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PREFACE

This is the fourth conference of the series of regional conferences in chemical engineering under AUN/SEED Net. The first conference was held in Manila, Philippines in 2009 and was hosted by De La Salle University (DLSU). The second was held in Ho Chi Minh City, Vietnam and was hosted by Ho Chi Minh City University of Technology (HCMUT) in 2010. Then, the conference was held in Manila again in 2011 and was again hosted by DLSU.

This CD contains the full papers presented in this conference. The papers are categorized into the following topics: Biofuel/Bioprocess, Material Science, Reaction Engineering, Environment, Process System Engineering, Separation Technology, Membrane Technology, Various Chemical Engineering Disciplines. In the conference there are 60 papers for oral presentation and 17 papers for poster presentation. Some of these papers will be considered publication in the Asean Journal of Engineering and Asean Chemical Engineering Journal.

Our deepest appreciation to all authors and co-authors for their excellent contribution and cooperation in preparing their papers on time. Although we did our best to prepare the proceedings properly, we would like to apologise to the authors for any possible errors during the editorial process.

The editorial effort would be difficult without the help of the technical committee, comprising of the staff of the Department of Chemical Engineering, University of Malaya. Special thanks to them all and in particular to Dr. Brahim Si Ali, Mr.Mohd Fauzi Zanil, Ms.Nurul Hazizah, Ms.NorHuda, Ms.Ezalia for their valuable assistance in the preparation of the proceedings and technical programs.

Thank you.

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RECALCITRAN CIBACRON RED DYE ADSORPTION BY LOCALLY SOURCED DOLOMITE ADSORBENT

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ABSTRACT

Restorative step towards serene environment collapse was attempted by harnessing potentials of locally available dolomite material from Perak state in Malaysia. The dolomite material was crushed, sieved and then calcined. The calcined dolomite's adsorptivity was tested on treatment of synthetic textile waste-waters containing reactive Cibacron Red dye (CBD) through batch adsorption studies which yielded a maximum adsorption capacity of 100 mg/g. Pseudo-first-order and pseudo-second-order kinetic models studies administered on the adsorption process data revealed that both models described the process very well with pseudo-second-order model having an edge over pseudo-first-order model. Langmuir and Freundlich isotherms were suitable representation of the process more than Temkin isotherm model. Thermodynamic studies revealed that the adsorption process was spontaneous and endothermic in nature; and also, entropy of the process increased with increase in temperature of the system. Boundary layer and intra-particle diffusion steps were necessary for the adsorption of CBD on the adsorbent. The locally sourced dolomite adsorbent was found to be very good for removal of CBD from waste-waters and can be used adequately as a cheaper alternative to expensive commercial activated carbon.

1.0 Introduction

The insurmountable human activities which are mostly accompanied with discharge of waste pollutants into the ecosystem has prompted researchers to look for cheaper alternative means to salvaging it in an attempt to sustain good environment with ease. Dyes discharge into the environment comes from different sources with high roots like textiles, leather, paper, printing industries etc. Among methods used to tackle this menace, adsorption process is one of the methods that have an edge over others, but expensive commercial activated carbon adsorbent often used in the system negates its desiring applicability. Several alternatives to commercial activated carbon adsorbents used for adsorption processes has been reported which includes agricultural waste materials [1], clays [2], silica [3], sewage sludge [4] and so on.

An important natural material dolomite, has found applications in industries such as chemical and ceramics, food, pharmaceutical, fertilizer, glass, trans-esterification and adsorption of metals; there are very few reports on its applicability on dyes adsorption [5]. The potentials of it are usually harnessed when it has undergone thermal treatment leading to structural realignment of the material. Calcinations of dolomite compound leads to ample increase in specific surface area and pore volume of calcium carbonate (calcite) and magnesium oxide which are constituents of its decomposition [6].

This study is aimed at harnessing potentials of locally sourced dolomite material to investigate its usefulness for treatment of synthetic textile waste-water containing recalcitrant reactive Cibacron dye.

2.0 Materials and methods

Cibacron Brilliant Red 3B-A with 50% dye content was obtained from Sigma-Aldrich, Malaysia. It has an empirical formula (Hill notation) of $C_{32}H_{24}ClN_8Na_4O_{14}S_4$, molecular weight of 1000.25 and color index number of 18105. The dye was used without further purification and its structural formula is shown in Scheme 1. Dolomite pebbles were ground into 63-75 µm and calcined in furnace at 850 ^{o}C for 5 h. The calcined dolomite was packaged in an airtight container for use.

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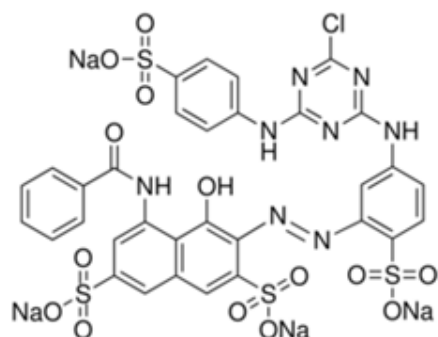
Scheme 1 molecular structure of CBR

2.1 Batch equilibrium studies

The study was conducted in a set of 250 mL Erlenmeyer flasks containing 200 mL of various initial dye concentrations (50-350 mg/L) where 0.4 g of calcined dolomite (CD) was added to each flask. This mixture was placed in an isothermal water-bath shaker at 30 $^{\circ}$C with shaker speed of 135 rpm for 24 h until equilibrium was attained. Samples of the solution were withdrawn at equilibrium and CBR concentration residue determined with the aid of UV-Vis spectrophotometer (Shimadzu UV/Vis 1700 spectrophotometer, Japan) at the maximum wavelength of 541. The procedure was repeated at different isothermal shaker temperature of 40 and 50 $^{\circ}$C. The amount of CBR adsorbed Q_e (mg/g) at equilibrium was calculated using:

$$Q_e = \frac{(C_o - C_e)V}{W} \qquad (1)$$

where C_e and C_o (mg/L) are the liquid-phase concentration of the CBR at equilibrium and at initial, respectively; V (L) is the volume of the solution; and W (g) is the mass of the CD used.

2.2 Batch kinetic studies

Similar to steps taken during equilibrium adsorption studies was the method used for kinetic studies with determination of CBR concentration at time intervals. The amount of CBR adsorbed at time t, Q_t (mg/g) was evaluated by

$$Q_t = \frac{(C_o - C_t)V}{W} \qquad (2)$$

where C_o and C_t (mg/L) are the liquid-phase concentration of the CBR at the initial and any time t, respectively; V (L) is the volume of the solution; and W (g) is the mass of CD used.

3.0 Results and discussion

3.1 Effect of initial CBR concentration and time

The Fig. 1 clearly revealed that rapid adsorption took place at the initial time of the process and gradually slowed down until equilibrium was attained at all the various initial concentrations investigated. This was attributed to the abundant yearning active vacant sites present at the initial time of the adsorption process. Higher adsorption of CBR on CD was also observed when the concentration gradient in the system was increased; this was due to increased in mass transfer of the system as the concentrations were increased. The adsorption capacity calculated at 50 and 350 mg/L were 24.65 and 94.98 mg/g, respectively. This is in accordance with results obtained result for anionic dye removal by naturally untreated clay material [7].
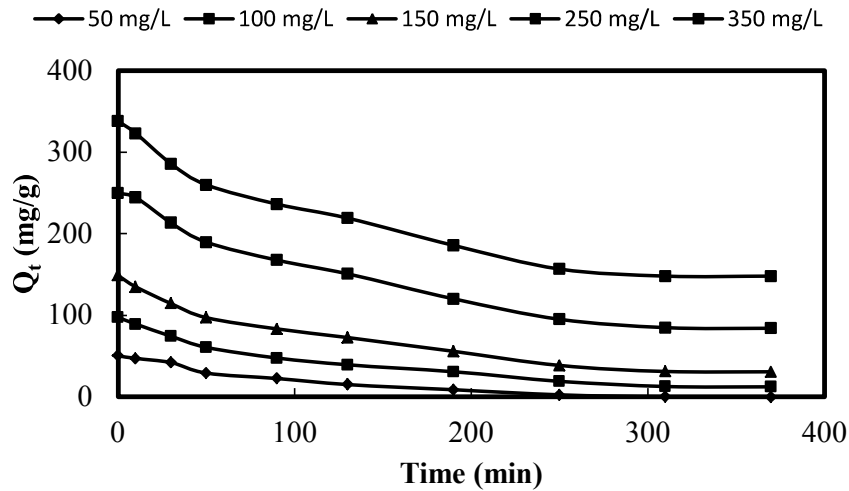
Fig. 1 Effect of initial concentration of CBR adsorption on CD at 30 °C

3.2 Adsorption isotherms

Three isotherm models namely Langmuir, Freundlich and Temkin were investigated to study interaction between CBR and CD and as a step to enhance the design of the adsorption process.

Langmuir in 1918 on his theory proposed for description of gas molecules onto metal surfaces was based on the following assumptions: fixed numbers of sites on the adsorbent adsorb the adsorbate; a molecule is adsorbed on each site; every site has equivalent energy of adsorption; that no interaction whatsoever between adsorbates adsorbed on different sites. Non-linear Langmuir model equation is given as:

$$Q_e = \frac{Q_o C_e b}{(1+bC_e)} \tag{3}$$

where C_e (mg/L), is the equilibrium concentration of CBR adsorbed, Q_e (mg/g), is the amount of CBR adsorbed, Q_m and b (Langmuir constants), the monolayer adsorption capacity and

affinity of adsorbent towards adsorbate, respectively. A plot of Q_e against C_e gave a fitted curve, and the Langmuir constants were generated from the plot of sorption data shown in Fig. 2.

The non-linear form of the Freundlich model empirical model used to give information on how heterogeneity can be expressed as:

$$Q_e = k_f C_e^{1/n} \tag{4}$$

where Q_e (mg/g), is the amount of dye adsorbed at equilibrium; C_e (mg/L), is the equilibrium concentration of the adsorbate; k_f and n are the Freundlich equilibrium coefficients. The value of n gives information on favourability of adsorption process and k_f is the adsorption capacity of the adsorbate.

Temkin isotherm which describes adsorbent-adsorbate interaction on the assumptions that decrease of heat of adsorption of molecules in a layer is due to increase of coverage from adsorbate-adsorbent interaction and, that about some maximum binding energies of adsorption is uniformly distributed [8]. Non-linear Temkin model equation is given as:

$$Q_e = BIn(K_T C_e) \tag{5}$$

where K_T is the equilibrium binding constant corresponding to the maximum binding energy, B is related to the heat of adsorption, Q_e is the experimental adsorption capacity (mg/g), C_e is the concentration of the CBR adsorbed at equilibrium position (mg/L);

$$B = \frac{RT}{b_T} \tag{6}$$

where $1/b_T$ indicates the adsorption potential of the adsorbent; R is the universal gas constant (8.314 J/kmol); and T is the temperature in Kelvin (K).

The result for Temkin isotherm investigation showed that the model did not fit well with the CBR adsorption on CD as evidenced by the low correlation coefficient R^2 values obtained (Table not shown), the Temkin isotherm model plots is shown in Fig. 2.

The results of the parameters of the three models (Table not shown) revealed that Langmuir and Freundlich models both described CBR adsorption on CD while Temkin model did not. This was adjudged by the high values of their correlation coefficient R^2 values and the fitness of their plots as shown in Fig. 2. Similar result were obtained when both Langmuir and Freundlich isotherms described the adsorption process when comparative studies were carried out for adsorption of Methylene Blue by commercial activated carbon and locally prepared activated carbons from bamboo dust, coconut shell, groundnut shell, rice husk, and straw [9].
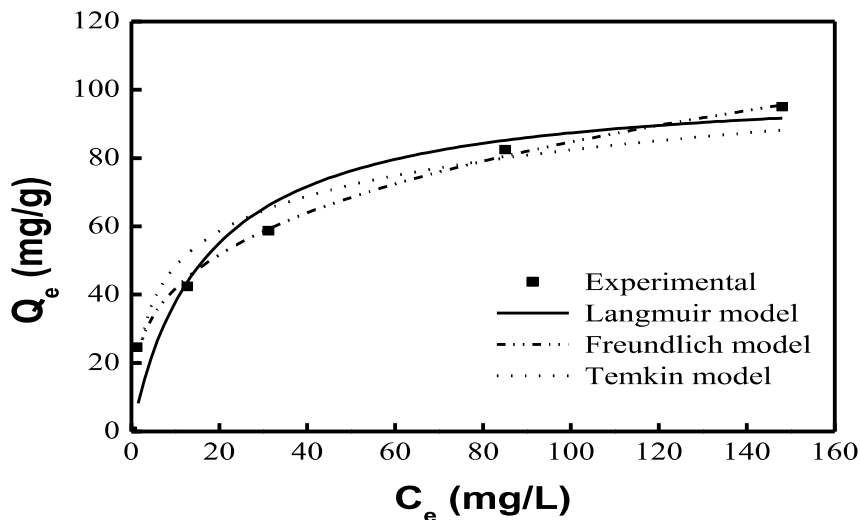

Fig. 2 Langmuir, Freundlich and Temkin models plots for CBR adsorption on CD

3.3 Adsorption kinetics

Pseudo-first-order and Pseudo-second-order kinetic models were used to evaluate the rate of CBR adsorption on CD.

3.3.1 Pseudo-first order model

Non-linear form of pseudo-first order equation [10] is given as:

$$Q_t = Q_e\left(1 - e^{-K_1 t}\right) \tag{7}$$

where Q_e and Q_t are the amount of CBR adsorbed (mg/g) at equilibrium and at time t (min) respectively; k_1 is the rate constant of adsorption (h^{-1}). Values of Q_t against Q_e at various temperatures studied were plotted (Fig. not shown).

3.3.2 Pseudo-second order model

The non-linear form of pseudo-second order equilibrium adsorption model [11] is given as:

$$Q_t = \frac{K_2 Q_e^2 t}{(1 + K_2 Q_e t)} \tag{8}$$

where k_2 (g/mgh) is the rate constant of second order adsorption. Plots of Q_t versus t at various temperatures studied gave very good curves as shown in Fig. 3.

The parameters for the two models as shown in Table 1 revealed that pseudo-second-order kinetic model fitted better to the adsorption process as compared with Pseudo-first-order model. This was evidence by the correlation coefficients R^2 of the model which were all above 0.900 and the better fitted curves. This model fitness predicted the whole of range of adsorption of CBR on CD unlike Pseudo-first-order model which is only applicable at the initial part of the adsorption process. Pseudo-second-order model was also found to be the fitted model that best described cationic dye adsorption by novel biosorbent (*Canola hull*) [12].
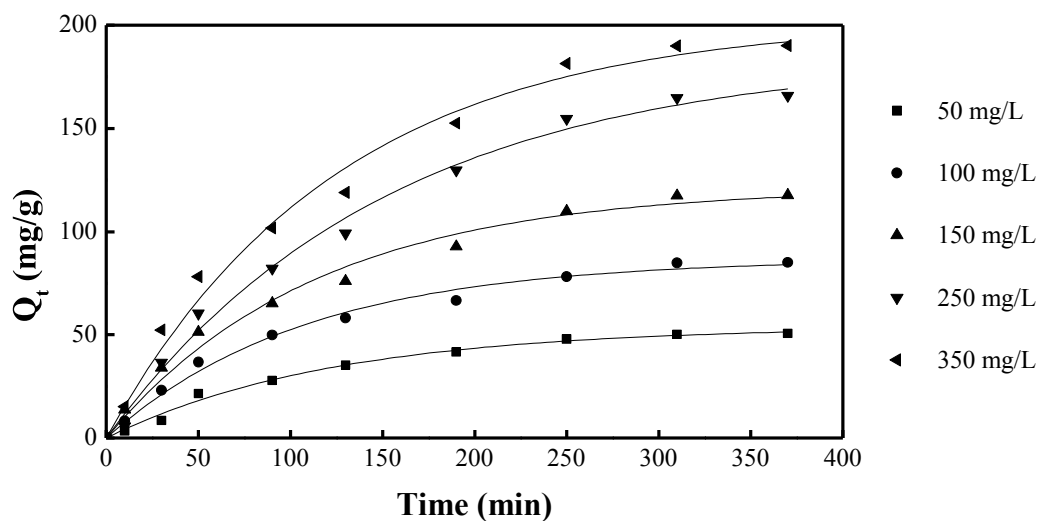

Fig. 3 Pseudo-second-order kinetics of CBR adsorption on CD at 30 ^{o}C

Table 1 Kinetics and mechanism of adsorption parameters of CBR adsorption on CD at 30 ^{o}C

Dye conc. (mg/L)	Q_{exp} (mg/g)	Pseudo-first-order parameters				Pseudo-second-order parameters				Intra-particle diffusion model					
		K_1 (h^{-1}) $\times 10^3$	Q_{cal}	R^2		K_2 (10^4)	Q_{cal}	R^2		K_{i1} (mg/g.min$^{0.5}$)	C	R^2	K_{i2} (mg/g.min$^{0.5}$)	C	R^2
50	24.65	8.21	53.94	0.89		6.10	54.23	0.98		3.78	8.72	0.85	0.775	35.98	0.97
100	42.41	9.30	86.77	0.83		2.06	117.34	0.96		5.57	6.30	0.80	2.046	46.79	0.98
150	58.72	8.84	121.48	0.92		1.20	149.72	0.97		7.26	5.44	0.81	2.291	74.81	0.99
250	82.44	6.59	185.41	0.90		1.08	207.89	0.98		11.30	26	0.84	3.282	104.2	0.99
350	94.98	8.01	202.46	0.85		1.08	249.06	0.99		12.40	18	0.89	2.579	141.8	0.99

3.4 Mechanism of adsorption

Adsorption process involves series of steps which includes external film diffusion, internal particle diffusion and surface adsorption; this becomes paramount to predict the rate limiting step of the process. An investigation into whether intra-particle diffusion model or film diffusion was rate-controlling step was tested on CBR adsorption by CD even though the former is often associated with batch reactor and the later with continuous flow processes. The intra-particle diffusion model equation is given as:

$$Q_t = k_{ip}t^{1/2} + C \qquad (9)$$

where, k_{ip} (mg/(g.min$^{1/2}$)) is intra-particle diffusion rate constant (slope) and C (intercept) is boundary thickness. The plots of Q_t against t (Fig. not shown) revealed that boundary layer diffusion and intra-particle diffusion represented by the steepy and gradual slopes portions, respectively of the plots were all involved in CBR rate-controlling adsorption by CD. The

results of slope and intercept shown in Table 1 indicated that boundary layer slope had larger diffusion rate constants (k_{i1}) and smaller boundary thickness (C). Therefore, since the intercept and the boundary layer thickness of the intra-particle diffusion had greater boundary layer effect and also had the least rate constants (k_{i2}); intra-particle diffusion was the rate limiting step on CBR adsorption on CD.

3.5 Adsorption thermodynamics

The actual application of the adsorption process was investigated by determining the Gibbs free energy (ΔG, kJ/mol) which is also known as chemical potential, from entropy (ΔS, kJ/mol K) and enthalpy (ΔH, kJ/mol). This study was carried out at various temperatures of 30, 40 and 50 ^{o}C and the parameters were evaluated using the following equations:

$$\Delta G = -RT \ln K_o \tag{10}$$

where R is the universal gas constant (8.314 J/Kmol); T, the absolute temperature (K); and K_o is the distribution coefficient expressed as $K_o = Q_e/C_e$.

Van't Hoff equation was used to determine the average standard enthalpy change, the equation is expressed as:

$$\ln K_o = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{11}$$

By plotting a graph of ln K_o versus 1/T, we can estimate the values ΔH and ΔS from the slopes and intercepts (Fig. not shown).

The thermodynamics parameters obtained are summarized in Table 2. Negative values of ΔG and positive values of ΔH were obtained signifying that the process was spontaneous and endothermic in nature. The Gibbs free energy of the CBR adsorption on CD was classified as physisorption since the ΔG values obtained were between 0 and -20 kJ/mol unlike chemisorption reactions whose values ranges from -80 to -400 kJ/mol [13,14]. In the adsorption

of cationic dyes using kaolin adsorbent, the process thermodynamic parameters obtained were similar to this CBR adsorption on CD [15].

Table 2 Thermodynamic parameters of CBR adsorption on CD

ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)		
		303 K	313 K	323 K
19.28	0.063	-2.441	-3.333	-4.139

Conclusion

This study has further proven that some solutions to our problems are just a stone throw from us which takes research to access. The CD gave good removal of CBR from aqueous solution with an adsorption capacity of 100 mg/g. The rate of the adsorption was best described by Pseudo-second-rate kinetics whose mechanism revealed that the process rate-limiting step was controlled by intra-particle diffusion and not boundary layer diffusion even though it participated. The process was also found to be spontaneous and endothermic, with the level of dispersion increasing with temperature. Results of this study revealed that the locally sourced dolomite is an adsorbent to reckon with in adsorption of reactive dyes.

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