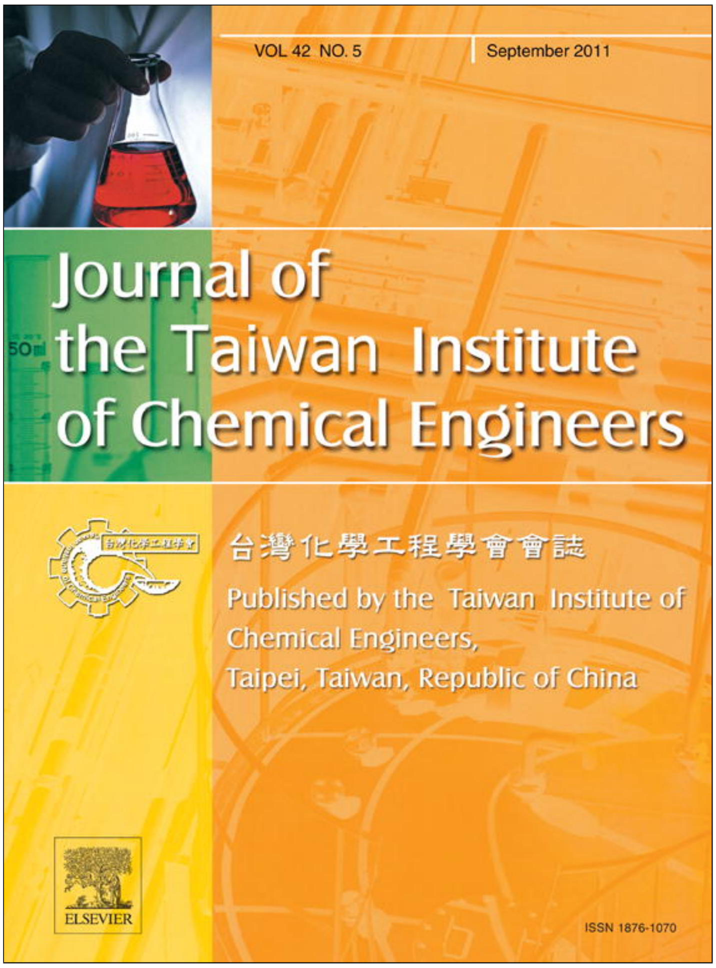
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Potential utilization of *Jatropha curcas L.* press-cake residue as new precursor for activated carbon preparation: Application in methylene blue removal from aqueous solution

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ABSTRACT

Low cost activated carbon was prepared from the press-cake residue of *Jatropha curcas L.* The effectiveness of this activated carbon and its modified forms (chemical and thermal activation) was evaluated for methylene blue (MB) dye removal from aqueous solution. Adsorption experiments were conducted in batch system at various pH and temperatures. The widely used isotherm models, Langmuir and Freundlich, were employed to represent equilibrium data. Kinetic data were analyzed using pseudo-first order and pseudo-second order model. Thermodynamic properties (ΔG^0, ΔH^0 and ΔS^0) of the adsorption of methylene blue onto Jatropha carbons were also obtained. The thermal activated carbon (JAC-3) was more effective for MB dye removal compared to chemical (JAC-2) and parent (JAC-1) activated carbon.

1. Introduction

The textile and dye manufacturing industries play a significant role in the economy growth of Indonesia. Wastewater from these industries contain considerable amount of unused dyes, which are not readily biodegradable in natural environment. The direct discharge of colored wastewater from these kinds of industries into the aquatic streams harm the environment due to its toxicity and ability to impede the transmission of sunlight, retards photosynthesis activity by plant and phytoplankton, and inhibits the growth of biota and harm the stability of food web (Gad and El-Sayed, 2009). Additionally, most of synthetic dyes are very harmful to human life due to their acute and chronic effects. It is obvious that dyes are hazardous material hence their removal from industrial effluent is considered as an important step in the environmental protection.

A number of treatment methods are available for dyes removal such as coagulation, oxidation, biodegradation, photolysis, filtration and adsorption (Fernandez *et al.*, 2010). Among them, adsorption is generally considered as an effective method for reducing the concentration of dissolved dyes in industrial wastewater. Since adsorption process is widely known as promising technique, which produces treated dye effluents with very low concentration, therefore in the past few years, the hundreds of studies have been conducted to develop different kind of cost effective/low cost adsorbents (Bhatnagar and Sillanpaa, 2010). In this regard, activated carbons have been developed extensively for the removal of different classes of dyes such as acid, direct, basic, reactive, disperse, sulphur and metallic.

Activated carbon is a versatile adsorbent from an industrial view of point due to its high adsorptive properties. It has complex nature and various surface properties with pore sizes ranging from micropores (<20 Å slit width) to macropores (>500 Å slit width). However, the large scale use of activated carbon in industrial wastewater treatment still limited due to its high cost. A method to overcome this limitation is by using agricultural or forestry wastes as precursor for activated carbon preparation, such as bagasse pith (Gad and El-Sayed, 2009), cashew nut shell (Kumar *et al.*, 2011), rice straw (Fierro *et al.*, 2010), cherry stones (Jaramillo *et al.*, 2010), oak cups pulp (Timur *et al.*, 2010), flower (Nethaji *et al.*, 2010) and also various biodiesel solid residues (Foo and Hameed, 2009; Karagoz *et al.*, 2008; Nunes *et al.*, 2009).

Jatropha curcas L. press-cake residue is one of promising biomass wastes that can be utilized as precursor for active carbon preparation. Their seeds contain high enough oil and have been widely used for biodiesel production in several Asia countries. However, the solid residues that produced after seed-pressing process just ended as mere waste. In Indonesia, approximately 2,105,400 tons of *J. curcas L.* seeds were produced in 2009 and 70% of it end up as solid residue. Accumulation of these wastes for long period of time often create environmental problem due to its

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unpleasant odor. Since the fixed carbon content in Jatropha press-cake residue is quite high, hence the utilization of this waste as activated carbon precursor can minimize the environmental problem. To the best of our knowledge, to the present, there is no information about the preparation and modification of activated carbon from *J. curcas L.* press-cake residue available in the literature. The main objective of this present study is to develop low cost activated carbon from Jatropha waste and to investigate its adsorption performance for basic dye (methylene blue) removal from aqueous solution.

2. Materials and methods

2.1. Activated carbon preparation

J. curcas L. press-cake residue was used as activated carbon precursor in this study. Prior to used, the biomass was washed several times with tap water to remove physical impurities then dried in oven for overnight at 120 °C. Subsequently, the dry biomass was crushed into powder using microhammer mill and sieved to particle size fraction of 38–106 μm.

The preparation of activated carbon was conducted by following procedure: 500 g of pretreated biomass were soaked in KOH solution for 24 h with impregnation ratio of 2:1. The choice of impregnation ratio 2:1 based on our preliminary experiments; at this impregnation ratio the pore structure of activated carbon was more developed than other impregnation ratio. The soaked biomass was then subjected to a two-step heating process at 120 °C for 2 h in an oven and then at 500 °C for 4 h in a horizontal tubular furnace at a constant heating rate of 10 °C/min under N_2 stream at flow rate of 150 cm^3/min (STP).

After carbonization process, the char that produced was cooled to room temperature under the same gaseous flow then rinsed with 0.5 N HCl and hot distilled water until no significant change in pH detected. The char (JAC-1) was then dried in an oven at 120 °C for 24 h and kept in dessicator for further use. The ultimate and proximate analysis of *J. curcas L.* press-cake residue and JAC-1 was given in Table 1.

2.2. Chemical and thermal activation of JAC-1

Chemical activation of JAC-1 was conducted by following procedure (Huang *et al.*, 2009): 50 g of JAC-1 was added into 500 mL round bottle flask containing 200 mL of concentrated nitric acid. The mixture was then heated at 80 °C for 7 h under continuous stirring at 100 rpm. Subsequently, the oxidized carbon was rinsed with deionized water until no significant change in pH detected. Finally, the activated carbon sample was dried in an oven at 120 °C for 24 h and kept in dessicator.

Thermal activation of JAC-1 was carried out in a horizontal tubular furnace (Thermolyne 21100) with the procedure as follows: 20 g of JAC-1 were placed in a stainless steel tubular reactor and heated from room temperature to 750 °C at a constant heating rate of 10 °C/min under N_2 flow. Once the carbonization temperature was reached, the N_2 flow was switched to air (150 cm^3/min) and maintained for 30 min. The activated carbon sample was then cooled to room temperature under N_2 flow and stored in dessicator. Here, chemical activation carbon and thermal activation carbon are referred as JAC-2 and JAC-3, respectively.

Table 1
Proximate and ultimate analysis of *Jatropha* press-cake residue and JAC-1.

	Press-cake residue	JAC-1
Ultimate analysis (wt%)		
Carbon	47.8	92.3
Hydrogen	6.7	1.2
Nitrogen	4.3	0.1
Oxygen (*measured by difference)	41.2	6.4
Proximate analysis (wt%)		
Volatile matter	50.9	2.3
Fixed carbon	39.2	86.6
Ash	2.6	11.1
Moisture	7.3	–

2.3. Characterizations of active carbons

The pore structure of JAC was analyzed by nitrogen sorption at 77 K using an automatic Micromeritics ASAP-2010 volumetric sorption analyzer. Prior to the gas adsorption measurements, the carbon samples were degassed at 573 K in a vacuum condition for a period of at least 24 h. Nitrogen sorption isotherms were measured over a relative pressure (P/P_0) range from approximately 10^{-5} to 0.995.

The surface oxides of JAC were characterized by Boehm titration (Boehm, 2002). The Boehm titration is described as follow: 0.5 g of carbon sample was added to a series of conical flasks containing 50 cm^3 of 0.05 M: NaOH, Na_2CO_3, $NaHCO_3$ and HCl solutions. The conical flasks were then sealed and shaken for 24 h at room temperature. The solid suspension was decanted and 10 cm^3 of the remaining solution was titrated with 0.05 M HCl or NaOH, depends on the original solution used. The number of acidic groups was calculated under the assumptions that NaOH neutralizes carboxylic, phenolic and lactonic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups; and $NaHCO_3$ neutralizes only carboxylic groups. The number of basic sites presented on the carbon surface was determined from the amount of HCl reacted with sample.

The pH_{pzc} of JAC was analyzed using pH-drift technique (Faria *et al.*, 2004). The pH-drift procedure is described as follows: 50 cm^3 of 0.01 N NaCl solution was placed in several conical flasks. The pH was adjusted to value between 2 and 11 by adding 0.1 M HCl or 0.1 M NaOH solutions. After that, 0.15 g of carbon was added to the solution and the final pH was measured after 48 h (using digital pH meter Schott CG-825) under agitation at room temperature.

The surface functional groups of JAC were also characterized using infrared spectroscopy (FTIR SHIMADZU 8400S). This qualitative analysis was performed using KBr pelleting technique and all of the carbon spectra were recorded in mid-IR wave number range (500–4000 cm^{-1}).

2.4. Adsorption experiments

Methylene blue (Basic Blue 9; C.I. 52015; chemical formula $C_{16}H_{18}N_3SCl.3H_2O$; MW: 373.90 g mol^{-1}) was used as adsorbate in this study. It was purchased from Sigma–Aldrich as analytical reagent grade and directly used without any further treatment. The maximum wavelength of this dye is 664.1 nm. The dye stock solution was prepared by dissolving a fixed amount of methylene blue into 1 L of deionized water. To prevent the decolorization by direct sunlight, the dye stock solution was stored in dark bottle and kept in dark place before used.

Adsorption equilibrium and kinetic studies were carried out in batch system. Adsorption equilibrium data were obtained by adding various mass of carbon (0.1–1.1 g) into a series of 250 mL conical flasks, containing 100 mL of dye solution with initial concentration of 1000 mg/L. The conical flasks were then covered with aluminum foil, placed in thermostat shaker (MEMMERT) and shaken with constant speed at desired operating temperature until equilibrium state was achieved. Product analysis showed that the equilibrium state was achieved within 6–10 h. After equilibrium time reached, the dye solution was centrifuged at 4000 rpm for 5 min (MLW T.51.1) to remove solid particles. The supernatant was then carefully taken and measured its residual dye concentration by UV/vis spectrophotometer (SHIMADZU UV/VIS-1700 PharmaSpec). The pH of dye solution was also measured at the start and at the end of each experiment using digital pH-meter (Schott CG-825) to check for any drift. The results indicated that no significant change in pH was detected in all experiments. Isotherm experiments were conducted at various pH (3, 7 and 11) and temperatures (30 °C, 45 °C and 60 °C). To adjust the pH, an appropriate amount of 0.1 M NaOH or 0.1 M HCl solutions were added to the system.

Adsorption kinetic experiments were performed in glass vessel of 11 cm in inner diameter, 15 cm in height and fitted with four glass baffles (1 cm in width). The dye solution was prepared by mixing a known amount of MB dye with deionized water to yield various initial concentrations of 200, 500 and 800 mg/L. Prior to the addition of carbon (0.6 g), the glass vessel containing 500 mL of dye solution was placed in the thermostat water-bath at 30 °C. The mixture was then agitated at 500 rpm for 7 h. During the experiments, at predetermined interval of time, the dye solution was taken from the vessel (1 mL using micropipette), diluted with deionized water, centrifuged and analyzed its residual dye concentration spectrophotometrically. All of adsorption experiments in this study were conducted in triplicate and the experimental results were given as averages.

The following equation was used to calculate the amount of MB dye adsorbed at equilibrium and at a certain time t:

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{1}$$

$$q_t = \frac{C_0 - C_t}{m} \times V \tag{2}$$

where q_e and q_t is the amount of dye adsorbed at equilibrium and at a certain time t (mg/g), C_0 and C_e are the initial and equilibrium dye concentration in liquid phase (mg/L), respectively, m is the amount of adsorbent used (g) and V is the volume of dye solution (L).

3. Results and discussion

3.1. Textural characterizations of active carbons

The physical characteristics of the adsorbent are related to the pore structure of adsorbent such as micropore surface area (S_{micro}), mesopore surface area (S_{meso}), micropore volume (V_{micro}), and specific surface area (S_{BET}). The pore structure of JAC was analyzed by nitrogen sorption technique. The specific BET surface area (S_{BET}), micropore volume (V_{micro}) and micropore surface area (S_{micro}) was determined by application of the Brunauer–Emmett–Teller (BET) and Dubinin–Asthakov (DA) analysis software available within the instrument, respectively. The specific BET surface area of JAC was determined by means of the standard BET equation applied in the relative pressure range from 0.06 to 0.3 while for the micropore volume (V_{micro}) and micropore surface area (S_{micro}) were determined by application of the t-plot method on the adsorption isotherm. The values of physical characteristic of JAC carbons are given in Table 2. The pore size distribution of JAC was determined from adsorption isotherm data using the Density Functional Theory (DFT) software with medium regularization. Nitrogen sorption results (Fig. 1) show the largely microporous nature of the carbons, with some mesopores leading to gradual increase in the adsorption after the initial filling of the micropores, followed by rapid increase near saturation. This statement was also supported by DFT results (Fig. 2), which showed that all JAC exhibited several peaks at pore width ranging from 5 to 30 Å.

Table 2
Physical properties of JAC.

Active carbon	Surface characteristic			
	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{meso} (m^2/g)	V_{micro} (cm^3/g)
JAC-1	845.55	761.81	83.74	0.396
JAC-2	792.23	714.32	77.91	0.374
JAC-3	904.72	817.19	87.53	0.427

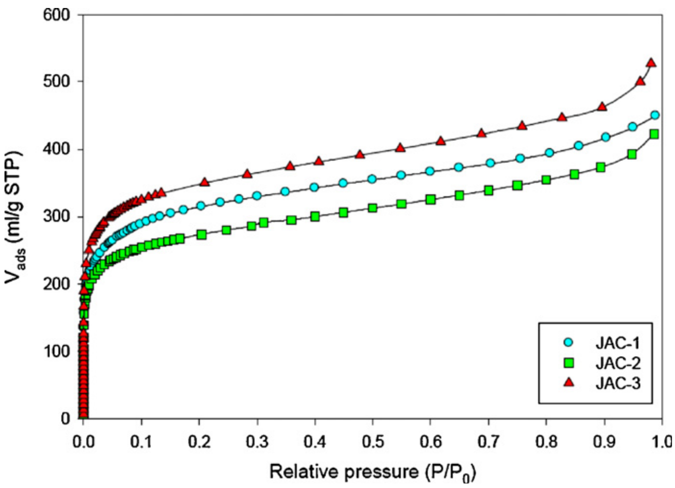

Fig. 1. Nitrogen sorption isotherms of JAC.

Chemical treatment on activated carbon using various oxidizing agents such as HNO_3, H_2O_2, $Fe(NO_3)_3$, $(NH_4)_2S_2O_8$, etc. can increase the amount of acidic surface groups, mainly carboxylic acid and also anhydrides, lactone and phenol groups in less extent. Among them, chemical treatment by HNO_3 is generally considered as the most effective method to increase the acidic groups on carbon surface (Faria *et al.*, 2004). The acidic groups, specifically carboxylic acids are known to be the binding sites for basic dyes such as methylene blue hence the presence of this group can improve the adsorption capacity of activated carbon. It was also known that chemical (wet) oxidation can reduce the surface area of carbon (JAC-2) due to the presence of numerous oxygenated groups that partially blocked the access of N_2 molecules to the small pores. Moreover, oxidation of carbon by HNO_3 also caused nitration attack by nitronium ions (NO_2^+) on the polyaromatic sheets. The nitronium ion is a strong electrophile (Lewis acid), which can substitute hydrogen atom in aromatic ring based on electrophilic aromatic substitution mechanism (Draper and Ridd, 1978).

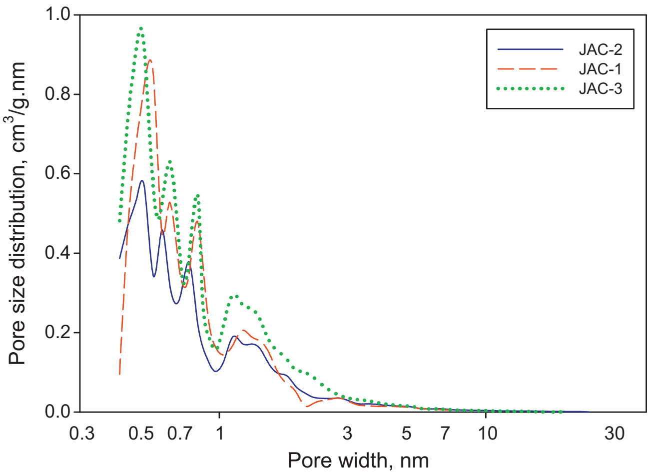

Fig. 2. Pore size distribution of JAC.

In thermal treatment, most of the oxygenated groups on carbon surface (carboxylic acid, lactone and phenol) were decomposed to CO_2 and CO at high temperature carbonization, resulting in the extension of carbon surface area and the generation of large amounts of reactive sites on the carbon basal planes which have electron rich oxygen free-radical character (Leon *et al.*, 1992). These reactive sites reacted with oxygen contained in the air thus producing new surface oxides, which can be assigned to carbonyl, pyrone or chromene type structures. These surface groups have basic surface properties, corresponding to the basic nature of JAC-3. By comparing nitrogen sorption and pore size distribution results of all JAC that have similar characteristic, it is obvious that both chemical and thermal treatment gave insignificant effect on the textural properties hence the adsorption capacity of JAC for MB dye removal will also depend on their surface chemistry properties.

3.2. Surface chemistry characterization of active carbons

The surface functional groups of JAC were analyzed by FTIR spectroscopy. The analysis results showed that several major peaks on JAC-1 was appeared at the following wave numbers: 805 cm^{-1} attributed to O–H stretch in out-of-plane bending; 1176 cm^{-1} related to the C=O stretch in lactone; 1589 cm^{-1} associated to C=C stretch in aromatic skeletal; 1729 cm^{-1} attributed to C=O stretch in carboxylic acid; 2945 cm^{-1} ascribed to the presence of symmetric C–H stretch in methylene ($-CH_2$) groups; 3021 cm^{-1} revealed to C–H stretch in aromatic ring and the last peak at 3440 cm^{-1} contributed to the presence of O–H stretch in phenolic groups.

The intensity of some peaks in JAC-2 spectra that are characteristic of C=O functional groups at wave number of 1730 cm^{-1} (carboxylic acid), 1177 cm^{-1} (lactone) and 3400 cm^{-1} (phenol) increased during chemical oxidation by HNO_3. New peak was also observed at wave number of 1600 cm^{-1}, which assigned to the nitro groups as the result of nitration attack by NO_2^+ ions on the aromatic ring groups in carbon skeletal.

The FTIR spectra of JAC-3 reflected similar characteristic with JAC-1, denoting that JAC-3 carbon had essentially the same species of surface groups except for the new peak assignment that appeared at wave number of 1582 cm^{-1}. This peak may assign to carbonyl or quinone groups, which have basic surface nature (Lewis basicity). Furthermore, the decrease in intensity of several peaks that attributed to carboxylic acid, phenol and lactone was also noticed due to the decomposition of these oxygenated groups during carbonization process at 750 °C. The surface oxides of JAC carbons obtained by Boehm titration are summarized in Table 3.

3.3. Chemisorption mechanisms of MB dye onto JAC

In order to investigate the dominant mechanism that may occur in the adsorption of methylene blue, some information relating to adsorbent nature and pH must be imparted. It is known that pH is one of key parameter in the adsorption study as it affects the chemistry of the solution, the ionic species of adsorbate as well as the surface charge density of adsorbent. In this study, the chemisorption mechanisms of MB dye onto JAC were proposed using molecular modeling by ChemDraw software package (Fig. 3).

At pH 3 ($pH < pH_{pzc}$), the surface all of JAC were influenced mainly by positive charge due to the excessive protonation on the carbon basal planes through electrostatic interaction with the π-electrons of the graphene layers (Montes-Moran *et al.*, 2004). As the carbon surface exhibited positive charge, the MB dye existed in triple protonated form (Khalid, 2001). Under this condition, the dye uptake was limited by repulsion forces which occurred between MB dye cations and positively charged of carbon surface. Electrostatic interaction also existed between MB dye cations and carboxylate anions (COO^-) on the JAC surface, however, this interaction much weaker compared to the repulsion forces resulting low dye uptake in this pH value.

The carboxylic groups on JAC surface were in the order of JAC-2 > JAC-1 > JAC-3, in which the MB dye uptake must follows this order. It is also known that carboxylic groups can dissociate in water when the pH of the system lies between 2 and 6, resulting in the formation of carboxylate anions. The carboxylate anions are known to be the active binding sites for basic dyes such as methylene blue hence the presence of this group enhanced the dye uptake. However, the inconsistency in the experimental results was observed (JAC-3 > JAC-2 > JAC-1), an indication that another interaction may also took place during dye adsorption process.

The high dye uptake by JAC-3 (basic nature carbon) due to the existence of two parallel mechanisms: electrostatic and dispersive interactions. The latter interaction was occurred between the delocalized π-electrons on the carbon basal planes and the free electrons of dye molecules present in the aromatic rings or multiple bonds (–N=C–C=C–). This interaction played a dominant role in the adsorption process of methylene blue on JAC-3. The pore characteristic of JAC-3 also contributes a significant role in the dye removal due to the enlargement in the micropores and mesopores structures as a result of the decomposition of surface oxygenated groups during heat treatment.

Low dye uptake by JAC-2 (acid nature carbon) suggests that other interaction such as water bonding and electrostatic repulsion may also play an important role in the adsorption process. It was reported that water molecules can bind into acidic surface oxides, especially carboxylic groups through H-bonding (Coughlin and Ezra, 1968) hence the presence of this group could reduce the amount of dye uptake due to the blockade on the micropores region by water. Chemical oxidation on carbon using HNO_3 also gave a negative effect on the dye uptake due to the insertion of nitrogen functionalities (NO_2) which provides more positive surface sites. The presence of abundant positive surface sites increased the repulsion forces therefore less molecules dye adsorbed in the surface of carbon. Higher dye by JAC-2 compared to JAC-1 (parent carbon) may correspond to the stronger effect of electrostatic interaction of carboxylate anions and MB molecules. As mentioned before, the JAC-2 possesses more carboxylics groups than JAC-1, therefore more carboxylate anions are available on the JAC-2 surface. In addition, low dye uptake at pH 3 was also caused by the competition between protons (H^+) and MB dye cations in bulk solution onto the active binding sites on carbon surface.

In neutral pH, the JAC-2 surface is predominated by negative charge ($pH > pH_{pzc}$) while for JAC-1 and JAC-3, the overall charge

Table 3
Surface chemistry of JAC.

Active carbon	pH_{pzc}	Carboxylic (mequiv./g)	Lactone (mequiv./g)	Phenol (mequiv./g)	Acidity (mequiv./g)	Basicity (mequiv./g)	All groups (mequiv./g)
JAC-1	8.2	0.143	0.095	0.109	0.347	0.521	0.868
JAC-2	3.7	0.372	0.157	0.264	0.793	0.214	1.007
JAC-3	10.1	0.061	0.012	0.043	0.116	0.817	0.933

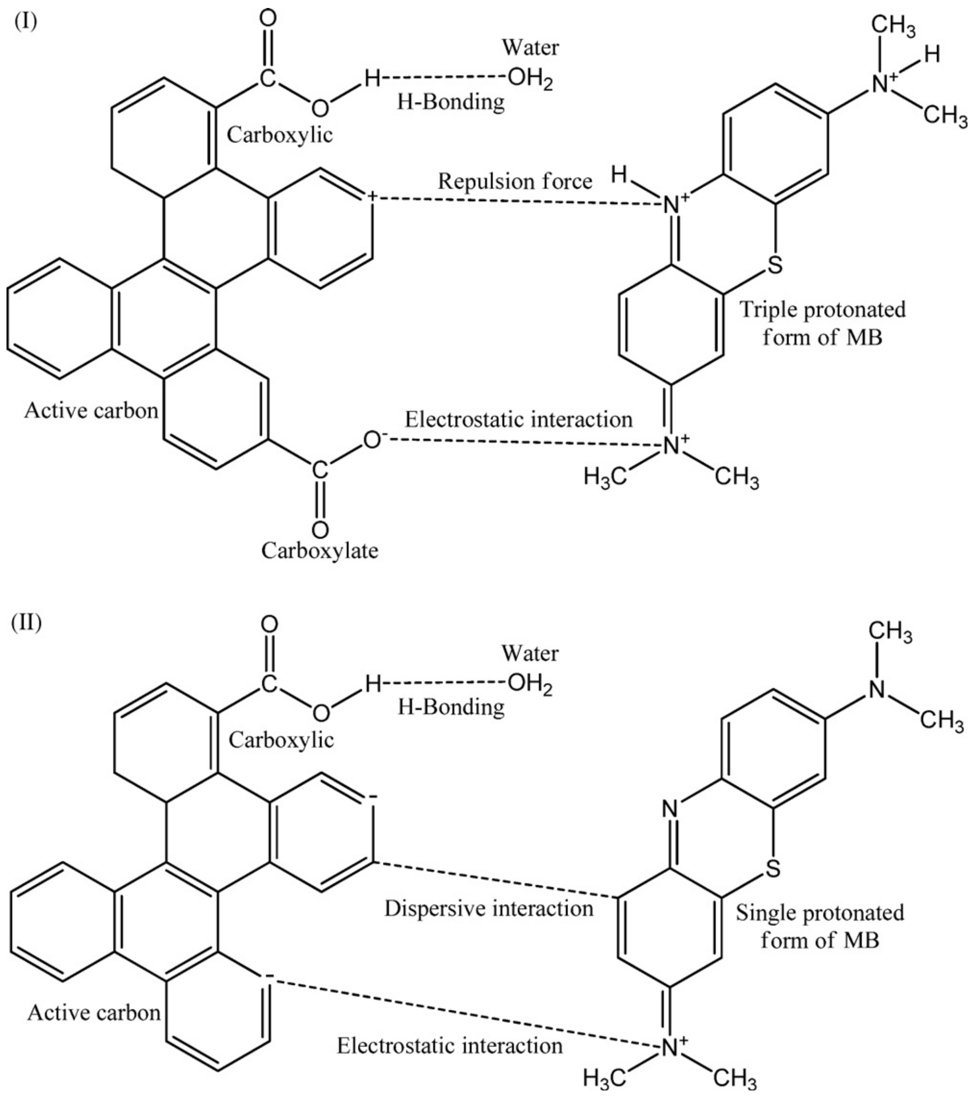

Fig. 3. Chemisorption mechanism of MB dye onto JAC at pH 3 (I) and pH 11 (II).

on their surface is positive ($pH_{pzc} > pH$). As given in Fig. 4, the dye uptake at pH 7 are in the order of JAC-3 > JAC-2 > JAC-1, indicates the mechanisms involved in the adsorption of dye in pH 7 are similar with pH 3. The dye uptake at pH 7 was higher than pH 3. At pH 7, the presence of protons (H^+) in the solution was much less than at pH 3, therefore less competition between protons (H^+) and MB dye cations in bulk solution onto the active binding sites on carbon surface occurred.

In basic solution (pH 11), the surface of all JAC were predominated by negative surface sites due to $pH > pH_{pzc}$ and the dissociation of phenol groups on carbon surface occurred, leading to the formation of phenolate anions, while MB dye existed in single protonated form. In this case, the MB dye uptake onto JAC caused by the electrostatic interaction between negatively charged on the carbon surface and dye cations. Another interaction, the π–π dispersion, may also take place during adsorption of dye. This interaction was generated between the π-electrons on carbon basal planes and the π-electrons on aromatic rings of dye molecules. Furthermore, the excessive presence of hydroxyl groups (OH^-) in bulk solution also gives a positive effect on the π–π dispersion interaction, which increased the π-electron density on carbon basal planes, hence enhanced the adsorption of MB dye. Highest dye uptake at pH 11 compared with other systems (pH 3 and pH 7) due to the existence of two parallel mechanisms, the π–π dispersion and electrostatic interaction.

3.4. Adsorption isotherms

Equilibrium relationship between adsorbate and adsorbent can be determined by adsorption isotherm study, which describes how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption reaches equilibrium. Various adsorption isotherm models for the gas phase adsorption such as Langmuir, Freundlich, Toth, Sips, etc., can in principle be extended to liquid phase adsorption. Among these isotherms, the Langmuir and the Freundlich isotherm are the most widely used models to represent the liquid phase adsorption experimental data (Ai *et al.*, 2010; Demirbas *et al.*, 2009; Liu *et al.*, 2011). The Langmuir isotherm is expressed as follows:

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \tag{3}$$

where q_{max} and K_L are the Langmuir parameters corresponded to the maximum adsorption capacity for specific adsorbent (mg/g) and the equilibrium constant (L/mg), respectively. The essential characteristic of the Langmuir isotherm can be expressed by

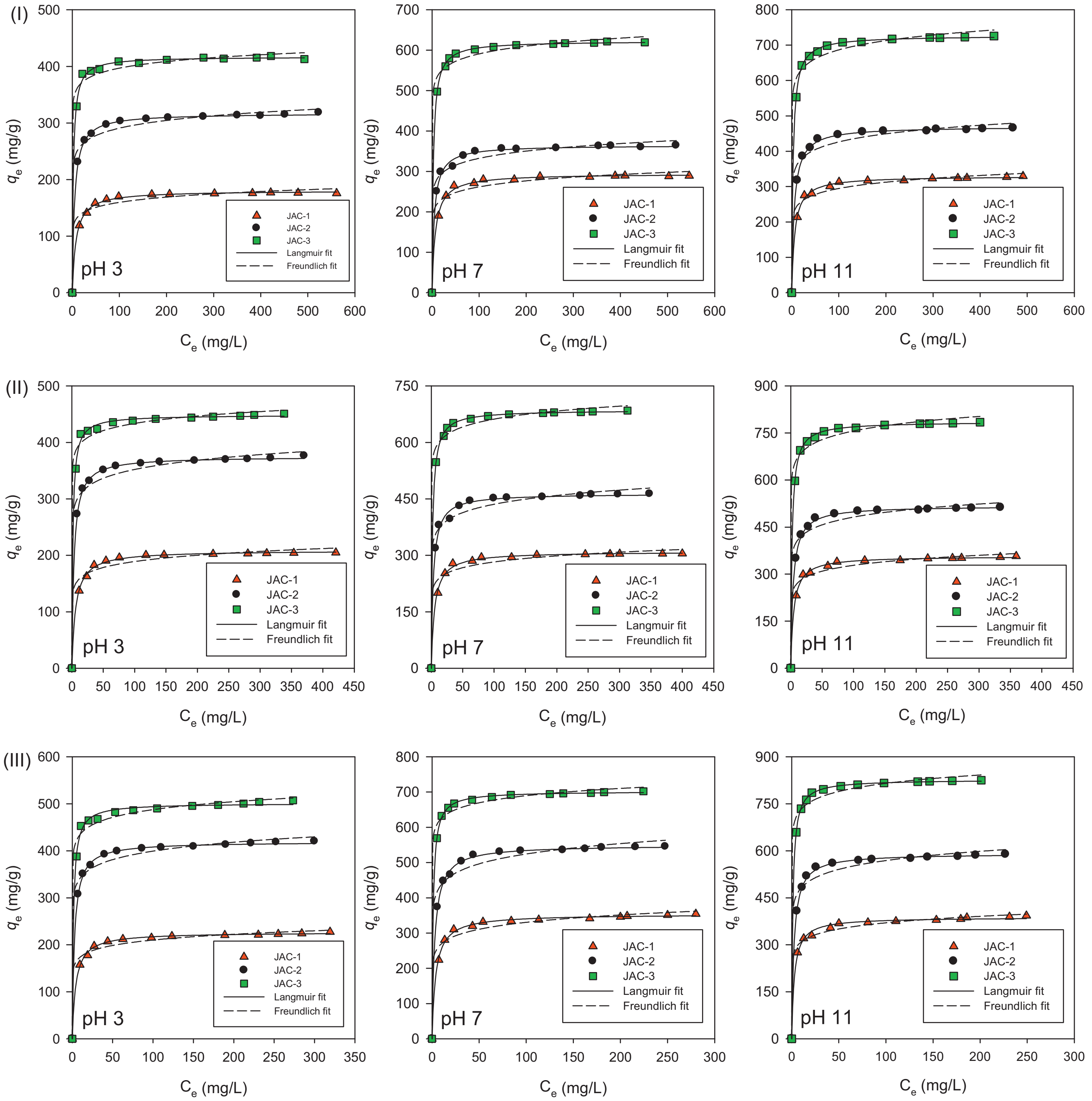

Fig. 4. Isotherm plots of MB dye uptake onto JAC at 30 °C (I), 45 °C (II) and 60 °C (III).

dimensionless constant called equilibrium parameter, R_L, which defined by following equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

The value of R_L indicates the various nature of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).

Another empirical isotherm model that widely used to represent equilibrium data is Freundlich model, which has the form:

$$q_e = K_F \times C_e^{1/n} \tag{5}$$

where K_F and n are the Freundlich parameters represented the adsorption affinity $[(\text{mg/g})(\text{L/mg})^{1/n}]$ and the heterogeneity of the system, respectively.

The isotherm plots of Langmuir and Freundlich models at various pH and temperatures are given in Fig. 4. As shown in this figure, Langmuir model could represent the experimental data better ($R^2 > 0.99$) than Freundlich equation. The parameters of

Table 4
Isotherm model parameters for MB dye adsorption onto JAC.

Active carbon	Isotherm model	Parameter	pH	T (K)			pH	T (K)			pH	T (K)		
				303.15	318.15	333.15		303.15	318.15	333.15		303.15	318.15	333.15
JAC-1	Langmuir	K_L (L/mg)	3	1.8854	2.8219	3.7501	7	2.6365	4.1524	5.1971	11	3.5549	5.1832	7.2228
		q_{max} (mg/g)		177.92	206.73	230.51		292.05	306.63	357.59		327.56	359.11	393.06
		R_L		0.0078	0.0059	0.0044		0.0070	0.0052	0.0039		0.0063	0.0046	0.0028
		R^2		0.9987	0.9984	0.9982		0.9980	0.9982	0.9978		0.9982	0.9989	0.9963
	Freundlich	K_F [(mg/g) (mg/L)$^{-1/n}$]		111.42	128.89	144.37		182.70	195.11	219.72		201.11	221.94	257.55
		n		0.0798	0.1567	0.3312		0.0688	0.1241	0.3154		0.0835	0.1552	0.3461
		R^2		0.9731	0.9735	0.9850		0.9717	0.9722	0.9761		0.9799	0.9749	0.9918
JAC-2	Langmuir	K_L (L/mg)		2.2149	3.2861	4.6307		2.8537	4.0663	5.9347		3.6859	5.5241	7.5831
		q_{max} (mg/g)		317.63	379.52	424.42		366.76	467.19	546.93		469.36	515.45	590.65
		R_L		0.0047	0.0033	0.0027		0.0048	0.0032	0.0029		0.0054	0.0039	0.0025
		R^2		0.9995	0.9996	0.9994		0.9965	0.9968	0.9991		0.9994	0.9996	0.9994
	Freundlich	K_F [(mg/g) (mg/L)$^{-1/n}$]		217.09	260.24	293.24		234.71	307.60	364.44		302.36	340.03	406.39
		n		0.0643	0.1458	0.3126		0.0570	0.1135	0.3083		0.0646	0.1462	0.3282
		R^2		0.9884	0.9880	0.9895		0.9824	0.9828	0.9822		0.9793	0.9794	0.9814
JAC-3	Langmuir	K_L (L/mg)		2.8564	4.5264	6.2962		3.6321	5.7313	7.7755		5.1553	7.1871	9.6732
		q_{max} (mg/g)		419.75	453.26	510.32		624.55	685.49	706.88		730.34	785.33	827.34
		R_L		0.0023	0.0016	0.0015		0.0028	0.0016	0.0012		0.0030	0.0021	0.0012
		R^2		0.9987	0.9985	0.9977		0.9998	0.9995	0.9998		0.9997	0.9990	0.9999
	Freundlich	K_F [(mg/g) (mg/L)$^{-1/n}$]		321.75	355.83	388.49		475.24	535.16	566.66		531.55	589.73	657.94
		n		0.0640	0.1371	0.3014		0.0561	0.1062	0.3004		0.0563	0.1396	0.3218
		R^2		0.9895	0.9905	0.9914		0.9926	0.9926	0.9936		0.9895	0.9902	0.9924

each model were obtained by non-linear regression method (Table 4). Based on the value of R_L ($0 < R_L < 1$), all systems show favorable adsorption process. The value of parameters K_L and q_{max} in Langmuir model increased as the temperature increased. Similar trend was also observed in Freundlich model. The increase of these parameters with the increase of temperature indicated that the adsorption process of MB in JAC carbons was an endothermic process. Table 5 shows the comparison of the maximum adsorption capacity of various low cost and commercial active carbons for MB dye removal. The adsorption capacity of JAC-3 is higher than other adsorbents, indicates that JAC-3 is suitable as the adsorbent for dye removal from wastewater.

3.5. Adsorption kinetics

In the design of the adsorption system, the data obtained from the adsorption kinetic study are very important since it contain the information about the adsorption mechanism, the potential rate controlling steps, etc. This information is required to select the optimum condition for full scale batch metal removal processes. Several adsorption kinetic models have been developed to understand the adsorption kinetics and rate limiting step. The pseudo-first and second order kinetic models are well known models to correlate the adsorption dynamic or kinetic data for various systems. The pseudo-first order, which also known as Lagergren kinetic model (Lagergren, 1898) has the form:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

Integrating Eq. (6) with the boundary conditions $t = 0 \rightarrow t = t$ and $q_t = 0 \rightarrow q_t = q_t$ gives:

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{7}$$

While the pseudo-second order model (Ho and McKay, 1999) can be expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{8}$$

Integrating Eq. (8) with the boundary condition: $t = 0 \rightarrow t = t$ and $q_t = 0 \rightarrow q_t = q_t$ gives

$$q_t = q_e\left(\frac{q_e k_2 t}{1 + q_e k_2 t}\right) \tag{9}$$

where k_1 and k_2 are the pseudo-first order (min^{-1}) and pseudo-second order (g mg^{-1} min^{-1}) rate constants, respectively.

Table 5
Maximum adsorption capacity (q_{max}) of several adsorbents for MB dye removal.

	q_{max} (mg/g)	Reference
Commercial active carbon		
Filtrasorb 300	240	Stavropoulos and Zabaniotou (2005)
Filtrasorb 400	476	El Qada *et al.* (2008)
Norit	276	Raposo *et al.* (2009)
Picacarb	246	Raposo *et al.* (2009)
Biomass based – active carbon		
Vetiver roots	375–423	Altenor *et al.* (2009)
Oak cups pulp	384.6–454.5	Timur *et al.* (2010)
Corncob hull	684.24	Wu *et al.* (2011)
Bamboo	195.8–618.5	Liu *et al.* (2011)
Olive seed waste residue	190–263	Stavropoulos and Zabaniotou (2005)
Defective coffee press-cake residue	14.9	Nunes *et al.* (2009)
Sunflower oil cake	16.4	Karagoz *et al.* (2008)
JAC-1	177.9–393.0	This study
JAC-2	317.6–590.6	This study
JAC-3	419.7–827.3	This study

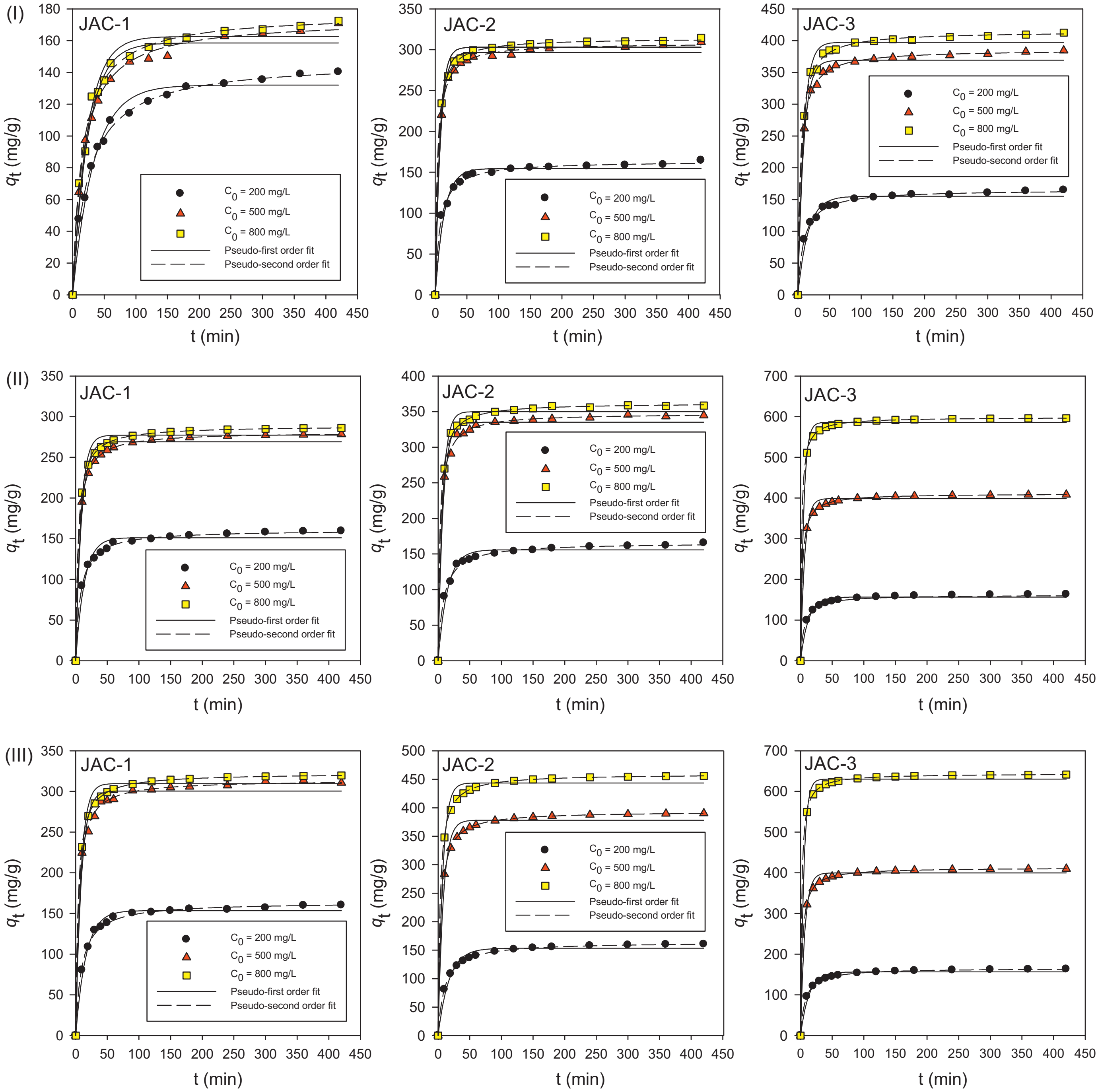

Fig. 5. Kinetic plots of pseudo-first order (Lagergren) and pseudo-second order model for MB dye uptake onto JAC at pH 3 (I), pH 7 (II) and pH 11 (III).

The adsorption kinetics data of MB in JAC carbons and the fitted models are depicted in Fig. 5, and the fitted kinetic parameters of pseudo-first order and pseudo-second order are summarized in Tables 6 and 7, respectively. In this figure, the kinetic plots are characterized by fast dye uptake and the sharp rise in solid phase concentration. By comparing the fitting result by pseudo first order and pseudo second order, the latter seems to give better representation. Additionally, the fitted parameter q_e in pseudo-second order agree quite well with the experimental data. The applicability of the pseudo-second order model to correlate the adsorption kinetic data of MB on JAC carbons suggested that the rate-controlling step in MB dye uptake onto JAC is chemisorption involving valence forces through the exchange or sharing of electrons between the adsorbate molecules and the surface functional groups of adsorbent.

3.6. Thermodynamic aspects

In order to gain complete understanding about the MB adsorption onto JAC surface, the thermodynamic properties such as the change in standard Gibb's free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) also have been investigated. The standard Gibb's free energy change was calculated by following equation:

$$\Delta G^0 = -RT \ln K_D \tag{10}$$

Table 6
Kinetic parameters of pseudo-first order for MB dye adsorption onto JAC.

C_0, mg/L	JAC-1			JAC-2			JAC-3		
	k_1 (1/min)	q_e (mg/g)	q_e exp (mg/g)	k_1 (1/min)	q_e (mg/g)	q_e exp (mg/g)	k_1 (1/min)	q_e (mg/g)	q_e exp (mg/g)
pH 3									
200	0.0298	132.06	146.33	0.0624	154.52	163.21	0.0724	155.07	164.65
500	0.0410	158.57	173.92	0.1097	296.60	307.29	0.1147	369.23	383.33
800	0.0425	162.65	175.50	0.1116	303.08	313.68	0.1332	397.37	413.13
pH 7									
200	0.0680	151.32	160.85	0.0733	155.92	163.31	0.0817	156.61	165.61
500	0.1306	269.25	281.28	0.1115	335.02	346.28	0.1567	398.82	411.06
800	0.1385	277.33	288.93	0.1103	350.02	360.93	0.1964	586.17	598.80
pH 11									
200	0.0581	150.58	162.23	0.0618	153.27	164.26	0.0760	156.35	165.78
500	0.1118	300.61	313.78	0.1133	378.16	393.77	0.1499	399.78	411.77
800	0.1388	309.77	322.61	0.1116	443.49	459.39	0.1954	630.45	644.18

Table 7
Kinetic parameters of pseudo-second order for MB dye adsorption onto JAC.

C_0, mg/L	JAC-1			JAC-2			JAC-3		
	k_2 (g/mg min)	q_e (mg/g)	q_e exp (mg/g)	k_2 (g/mg min)	q_e (mg/g)	q_e exp (mg/g)	k_2 (g/mg min)	q_e (mg/g)	q_e exp (mg/g)
pH 3									
200	0.0003	147.38	146.33	0.0006	163.79	163.21	0.0008	165.73	164.65
500	0.0004	173.42	173.92	0.0006	308.50	307.29	0.0009	385.99	383.33
800	0.0004	177.11	175.50	0.0005	314.38	313.68	0.0009	414.11	413.13
pH 7									
200	0.0007	160.85	160.85	0.0008	164.05	163.31	0.0009	165.98	165.61
500	0.0008	282.31	281.28	0.0008	347.60	346.28	0.0009	410.38	411.06
800	0.0009	288.03	288.93	0.0009	361.26	360.93	0.0010	597.93	598.80
pH 11									
200	0.0006	161.97	162.23	0.0006	163.94	164.26	0.0008	166.07	165.78
500	0.0006	314.17	313.78	0.0007	392.98	393.77	0.0009	411.39	411.77
800	0.0007	323.31	322.61	0.0008	459.39	459.39	0.0009	645.08	644.18

where R is the universal gas constant (8.314 J/mol K), T is temperature (K) and K_D is the thermodynamic distribution coefficient ($K_D = q_e/C_e$). The enthalpy and entropy change were correlated to the K_D by Van't Hoff equation which expressed as follow:

$$\ln K_D = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{11}$$

The value of ΔH^0 and ΔS^0 was obtained from the slope and the intercept from the linear plot of $\ln K_D$ versus $1/T$ (Fig. 6), respectively. The calculated thermodynamic parameters were summarized in Table 8. From this table it can be seen that all systems showed the favorability of the process and spontaneous nature of dye adsorption onto JAC carbons.

By increasing the temperature, more negative value of ΔG^0 was observed; this phenomenon indicates that higher temperatures are more preferred for higher sorption results. The binding affinity of adsorbate molecules toward adsorbent surface increased with the increased of temperature. The positive value of ΔH^0 reveals that the adsorption process is endothermic in nature and could be classified into chemisorption since all of ΔH^0 values fall into the range of 20.9–418.4 kJ/mol (Tan *et al.*, 2011). On the other hand, the positive value of ΔS^0 denotes the increased in randomness at solid–solution interface during

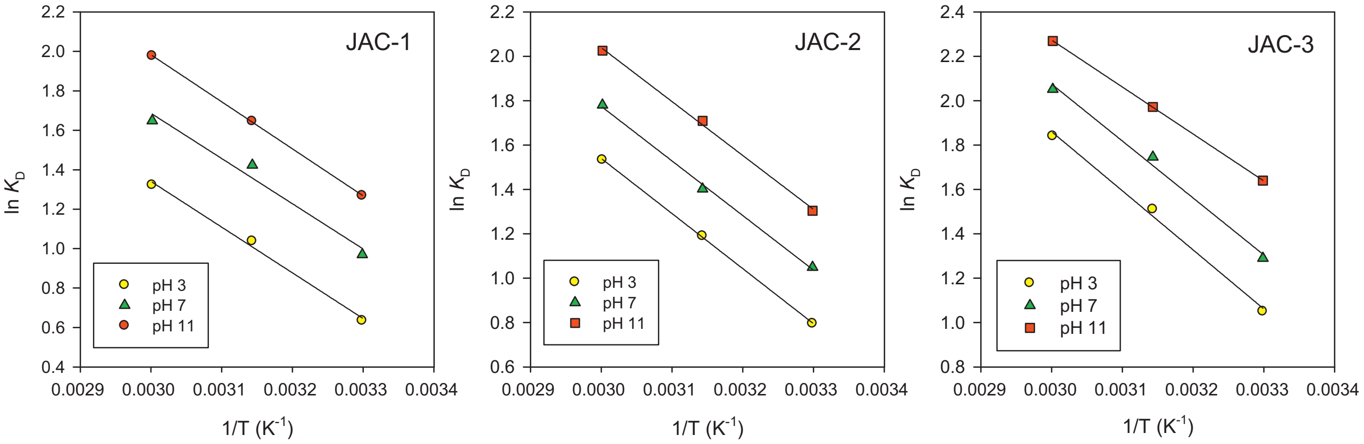

Fig. 6. Thermodynamic plots of $\ln K_D$ versus $1/T$ for MB dye adsorption onto JAC.

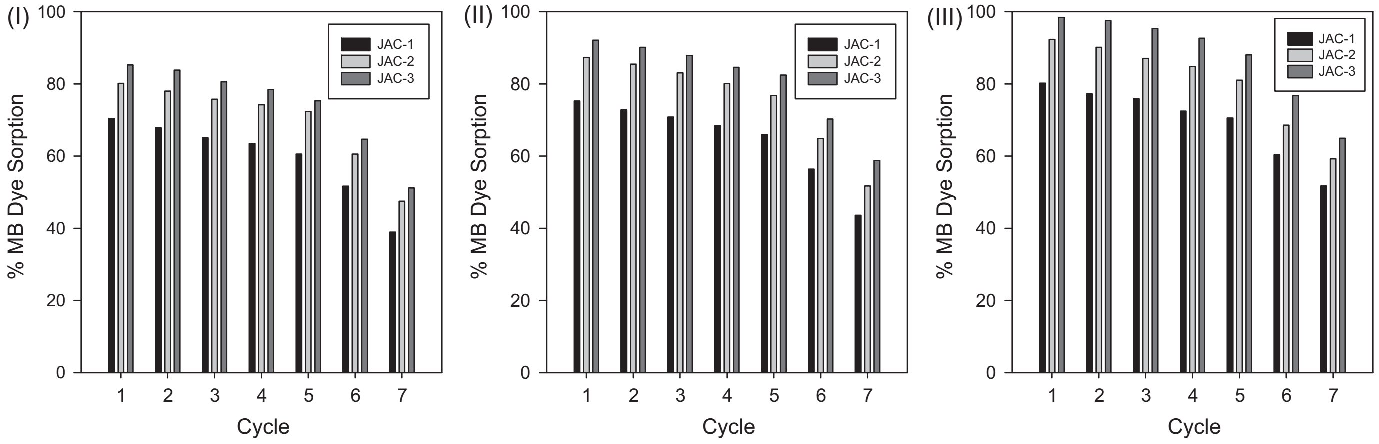

Fig. 7. Effect of recycling time on MB dye adsorption by JAC at pH 3 (I), pH 7 (II) and pH 11 (III).

Table 8
Thermodynamic parameters for MB dye adsorption onto JAC.

pH	T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)	R^2
JAC-1					
3	303.15	−1.5983	21.2082	0.0690	0.9948
	318.15	−2.7441			
	333.15	−3.6611			
7	303.15	−2.4434	21.1790	0.0713	0.9727
	318.15	−3.5078			
	333.15	−4.5649			
11	303.15	−3.1967	21.1567	0.0760	0.9999
	318.15	−4.5323			
	333.15	−5.4766			
JAC-2					
3	303.15	−2.0043	21.6492	0.0747	0.9998
	318.15	−3.1469			
	333.15	−4.2453			
7	303.15	−2.6429	21.4678	0.0762	0.9979
	318.15	−3.7104			
	333.15	−4.9325			
11	303.15	−3.2879	21.2148	0.0776	0.9982
	318.15	−4.5208			
	333.15	−5.6114			
JAC-3					
3	303.15	−2.6453	22.1634	0.0820	0.9954
	318.15	−3.9939			
	333.15	−5.0963			
7	303.15	−3.2508	21.8355	0.0830	0.9925
	318.15	−4.6182			
	333.15	−5.6808			
11	303.15	−4.1335	21.5060	0.0857	0.9998
	318.15	−5.2169			
	333.15	−6.2857			

adsorption of dyes while the negative value of ΔS^0 describes the opposite phenomena.

3.7. *Reusability of the adsorbent*

The reusability of the adsorbent is important in industrial practice. To assess the stability of the repeated used of JAC for MB dye removal, the adsorption–desorption cycles was also conducted. In this study, dilute hydrochloric acid was used as elution solution and the procedure was repeated seven times under following operating condition (initial dye concentration = 1000 mg/L; contact time = 4 h; T = 30 °C; mass of adsorbent = 1 g). The effect of recycling time on the adsorption capacity of JAC is given in Fig. 7. In this figure, it can be seen that all of JAC can be repeatedly used at least five times without significantly losing its adsorption capacity toward MB dye.

4. Conclusions

J. curcas L. press-cake residue can be utilized as new precursor for low cost activated carbon preparation. In order to improve the adsorption capacity for dyes removal, the surface properties of carbon could be tailored appropriately by chemical and thermal treatment. Based on the experimental results, it was found that thermal activated carbon (JAC-3) showed higher adsorption capacity for MB dye removal than the parent carbon (JAC-1) and oxidized carbon (JAC-2). The Langmuir model represented the experimental data better than Freundlich equation. The pseudo-second order model gave better representation in correlating kinetic data than pseudo-first order model. The adsorption of MB dye onto JAC was controlled by chemisorption mechanism. The thermodynamic behavior of the adsorption MB onto JAC carbons was endothermic ($\Delta H^0 > 0$), irreversible ($\Delta S^0 > 0$) and spontaneous ($\Delta G^0 < 0$). Desorption studies indicated that all of JAC could be regenerated and reused at least five times without significantly losing its adsorption capacity.

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