Jurnal Teknologi

Full paper

Metals Chloride-Activated Castor Bean Residue for Methylene Blue Removal

Lee Lin Zhi[a,b], Muhammad Abbas Ahmad Zaini[a,b*]

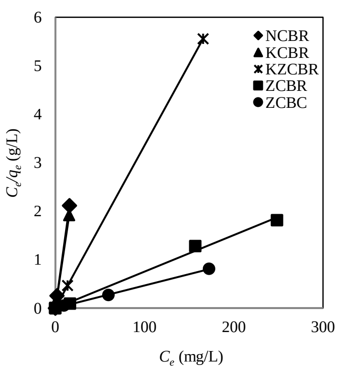
[a]*Centre of Lipids Engineering & Applied Research (CLEAR), Ibnu Sina ISIR, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia*
[b]*Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Malaysia*

*Corresponding author: abbas@cheme.utm.my

Article history

Received : 2 March 2015
Received in revised form :
24 April 2015
Accepted : 10 May 2015

Graphical abstract



Abstract

This work aims to evaluate the feasibility of castor bean residue as the precursor of activated carbon by metal chloride salts as activating agent. $ZnCl_2$, NaCl and KCl were used to activate the castor bean residue and the performance was investigated by adsorption of methylene blue and its correlation with the specific surface area. $ZnCl_2$-activated castor bean cake with had the best adsorption result with maximum capacity of 213 mg/g and specific surface area of 643 m^2/g. The adsorption of methylene blue for all metals chloride-activated castor bean residue followed Langmuir isotherm which suggests monolayer adsorption onto the homogeneous surface.

Keywords: Activated carbon; adsorption; castor bean residue; metals chloride; methylene blue

1.0 INTRODUCTION

Dyes are widely used to add value on the appearance of the products such as textiles, printing and food. There are more than 7x10^5 tonnes of dyes produced annually, but 12% of them are discharged in effluent and result in environmental problem [1]. Dye is visible pollutant, its existence can severely affect the surface water quality, aquatic ecosystems and food chain [2]. Cationic dyes are water soluble and yield cations in solution. Few examples of cationic dyes are methylene blue, malachite green, rhodamine B., crystal violet and safranin. These dyes can cause eye burns in humans and animals, methemoglobinemia, cyanosis, convulsions, tachycardia, dyspnea, irritation to the skin, irritation to the gastrointestinal tract, nausea, vomiting and diarrhoea [3].

There are various treatment methodologies that have been investigated such as biodegradation, coagulation, oxidation, and adsorption. Adsorption is most economically attractive due to its flexibility and simplicity of the design, ease of operation and insensitivity to toxic pollutants [2, 4]. Activated carbon is regarded as the most effective adsorbent for dyes removal, due to its large porous surface area, controlled pore structure and inert properties [5]. They can be prepared from a variety of raw materials, especially agricultural by-products such as wood apple shell [6], rice husk [7], palm shell [8] and many others. Castor bean residue is the by-product of castor oil production, the remains after the extraction of the oil comprises about 50% of the castor bean weight [9]. Due to its rich source, which is 1.1 tons per 1 ton of castor oil production, castor bean residue is also a suitable precursor to replace the conventional activated carbon [10].

The use of $ZnCl_2$ as activating agent has been widely investigated in the synthesis of activated carbon from coffee ground [11], coir pith [12], safflower seed press cake [13], cassava peel [14] and so on, but there are concerns about the aquatic toxicity of $ZnCl_2$ in large-scale manufacturing processes. NaCl and KCl are the least toxic metal chloride salts which has opened up the possibility of replacing $ZnCl_2$ as activating agent to produce activated carbon.

Equilibrium isotherm plays a significant role in the theoretical evaluation, and interpretation of heat of adsorption and mechanisms involved for process optimization [15,16]. Langmuir and Freundlich are two common isotherm models in equilibrium studies.

The aim of this paper is to investigate the effect of metals chloride, namely $ZnCl_2$, NaCl and KCl in the preparation of activated carbon on the adsorption performance of methylene blue. Equilibrium data were analyzed using isotherm models to evaluate the feasibility of activated carbons derived from castor bean residue.

■2.0 MATERIALS AND METHODS

2.1 Preparation of Activated Carbon

Castor bean residue (CBR) for the preparation of activated carbon (AC) is the by-product from solvent extraction of castor bean. The castor bean was formerly purchased from Ancient Greenfileds Pvt Ltd, India. Methylene blue (MB), C.I. No. 52015, MW=319.85g/mol and λ_{max}=580nm was purchased from HmbG Chemicals. Zinc chloride, $ZnCl_2$ (98%), sodium chloride, NaCl (99.5%) and hydrochloride acid, HCl (37%) were purchased from R&M Marketing, Essex. Potassium chloride, KCl (99.5%) was purchased from Merck and sodium hydroxide pellet, NaOH (96%) was obtained from Bendosen. All chemicals are of analytical-grade reagents.

Activated carbons were prepared from two different precursors using four activating agents, as stated in Table 1.

Table 1 Preparation of activated carbon

Sample	Precursor	Activating agent
NCBR	Castor bean cake + shell	NaCl
KCBR	Castor bean cake + shell	KCl
KZCBR	Castor bean cake + shell	50wt% KCl + 50wt% $ZnCl_2$
ZCBR	Castor bean cake + shell	$ZnCl_2$
ZCBC	Castor bean cake	$ZnCl_2$

CBR was mixed with activating agent (dissolved in water) at weight ratio of 1.0, and the mixture was homogenized using hot plate at 90˚C for 1.5 h. The mixture was dried in an oven at 110˚C for 24 h. After that, the impregnated CBR was heated in furnace at 550˚C for 1.5 h, and the resultant activated carbon was washed with 3M HCl. Then, the activated carbon was washed with hot distilled water to remove excess minerals and acid until the pH value is near to 4. The activated carbon was dried in the oven at 110˚C overnight and used for MB adsorption and specific surface area measurement by Pulse Chemi Sorb 2705 with liquid N_2 at 77 K.

The yield of activated carbon was calculated as,

$$yield = \frac{m}{m_0} \times 100\% \qquad (1)$$

where m is the mass of activated carbon (g) and m_0 is the mass of CBR (g).

2.2 Proximate Analysis of CBR

CBR was put in a beaker and heated in the oven at 110ºC for 24 h. The beaker was taken out and weighed to get the final weight of dry CBR. The moisture content of CBR was calculated as,

$$\%\ moisture\ content = \frac{m_w - m_d}{m_d} \times 100\% \qquad (2)$$

where m_w is the weight of wet sample (g) and m_d is the weight of dry sample (g).

Dry CBR was put into a crucible and gasified in a furnace at 900ºC for 2 h. The crucible was taken out and weighed to get the final weight of ash. The ash content of CBR was calculated as,

$$\%\ ash\ content = \frac{m_a}{m_d} \times 100\% \qquad (3)$$

where m_a is the weight of ash (g).

2.3 Equilibrium Adsorption

Fifty mL of MB solutions were prepared at varying initial concentrations in the range of 5-400 ppm. Fifty mg of activated carbon was brought into intimate contact with the MB solutions, and the mixtures were allowed to equilibrate at 120 rpm and 25˚C for 72 h. The concentration of MB was analysed using HALO VIS-10 visible spectrophotometer.

Adsorption capacity was calculated by Equation 4,

$$q_e = \frac{(C_0 - C_e)}{m} V \qquad (4)$$

where q_e is the equilibrium dye concentration on the AC (mg/g), C_0 is the initial concentration of dye solution (mg/L), $C_e$is the equilibrium concentration of dye solution (mg/L), m is the mass of AC (g) and V is the volume of dye solution (L).

Two isotherm models were used to analyse the adsorption data. Langmuir model was used to indicate the monolayer adsorption by describing the formation of a monolayer adsorbate at the outer surface of the activated carbon with a finite number of identical binding sites [17]. The Langmuir equation is given as follows,

$$q_e = \frac{QbC_e}{1 + bC_e} \qquad (5)$$

where Q is the maximum monolayer capacity of adsorbent (mg/g), and b is the Langmuir adsorption constant (L/g). Constant b is the coefficient related to the affinity between the adsorbent and the adsorbate at low adsorbate concentration. The higher the b, the higher is the affinity of the adsorbent for adsorbate [18].

The essential features of the Langmuir isotherm were expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter [19]. It is given as,

$$R_L = \frac{1}{1 + bC_0} \qquad (6)$$

where C_0 is the maximum initial concentration (mg/L). R_L values indicating the nature of adsorption are given in Table 2.

Table 2 Nature of adsorption

R_L value	Nature
>1	unfavourable
1	linear
0-1	reversible
0	irreversible

Freundlich equation was used to represent the adsorption on heterogeneous surface of CBR-ACs. Theoretically, there is an infinite amount of adsorption that is possible to be occurred [20]. The Freundlich equation is given as follows,

$$q_e = KC_e^{1/n} \qquad (7)$$

where K and n are Freundlich constants.

Higher K indicates higher maximum adsorption capacity. If n=1 then the partition between the two phases is independent of the concentration. The adsorption process follows a normal Langmuir adsorption if the value of $1/n$ is lesser than 1 [21].

3.0 RESULTS AND DISCUSSION

3.1 Characteristics of Activated Carbon

Table 3 shows the characteristics of CBR and the derived activated carbons.

Table 3 Characteristics of CBR and activated carbons

Raw material	Castor bean cake + shell				Castor bean cake
Moisture content (%)	10.1				10.0
Ash content (%)	3.83				1.95
Activated Carbon	NCBR	KCBR	KZCBR	ZCBR	ZCBC
pH	3.86	3.88	3.47	3.14	3.18
Yield (%)	28.1	26.1	23.4	32.4	21.6
Specific surface area (m^2/g)	142	128	255	739	643

The values of moisture content and ash content are fairly close to those in previous reports. The slight difference in value is expected because of physical and environmental conditions, and oil extraction methods involved [22, 23].

The yield of activated carbon from castor bean cake and shell is in the range of 27.5±4.6%, which is higher than that of ZCBC. This is because castor bean cake is totally in the powder form, so the average size is smaller. More surface area was contacted and reacted with the activating agent that enhances the elimination of light and volatile matter by breaking aliphatic and aromatic bonds, thus leading to the loss in weight [24].

Both $ZnCl_2$-activated carbons have higher BET surface area as $ZnCl_2$ is a good activating agent although it resulted in increasing carbon "burn-off". The $ZnCl_2$-carbon reaction enhances the existing pores, and creates new porosities so as to increase the specific surface area and pore volume [25]. This indicates that the activated carbons could possess higher maximum adsorption capacity [6].

3.2 Adsorption of Methylene Blue

Figure 1 shows the equilibrium adsorption of methylene blue (MB) by metals chloride-activated castor bean residue.

All activated carbons demonstrated a clearly increasing trend in the equilibrium adsorption capacity, q_e and achieved a saturation point which is known as maximum uptake. Equilibrium is achieved when the amount of MB being adsorbed onto the activated carbon is equal to the amount being desorbed. At lower concentration, there are much of available sites of adsorption, so the percentage of adsorption is independent of the initial concentration. While at high concentration, the available sites of adsorption become fewer; when there are no active sites for further adsorption, then equilibrium is achieved [26].

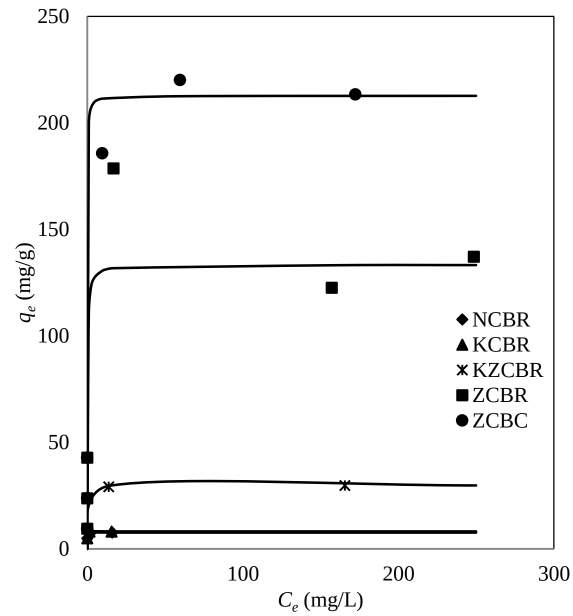


Figure 1 Equilibrium adsorption of methylene blue

ZCBC showed the best performance on MB adsorption. ZCBC is in the powder form while the other counterparts are in the mixture of plate and powder, and consequently, ZCBC has smaller size. The smaller size increases the percentage of dye adsorption because the external surface area of the adsorbent is larger, so there are more available sites for binding the dye onto the surface of activated carbon [27]. This result is supported by its specific surface area, which is one of the highest among the activated carbons studied, i.e., 643 m^2/g.

Oliveira *et al*. [28] reported that smaller size of metal ions of activating agent might yield activated carbon with smaller pores, which contributes to higher surface area and better dye adsorption. This is because the remaining activating agent deposited on the surface of the carbon matrix can be removed by washing with HCl solution for the evolution of additional pores. Therefore, smaller size metal ions may act as the template for creating smaller pores [13, 29]. In this study, ionic radius of Zn^{2+} (74 pm) is smaller than Na^+ (102pm) and K^+ (138 pm). This result is also in parallel with their specific surface area, which is in the order of ZCBR > NCBR > KCBR.

3.3 Isotherm Studies

Table 4 summarizes the constants of isotherm models for MB adsorption by metals chloride-activated castor bean residue. Figure 2 shows the linear regression of Langmuir adsorption isotherm for each activated carbon. It was found that the R^2 values for all five activated carbons are close to 1 by Langmuir model. This indicates the applicability of Langmuir isotherm in adsorption of MB by activated carbons. The adsorption process can be described as homogeneous in nature, in which the monolayer coverage of MB is formed on the surface of activated carbon.

Table 4 Langmuir and Freundlich isotherm constants

Activated carbon	Langmuir				Freundlich		
	***Q* (mg/g)**	***b* (L/mg)**	**R^2**	**R_L**	***K***	***n***	**R^2**
NCBR	7.59	94.1	1.000	4×10^{-4}	7.48	193	0.999
KCBR	8.10	176	1.000	2×10^{-4}	8.07	1.2×10^{6}	0.999
KZCBR	29.8	10.5	1.000	5×10^{-4}	28.5	116	0.623
ZCBR	133	5.00	0.996	5×10^{-4}	153	65170	0.907
ZCBC	213	15.7	0.999	2×10^{-4}	170	19.8	0.985

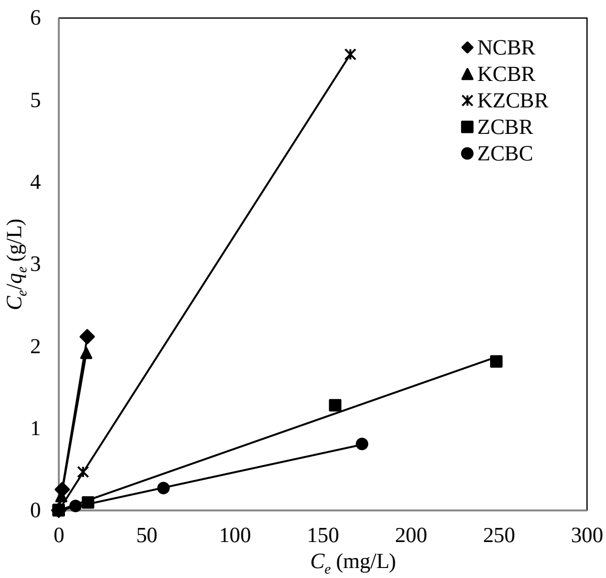


Figure 2 Langmuir adsorption isotherm

R_L values are in the range of 0 to 1, and this indicating that the adsorption process is favourable and reversible. It was also found that *n* values of Freundlich model are greater than 1 for all activated carbons, consequently, 1/*n* values obtained are below one. This indicates that the adsorption process follows a normal Langmuir isotherm [30]. From the Langmuir model, ZCBC has the highest *Q* which is 213 mg/g. This result is also supported by Freundlich model, where ZCBC has the highest *K* constant, which indicates that it as having the highest adsorption capacity.

■4.0 CONCLUSION

The performance of metals chloride-activated castor bean residue was investigated based on the adsorption of methylene blue. Activated carbon prepared from castor bean cake and activated by $ZnCl_2$ had the highest maximum adsorption capacity of methylene blue. The adsorption data were best fitted to Langmuir model. This model suggests that the adsorption process is a monolayer formation of methylene blue onto the surface of activated carbon. In short, non-valuable castor bean waste has potential to be converted as valuable activated carbon for dyes adsorption.

Acknowledgement

Authors acknowledge the Malaysia Ministry of Education and UTM Johor Bahru for the award of Fundamental Research Grant Scheme (FRGS, #4F305) and Flagship Grant (#03G07). L. Lin-Zhi thanks Malaysia Ministry of Education for the financial assistance through MyBrain15 scholarship.

References

[1] Easton, J. R. 1995. The Dye Maker's View. In Peter Cooper (ed.). *Colour in Dyehouse Effluent*. Bradford: Society of Dyers and Colourists.

[2] Robinson, T., MacMulian, G., Marchant, R. and Nicam, P. 2001. Remediation of Dyes Textile Effluent: A Critical Review on Current Treatment Technologies with a Proposed Alternative. *Bioresource Technol.* 58: 217–227.

[3] Senthilkumaar, S., Varadarajan, P. R., Porkodi, K. and Subbhuraam, C. V. 2005. Adsorption of Methylene Blue onto Jute Fiber Carbon: Kinetics and Equilibrium Studies. *J. Colloid Interface Sci.* 284(1): 78–82.

[4] Gupta, V. K. and Suhas. 2009. Application of Low-Cost Adsorbents for Dye Removal – A Review. *J. Environ. Manage.* 90: 2313–2342.

[5] Walker, G. M. and Weatherley, L. R. 1997. A Simplified Preductive Model for Biologically Activated Carbon Fixed Beds. *Process Biochem.* 76(13): 183–191.

[6] Karthikeyan, S. and Sivakumar, P. 2012. The Effect of Activating Agents on the Activated Carbon Prepared from Feronia limonia (L.) Swingle (Wood Apple) Shell. *J. Environ. Nanotechnol.* 1(1): 5–12.

[7] Yahaya, N. K. E. M., Latiff, M. F. P. M., Abustan, I. and Ahmad, M. A. 2010. Effect of Preparation Conditions of Activated Carbon Prepared from Rice Husk by $ZnCl_2$ Activation for Removal of Cu (II) from Aqueous Solution. *International Journal of Engineering & Technology.* 10(6): 28–32.

[8] Hussaro, K. 2014. Preparation of Activation Carbon from Palm Oil Shell by Chemical Activation with Na_2CO_3 and $ZnCl_2$ as Impregnated Agents for H_2S Adsorption. *American Journal of Environmental Sciences.* 10(4): 336–346.

[9] Robb, J.G., Laben, R. C., Walker, H. G. and Herrng, V. 1974. Castor Meal in Dairy Rations. *J. Dairy Sci*. 57: 443–450.

[10] Santos, N. A. V., Magriotis, Z. M., Saczk, A. A., Fassio, G. T. A. and Vieira, S. S. 2014. Kinetic Study of Pyrolysis of Castor Beans (Ricinuscommunis L.) Presscake: An Alternative Use for Solid Waste Arising from the Biodiesel Production. *Energy & Fuels.*

[11] Rufford, T. E., Hulicova-Jurcakova, D., Zhu, Z. and Lu, G. Q. 2010. A Comparative Study of Chemical Treatment by $FeCl_3$, $MgCl_2$ and $ZnCl_2$ on Microstructure, Surface Chemistry, and Double-Layer Capacitance of Carbons from Waste Biomass. *J. Mater. Res.* 25(8): 1451–1459.

[12] Subha, R. and Namasivayam, C. 2010. $ZnCl_2$-Modified Activated Carbon from Biomass Coir Pith for the Removal of 2-Chlorophenol by Adsorption Process. *Bioremediation Journal.* 14(1): 1–9.

[13] Angin, D., Altintig, E. and Kose, T. E. 2013. Influence of Process Parameters on the Surface and Chemical Properties of Activated Carbon Obtained from Biochar by Chemical Activation. *Bioresource Technol.* 148: 542–549.

[14] Salahudeen, N., Ajinomoh, C. S., Omaga, S. O. and Akpaka, C. S. 2014. Production of Activated Carbon from Cassava Peel. *Journal of Applied Hytotechnology in Environmental Sanitation.* 3(2): 75–80.

[15] Slejko, F. L. 1985. *Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application.* New York: Dekker.

[16] Srivastava, P. and Hasan, S. H. 2011. Biomass of *Mucor Heimalis* for the Biosorption of Cadmium from Aqueous Solutions: Equilibrium and Kinetic Studies. *Bioresources.* 6(4): 3656–3675.

[17] Hall, K. R., Eagleton, L. C., Acrivos, A. and Vermeulen, T. 1966. Pore and Solid-Diffusion Kinetics in Fixed-Bed Adsorption under Constant-Pattern Conditions. *Ind. Eng. Chem. Fund.* 5(2): 212–223.

[18] Langmuir, I. 1918. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *J. Am. Chem. Soc.* 40: 1361–1403.

[19] Webber, T. N. and Chakravarti, R. K. 1974. Pore and Solid Diffusion Models for Fixed Bed Adsorbers. *J. Am. Inst. Chem. Eng.* 20: 228–238.

[20] Freundlich, H. 1906. Over the Adsorption in Solution. *Z. Phy. Chem.* 57: 284–470.

[21] Mohan, S. and Karthikeyan, J. 1997. Removal of Lignin and Tannin Colour from Aqueous Solution by Adsorption on to Activated Charcoal. *Environ. Pollut.* 97: 183–187.

[22] Mohammed, T. H., Lakhmiri, R., Azmani, A. and Hassan, I. I. 2014. Bio-oil from Pyrolysis of Castor Shell. *International Journal of Basic and Applied Sciences.* 14(6): 1–5.

[23] Lacerda, R. S., Makishi, L. A., Chambib, H. N. M., Monica, A., Bittante, Q. B., Gomide, C. A., Costa, P. A., Sobral, P. J. A. 2014. Castor Bean (Ricinus communis) Cake Protein Extraction by Alkaline

Solubilization: Definition of Process Parameters. *Chemical Engineering Transactions*. 37: 775–780.

[24] Yorgun, S., Vural, N. and Demiral, H. 2009. Preparation of High-Surface Area Activated Carbons from Paulownia Wood by $ZnCl_2$ Activation. *Micropor*. *Mesopor*. *Mat*. 122: 189–194.

[25] Hayashi, J., Horikawa, T., Takeda, L., Muroyama, K. and Ani, F. N. 2002. Preparing Activated Carbon from Various Nutshells by Chemical Activation with K_2CO_3. *Carbon*. 40: 2381–2386.

[26] Hema, M. and Arivoli, S. 2007. Comparative Study on the Adsorption Kinetics and Thermodynamics of Dyes onto Acid Activated Low Cost Carbon. *Int. J. Phys*. *Sci*. 2(1): 10–17.

[27] Abbas, A., Murtaza, S. Shahid, K. Munir, M. Ayub, R. and Akber, S. 2012. Comparative Study of Adsorption Removal of Congo Red and Brilliant Green Dyes from Water Using Peanut Shell. *Middle East J. Sci*. *Res.* 11(6): 828–832.

[28] Oliveira, L. C. A., Pereira, E., Guimaraes, I. R., Vallone, A., Pereira, M., Mesquita, J. P. and Sapaq, K. 2009. Preparation of Activated Carbons from Coffee Husks Utilizing $FeCl_3$ and $ZnCl_2$ as Activating Agents. *J. Hazard. Mater*. 165: 87–94.

[29] Viswanathan, B., Indra Neel, P. and Varadarajan, T. K. 2009. *Methods of Activation and Specific Applications of Carbon Materials.* Chennai, India: National Centre for Catalysis Research.

[30] Tan, J. A. W., Ahmad, A. L. and Hameed, B. H. 2008. Enhancement of Basic Dye Adsorption Uptake from Aqueous Solutions Using Chemically Modified Oil Palm Shell Activated Carbon. *Colloid Surface A.* 318(1–3): 88–96.