove anionic dyes. Therefore, this study is to develop a quaternized palm kernel shell (MPKS) adsorbent to remove Reactive Red E (RRE) from aqueous solution.

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MATERIALS AND METHODS

Materials and chemicals: PKS is waste from crude palm oil production, was obtained from Rompin palm oil mill,Pahang, Malaysia. RRE supplied by Texchem-pack Bhd Bayan Lepas, Penang, Malaysia. N-(3-chloro-2-hydroxyproply trimethylammonuim chloride (CHMAC) 60% in water was purchased from Sigma-Aldrich. NaOH was purchased from Merk. Acetone, acetic acid and hydrochloric acid were all analytical grade purchased from Acros. All chemicals were used without further modification.

Quaternization of palm kernel shell: PKS was washed with hot water followed by acetone to remove oil and dried at under the sun for three days. Then, PKS was grinded and sieved to size between 1 and 0.25 mm. Granular PKS was mercerized with NaOH of 40 wt.% for 10 h. Mercerized PKS was rinsed with distilled water and dried at 60°C. Dried mercerized PKS was weight. Each gram of PKS was reacted to a solution consisting of 1.5: 4: 2.5 w/w ratio of NaOH, CHMAC and water, respectively (Liu *et al.*, 2011). Hence, the solution added to each gram of PKS contained 37 mmol of NaOH and 35 mmol of CHMAC. The mixture was kept in sealed container at room temperature for 24 h. Then the modified PKS (MPKS) was washed with 0.2% acetic acid solution to stop the reaction and followed by distilled water until pH 7. MPKS was dried at 60°C and kept in desiccator.

Characterization of MPKS: Infrared (IR) spectra were recorded on a Fourier Transform-Infrared (FT-IR) Spectrometer (Perkin Elmer 1750X). All the spectra were plotted as the percentage of transmittance versus wave number (cm^{-1}) for the range of 400-4000 cm^{-1} at room temperature to determine functional groups of samples. Surface morphology was acquired using Scanning Electron Microscopy (SEM) (Hitachi S-3400N). Samples were prior coated with a thin layer of Au/Pd. Specific surface area was measured by BET surface area analyzer (AutoSorb-1 Quantachrome). Pore size distribution, average pore size and pore volume of samples were determined using the Barrett, Johner and Halenda (BJH) equation. Determination of nitrogen content of MPKS was by using elemental analyzer (LECO CHNS-932).

Adsorption experiments: All the adsorption experiments were carried out in batch system using 250 mL Erlenmeyer flasks and 100 mL sample volume. All flasks were sealed properly using parafilm followed by aluminium foil to prevent leakage and evaporation. The shaking rate is 160 rpm (±2 rpm) and at temperature of 28°C (±2°C). The adjustment of pH was using 0.1 N HCl and 0.1 N NaOH

solutions. 1 g L^{-1} MPKS was added to each flask. The dye sample solution was filtered through a filter paper to separate the adsorbent before running analysis. Measurement of the solution concentration was by ultraviolet double beam spectrophotometer (GENEYES 10 ultraviolet, USA) at the maximum wavelength of 540 nm.

For effect of initial pH, 100 mg L^{-1} RRE solution was adjusted to pH 2, 3, 4, 5, 6, 7, 8 and 9, respectively and shaken for 1.5 h.

RRE solution of initial concentration 100 to 800 mg L^{-1} was prepared and pH was adjusted to the optimum adsorption pH and shaken for 8 days to reach equilibrium state.

For kinetic study, 250 mL RB5 solution of initial concentration 100, 300 and 500 mg L^{-1} with pH adjusted to the optimum adsorption pH was prepared and placed in 500 mL Erlenmeyer flask. 1 mL of sample was pipetted at different time intervals for analysis until the solution reached equilibrium state.

RESULTS AND DISCUSSION

Characterization: From FTIR spectra, PKS and MPKS have O-H stretching at 3353 and 3297 cm^{-1} and C-H stretching at 2923 and 2902 cm^{-1}, respectively. Peaks at 1462 and 1420 cm^{-1} with nearly equal intensity were assigned to C-H stretching of tert-butyl group on MPKS. Peaks at 935 cm^{-1} in MPKS spectrum attributed to C-N stretching which is not present in PKS spectrum prove that the NR$_4^+$ group was successfully quaternized in MPKS. From PKS and MPKS spectrum, C-O stretch mode appeared at 1030 and 1033 cm^{-1}, respectively.

The textural structure of granular PKS and MPKS were observed by SEM images as in Fig. 1a-d. Figure 1b shows mercerized PKS indicating that base treatment increases the pore diameter from micropores to macropores. Distinguished dark sport indicates the depth of the pore. In Figure 1c shows the surface of the MPKS became smooth with larger cleavage of macropores that make it possible to adsorb relatively larger molecules (Fig. 1a). Pores on MPKS after adsorption (Fig. 1d) became not visible because it had blocked by the dye molecules during adsorption.

As illustrated in Table 1, the average pore diameter of PKS is 2.2 nm which is mesopores, after treatment, MPKS has average pore diameter of 112.6 nm which is macropores. Enlargement of the pore size is due to the dissolved of lignin and hemicellulose in NaOH solution during the pre-treatment process in order to dispose the cellulose part which then reacted with quaternizing agent. MPKS shows slight decrease in surface area (S$_{BET}$) and pore volume from PKS because the texture of shell surface became smoother after reaction.
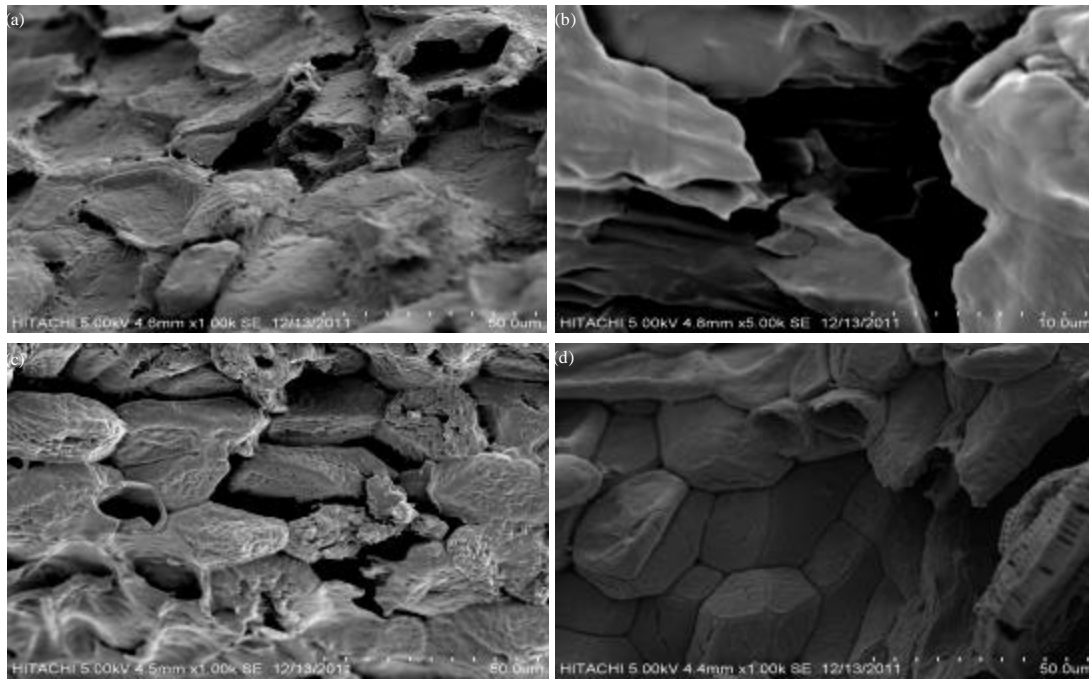
Fig. 1(a-d): SEM micrograph of PKS and MPKS (b) at 5K magnification and (a), (c), (d) at 1K magnification

Table 1: Properties of MPKS and PKS

Samples	$S_{BET}(m^2\ g^{-1})$	Average pore diameter (nm)	Pore volume ($cm^3\ g^{-1}$)	% of pore volume in stated pore size range (nm)		
				<2	2-50	>50
PKS	1.932	2.2	0.003	0	64.68	35.32
MPKS						
Element (%)	1.717 Carbon	112.6 Hydrogen	0.001 Nitrogen	0 Sulfur	0	100
PKS	47.24	4.87	0.24	0.00		
MPKS	45.08	5.41	0.98	0.12		

Assuming that percentage of nitrogen obtained represents the grafted amine groups contain on MPKS. CHNS elemental analysis (Table 1) shows that the nitrogen percentage increased from 0.24% to 0.98% after quaternization.

Effect of pH: In this study, the optimum pH for adsorption of RRE by MPKS is at pH 4 (Fig 2). The sulfonate groups of RRE were hydrolyzed into anionic form in aqueous solution. At pH 4, all the hydroxyl and amino group of MPKS will be protonated thus creates a net positive charge on surface of sorbent and hence enhancing the electrostatic attraction (Hanafiah *et al.*, 2012). As pH increased, the surface of MPKS became more negatively charged and repels the anionic RRE. At high pH, there will be competition between OH^- ions and RRE that hindered the dye

Table 2: Constants of Langmuir, Freundlich and Redlich-Peterson models for adsorption of RRE by MPKS

Isotherm models	Constants			
	K_L (L g^{-1})	α_L(L mg^{-1})	qm (mg g^{-1})	R^2
Langmuir	324.81	1.776	182.84	0.930
	K_F (L mg^{-1})	$1/n_F$		
Freundlich	115.50	0.081	0.869	
	K_S (L g^{-1})	$1/n_S$	α_S (L mg^{-1})	
Redlich-peterson	425.05	2.729	0.971	0.951

to be adsorbed. Therefore, pH 4 was determined as optimum pH for all the subsequent adsorption experiments.

Isotherm study: Three isotherm models namely Langmuir, Freundlich and Redlich-Peterson isotherms were used to analyze the data. The constant listed in Table 2 were identified using non-linear method. The sum of the square

Table 3: Parameters of pseudo-first-order and pseudo-second-order kinetic models for adsorption of RRE by MPKS

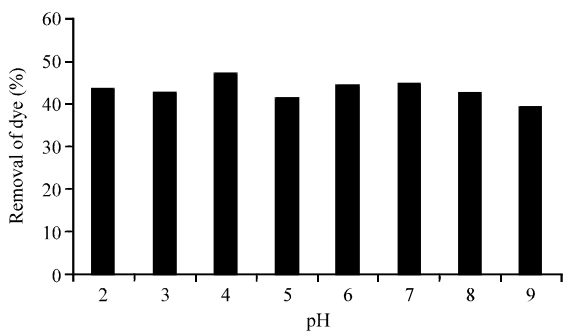| Initial RRE concentration (mg L^{-1})	qe$_{exp}$ (mg g^{-1})	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		q$_1$ (mg g^{-1})	k$_1$ (min^{-1})	R^2	q$_2$ (mg g^{-1})	k$_2$ (g mg^{-1} min)	R^2
100	96.66	57.07	9.21E-04	0.9517	98.04	5.40E-05	0.9991
300	229.02	279.83	6.91E-04	0.7536	243.90	4.34E-06	0.9144
500	231.65	180.38	4.61E-04	0.8352	222.22	8.10E-06	0.9274

Fig. 2: Effect of pH on adsorption of RRE on MPKS

of the errors function (ERRSQ) was used together with solver add-in with Microsoft's spreadsheet, Excel to minimize the error function across the concentration range studied (Gimbert *et al.*, 2008). Redlich-Peterson isotherm model is best describing adsorption of RRE on MPKS. It gives the highest correlation coefficient (R^2) value that is 0.951 among others. This can be concluded that the adsorption of RRE on MPKS is has both characteristic of Langmuir and Freundlich isotherm model.

Kinetic study: Pseudo-first-order kinetic model and pseudo-second-order kinetic model were used to study the adsorption kinetics of RRE on MPKS. From the equations, k$_1$ and k$_2$ (min^{-1} and g mg^{-1} min^{-1}) are the pseudo-first and pseudo-second order rate constant, respectively. q$_1$ and q$_2$ (mg g^{-1}) are the theoretical values of the amount of RRE adsorbed per gram of MPKS in equilibrium state by pseudo-first and pseudo-second order kinetic models, respectively. Table 3 shows the parameters and correlation coefficient (R^2) of pseudo-first and pseudo-second order kinetic models. Both the kinetic equations were rearranged to give the linear graft and parameters were obtained from the slope and intercept of the graph.

R^2 values for pseudo-second-order kinetic model were greater than 0.9991 for this study. Moreover, the calculated qe values are similar to the experimental qe values. Therefore, pseudo-second-order kinetic model is suitable to describe the kinetic mechanism of this study. Hence, adsorption kinetic of RRE on MPKS occurred by internal diffusion mechanism and chemisorption involved (Ho and McKay, 1999).

CONCLUSION

In this study, MPKS was successfully synthesized and proved to be effective to adsorb RRE in aqueous solution. The maximum amount of dye per unit mass of adsorbent was 183.8 mg g^{-1}. Redlich-Peterson isotherm was best describing adsorption process of RRE onto MPKS. The sorption process followed pseudo-second order kinetic process.

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REFERENCES

Bhatnagar, A. and M. Sillanpaa, 2010. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment-A review. Chem. Eng. J., 157: 277-296.

Dabrowski, A., 2001. Adsorption-from theory to practice. Adv. Colloid Interf. Sci., 93: 135-224.

El-Sayed, G.O., 2011. Removal of methylene blue and crystal violet from aqueous solutions by palm kernel fiber. Desalination, 272: 225-232.

Elizalde-Gonzalez, M.P., J. Mattusch and R. Wennrich, 2008. Chemically modified maize cobs waste with enhanced adsorption properties upon methyl orange and arsenic. Bioresour. Technol., 99: 5134-5139.

Gimbert, F., N. Morin-Crini, F. Renault, P.M. Badot and G. Crini, 2008. Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: Error analysis. J. Hazard. Mater., 157: 34-56.

Hanafiah, M.A.K.M., W.S.W. Ngah, S.H. Zolkafly, L.C. Teong and Z.A.A. Majid, 2012. Acid blue 25 adsorption on base treated *Shorea dasyphylla* sawdust: Kinetic, isotherm, thermodynamic and spectroscopic analysis. J. Environ. Sci., 24: 261-268.

Ho, Y.S. and G. McKay, 1999. Pseudo-second order model for sorption processes. Process Biochem., 34: 451-465.

Jumasiah, A., T.G. Chuah, J. Gimbon, T.S.Y. Choong and I. Azani, 2005. Adsorption of basic dye onto palm kernel shell activated carbon: Sorption equilibrium and kinetics studies. Desalination, 186: 57-64.

Liu, Z., Y. Ni, P. Fatehi and A. Saeed, 2011. Isolation and cationization of hemicelluloses from pre-hydrolysis liquor of kraft-based dissolving pulp production process. Biomass Bioenergy, 35: 1789-1796.

Low, K.S. and C.K. Lee, 1997. Quaternized rice husk as sorbent for reactive dyes. Bioresour. Technol., 61: 121-125.

MPOB, 2011. Oil palm planted areas as at September 2011. http://econ.mpob.gov.my/economy/area/Area_cate gory.pdf

Ng, W.P.Q., H.L. Lam, F.Y. Ng, M. Kamal and J.H.E. Lim, 2012. Waste-to-wealth: Green potential from palm biomass in Malaysia. J. Clean Product, 34: 57-65.

Ofomaja, A.E., 2007. Kinetics and mechanism of methylene blue sorption onto palm kernel fiber. Process Biochem., 42: 16-24.

Orlando, U.S., A.U. Baes, W. Nishijima and M. Okada, 2002. A new procedure to produce lignocellulosic anion exchangers from agricultural waste materials. Bioresour. Technol., 83: 195-198.

Pinheiro, H.M., E. Touraud and O. Thomas, 2004. Aromatic amines from azo dye reduction: Status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters. Dyes Pigments, 61: 121-139.

Robinson, T., B. Chandran, G. Sathya Naidu and P. Nigam, 2002. Studies on the removal of dyes from a synthetic textile effluent using barley husk in static-batch mode and in a continuous flow, packed-bed, reactor. Bioresour. Technol., 85: 43-49.

Simkovic, I., M.P. Yadav, M. Zalibera and K.B. Hicks, 2009. Chemical modification of corn fiber with ion-exchanging groups. Carbohydrate Polym., 76: 250-254.

Wang, L. and J. Li, 2013. Adsorption of c.I. Reactive red 228 dye from aqueous solution by modified cellulose from flax shive: Kinetics, equilibrium and thermodynamics. Ind. Crops Prod., 42: 153-158.

Wartelle, L.H. and W.E. Marshall, 2006. Quaternized agricultural by-products as anion exchange resins. J. Environ. Manage., 78: 157-162.

Xu, X., B.Y. Gao, Q.Y. Yue and Q.Q. Zhong, 2010. Preparation and utilization of wheat straw bearing amine groups for the sorption of acid and reactive dyes from aqueous solutions. J. Hazard Mater., 182: 1-9.