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Adsorption of Anion Dye from Aqueous Solution by Activated Carbon Coated Monolith in a Batch System

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Abstract

The adsorption of an anion dye, methyl orange, from aqueous solutions on polymer based carbon coated monolith was studied in a batch system. The kinetics of adsorption with respect to the initial dye concentration was investigated. Langmuir and Freundlich isotherms were applied to describe the experimental data. Equilibrium data fitted well to the Freundlich model for concentration range (0 – 160 mg/L). The maximum adsorption capacity of the carbon with BET surface area of 431 m^2/g obtained from the Freundlich model was 36.72 (mg/g) $(L/mg)^{1/n}$. The pseudo-first-order and pseudo-second-order kinetic models were employed to describe the kinetic data. The experimental data fitted well to the pseudo-second-order kinetic model with constant rates 5.42 $\times 10^{-4}$ and 2.22 $\times 10^{-4}$ g/(min-mg) for initial concentrations 50 and 100 mg/L, respectively.

Keywords: adsorption, anion dye, carbon coated monolith

1. Introduction

Dyes are extensively used in large quantity in many industries such as textile, leather, paper production, food technology, etc to color their products (Yener *et al.* 2008; Hameed and El-Khaiary, 2008). Untreated wastewaters directly dis-charged into water bodies from these industries will cause environmental damage to surface water (Crini and Badot, 2008). Visibly, dye is often the first contaminant to be recognized (Otero *et al.* 2003). Dyes, in generally, are synthetic in nature and have complex aromatic structures which make them carcinogenic, mutagenic, and chemically stable (Ofomaja, 2008; Aksu and Tezer, 2005). Methyl orange is anionic dye identified as that which dissociates in aqueous solution to give a negatively charged colored ion. This dye has harmful effects on living organisms on short periods of exposure. Several techniques are available for the treatment of industrial wastewaters. Among these methods, adsorption technique for wastewater treatment has become more popular in recent years. The most commonly used adsorbent in this process to remove dyes is activated carbon in form powder or granular (Al-Degs *et al.*, 2001). The use of carbon in the form of fixed bed is associated with high pressure drops, potential channeling, and other disadvantages. The problems encountered above can be overcome by the use of carbon monoliths. Compared to the conventional fixed bed column, monolithic columns provide the advantages of low pressure drop, larger external surface area, and shorter diffusion lengths (Kapteijn *et al.*, 1999). It can also be located in a vertical or horizontal position and in mobile system without losing shape and is easier to be scaled up due to its simple design and uniform flow distribution (Irandoust and Andersson, 1998).

This study is to examine the applicability of the new adsorbent, polymer based carbon coated monolith for the adsorption of methyl orange as a model dye from aqueous solution and to investigate the equilibrium isotherms and kinetics of the sorption process.

2. Methodology

2.1 Materials

The chemical compositions of the monolithic substrate used in this investigation are SiO_2 50.9 ± 1 %, Al_2O_3 35.2 ± 1 %, MgO 13.9 ± 0.5 %, and others < 1 %. The cell shape of the monolithic channels is square cross section with channel width 1.02 ± 0.02 mm equivalents to a channel density of 62 cell

cm^{-2} (400 cpsi) and wall thickness 0.25 ± 0.02 mm. These ceramic monoliths were obtained from Beihai Huihuang Chemical Packing Co. Ltd, China.

The starting chemicals for the preparation of carbon coated monolith are furfuryl alcohol 99% (FA) as carbon source, poly ethylene glycol (PEG) (molecular weights: 1500 g/mol), further called PEG-1500, as pore former agent, pyrrole 99% as binder, and nitric acid 65% as catalyst (Acros Organics, Belgium).

For adsorption application, methyl orange was used. The methyl orange (MO) was supplied in powder form by BDH Gurr-Cersistain, England and used without further treatment. The chemical formula of methyl orange is shown in Figure 1.

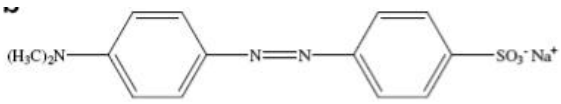

Figure 1. Structural Formula of Methyl Orange.

2.2 Textural Characterization

The texture of carbon coated monolith was analyzed by using nitrogen. Nitrogen adsorption was performed on Sorptometic 1990 series at 77 K. Pore volume and average pore size were calculated by the Barret-Joyner-Halenda (BJH) method for mesopore. The Brunauer-Emmett-Teller (BET) equation was also employed to estimate total surface area from adsorption isotherm (Ahmad *et al*, 2007).

2.3 Equilibrium Studies

The effect of solution of pH on equilibrium concentration was studied by agitating 0.9 g of carbon coated monolith (FA+PEG-1500) and 400 mL of dye solution of dye concentration 250 mg/L using Flocculator SW1 at ambient temperature. The experiment was conducted at different pH from 2.5 to 10 adjusted by 1N HCl or 0.1 N HCl and 0.1 N NaOH solutions. The solution was stirred with rate 60 rpm for 6 days contact time which was sufficient to reach equilibrium.

The equilibrium isotherms were also determined by contacting a constant mass of carbon coated monolith of 0.9 g with 400 mL sorbate solution in beakers at pH of 2.5 and different initial concentrations in range of 50-500 mg/L. The equi-librium concentrations of the solid phase sorbate, q_e (mg/g), were calculated from the material balance on the adsorption system.

$$q_e = (C_0 - C_e) \cdot V / m \quad (1)$$

a. Langmuir Isotherm

The Langmuir isotherm is given as:

$$q_e = \frac{Q_o \cdot a_L \cdot C_e}{(1 + a_L \cdot C_e)} \quad (2)$$

b. Freundlich Isotherm

The Freundlich isotherm is given as:

$$q_e = K_F (C_e)^{1/n} \quad (3)$$

2.4 Kinetic Studies

Kinetic studies provided kinetic data in the form of concentration decay versus time curves. In each experimental run, a weighed amount of carbon coated monolith of 1.6 g was brought into contact with 500 mL sorbate solution at two different initial concentrations (50 and 100 ppm). At regular time interval, about 2 mL samples of solution were withdrawn by a sampling system and then placed in sample bottles. Each sample was analyzed to determine the solute concentration using UV-vis spectrophoto-meter.

Table 1. Pore structure parameters of carbon measured by nitrogen adsorption at 77 K.

Sample	S_{BET} (m^2/g_{carbon})	Total pore volume (cm^3/g_{carbon})	Mesopore area (m^2/g_{carbon})	Mesopore volume (cm^3/g_{carbon})
FA + PEG-1500$_{unsup}$	431.00	0.380	186.55	0.2313
FA + PEG-1500$_{sup}$	21.31	0.002	-	-

3. Results and Discussion

3.1 Textural Characterization

Measurement of nitrogen isotherm at 77 K was shown in Figure 2. The isotherm of carbon coated monolith produced was of Type IV behavior defined by the International Union of Pure and Applied Chemistry (IUPAC) for characteristic of mesoporous material (Onal, 2006; Basar, 2006).

Table 1 contained mesopore volume and BET total surface area calculated from nitrogen adsorption data applying the BJH and the BET equations.

3.2 Effect of pH

The solution pH of adsorption medium being conducted was an important controlling parameter which dictated the uptake and release of solutes bound by sorption (Inbaraj *et al.*, 2008; Mittal *et al*., 2008; Dogan and Alkan, 2003). The magnitude of electrostatic charges imparted by the ionized dye molecules and functional groups on surface of adsorbent was primarily controlled by pH of medium (Dogan and Alkan, 2003).

Figure 3 illustrates the effect of pH on the adsorption of MO by using carbon coated monolith at ambient temperature by varying the initial pH of a 250 mg/L solution for fixed adsorbent mass of 0.9 g. The adsorption capacity increased signi-ficantly with decreasing the solution pH. At solution pH of 2.5, the amount of dye adsorbed was 102.1 mg/g.

Higher adsorption of the dye at low pH could be explained consideration the electro-static interaction between the surface of adsorbent, positively charged, and the anion dye MO (Pavan *et al.*, 2008). This indicated that the adsorption capacity of carbon coated monolith was pH dependent.

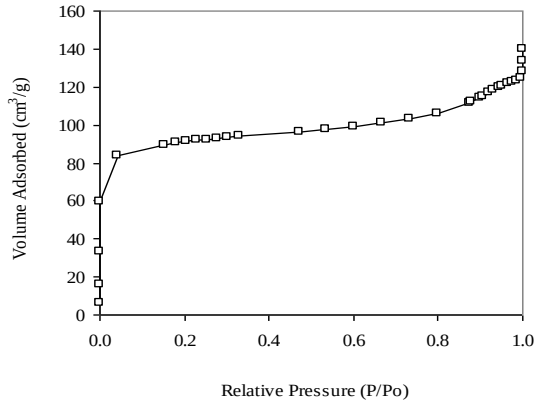

Figure 2. Adsorption isotherm of nitrogen at 77K on carbon

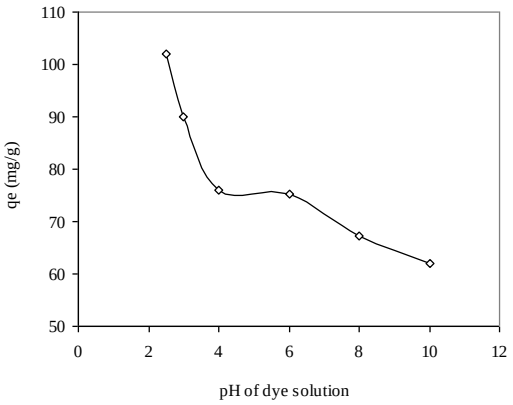

Figure 3. Kromatogram hasil reaksi dehidrogenasi etanol menggunakan katalis Cu/silika gel pada suhu 300°C.

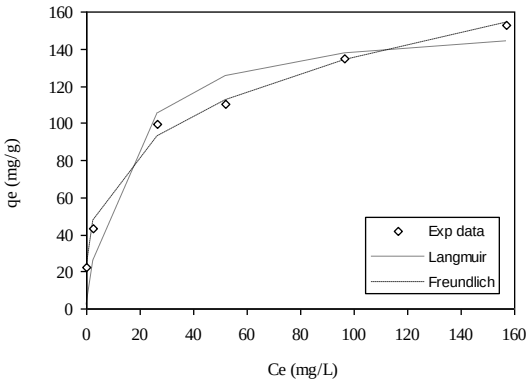

Figure 4. Equilibrium adsorption isotherm of MO on activated carbon coated monolith at pH of 2.5.

Table 2. Values of estimated Langmuir and Freundlich isotherms constants.

Langmuir isotherm		Freundlich isotherm	
Q_o (mg/g)	a_L (L/mg)	K_F (mg/g) (L/mg)$^{1/n}$	n
155.54	0.08	36.72	3.08

Table 3. Comparison of the first- and second-order adsorption rate constants and values of calculated and experimental q_e for two different initial dye concentrations.

Dye initial concentration	$q_{e,\,exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		k_1 (1/min) x 10^{-3}	$q_{e,\,cal}$ (mg/g)	R^2	k_2 (g/mg per min) x 10^{-4}	$q_{e,\,cal}$ (mg/g)	R^2
50 ppm	16.33	3.5	13.74	0.944	5.42	16.17	0.997
100 ppm	31.16	2.6	27.09	0.959	2.22	27.62	0.986

3.2 Adsorption Isotherm

Equilibrium adsorption data were collected at pH 2.5, agitation speed 60 rpm, and ambient temperature. The isotherms, in general, were fitted to experimental data and adsorption was generally favorable. Adsorption isotherms of MO showed that the data fitted better in Freundlich isotherm equation as illustrated in Figure 4. The values of the parameters of the isotherms were presented in Table 2.

3.3 Kinetics of Adsorption

The slopes and intercepts of plots of equations 4 and 5 for pseudo-first and second-order kinetic models, respectively were employed to calculate rate constants (k_1 and k_2) and q_e. The calculated results were listed in Table 3. A comparison of results with the correlation coefficients (R^2) was also presented in Table 3. The correlation coefficients for pseudo first-order kinetic model were rather low.

The straight lines in plots of $\frac{t}{q_t}$ versus t showed a good agreement of experimental data with pseudo-second-order model for two different initial concentrations as presented in Figure 6 and Table 3. On the contrary, the pseudo-first-order kinetic model fitted the experimental data poorly for the range under study as shown in Figure 5.

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

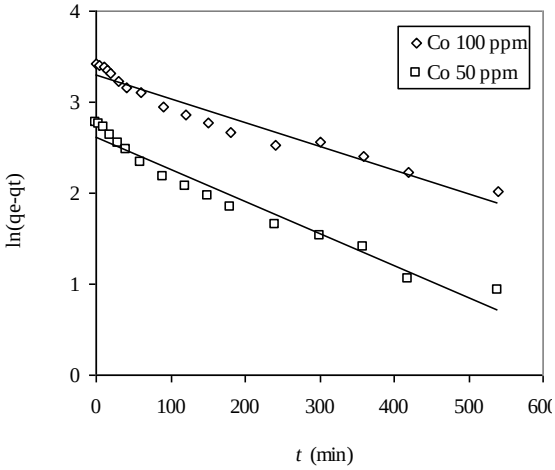

Figure 5. The fitting of pseudo first order model for the sorption of MO on carbon coated monolith at pH of 2.5.

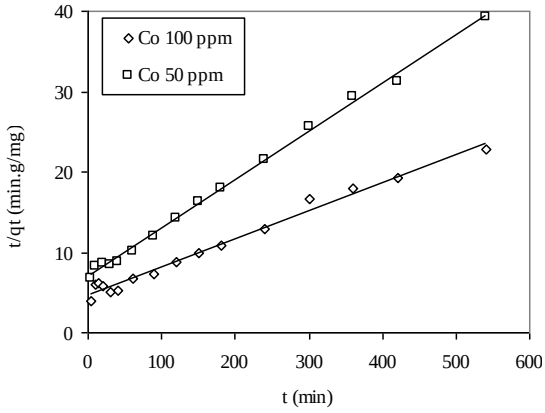

Figure 6. The fitting of pseudo second order model for the sorption of MO on carbon coated monolith at pH of 2.5.

4. Conclusions

The equilibrium and kinetics of adsorption for MO on polymer based carbon coated monolith have been studied. It is found that adsorption equilibrium by using the carbon with BET surface area of 431 m^2/g is practically

achieved in 6 days for carbon coated monolith dose of 0.9 g, pH of 2.5, and ambient temperature. The maximum MO adsorption capacity of 36.72 (mg/g) $(L/mg)^{1/n}$ is obtained. The results follow Langmuir and Freundlich isotherm equations. Of these two equations, the Freundlich fits better.

The rate constant of both the pseudo-first-order and second-order kinetic models has been obtained to decrease with increasing initial concentration. It is reported that the pseudo-second-order has a satisfactory fit with experimental data based on a correlation coefficient analysis.

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