Carbohydrate Polymers 102 (2014) 192–198

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Comparative study of calcium alginate, activated carbon, and their composite beads on methylene blue adsorption

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ARTICLE INFO

Article history:
Received 16 October 2013
Received in revised form 29 October 2013
Accepted 30 October 2013
Available online 27 November 2013

Keywords:
Alginate beads
Composite
Activated carbon
Coconut shells
Methylene blue

ABSTRACT

Three adsorbents, calcium alginate beads (AB), sodium hydroxide activated carbon based coconut shells (C), and calcium alginate/activated carbon composite beads (ACB) were prepared. Their textural properties were characterized by N_2-adsorption at −196 °C and scanning electron microscopy. The porosity, surface area and total pore volume of C > ACB > AB, but AB adsorbent was more acidic function groups more than the other adsorbents. Adsorption experiments were conducted to examine the effects of adsorbent dosage, pH, time, temperature and initial concentration of methylene blue. Methylene blue adsorption on C, AB and ACB was observed at pH > 6 to avoid the competition of H^+. The amount of dye adsorbed increases as the adsorbent dosage increase. Adsorption of dye follows pseudo-second order mechanism. Thermodynamic studies show spontaneous and endothermic nature of the overall adsorption process.

1. Introduction

The output of production of dyes generates colored wastewaters, which has aroused peoples concern regarding the environmental safety. The recycling from the manufacturing sectors and the textile industries into seas and rivers, alter the biomedical stability of the surrounding (Sheng, Xie, & Zhou, 2009). Removal of dyes and pigments from the waste has been fully considered over the last decade.

Methylene blue is one of the most commonly dyes used for industrial applications. Although the dye is not considered as highly toxic, methylene blue has various dangerous effects on human and animals. It can cause heart rate increasing, nausea and vomiting. Therefore, many different ways are available in order to eliminate these dyes from the industrial wastes. The most common used are degradation (El-Sheekh, Gharieb, & Abou-El-Souod, 2009), flocculation–coagulation (Cañizares, Martínez, Jiménez, Lobato, & Rodrigo, 2006), oxidation (Salem & El-Maazawi, 2000) and adsorption. Among these ways, adsorption has been proven more effective and attractive for the treatment of dye-bearing industrial wastes (Yao, Xu, Chen, Xu, & Zhu, 2010). Adsorption is also cheap and highly effective method in the removal of methylene blue from wastewaters.

The adsorption of methylene blue by using different adsorbents, such as activated carbon (AC), wastes from agriculture, silicate, clay, solid wastes from the industry (Rafatullah, Sulaiman, Hashim, & Ahmad, 2010) etc., have been investigated. Among these adsorbents, perhaps activated carbon is one of the most common used adsorbent for methylene blue removal, based on the highly adsorption capacity and the fast removal rate because of their higher specific surface area and surface reactivity too (Park & Kim, 1999). But it is prohibitively expensive. The wastewater materials and agriculture wastes are assumed to be low-cost adsorbents due to their most abundance in nature and with many surface functional groups. The raw agricultural wastes such as leaves (Han et al., 2009; Weng, Lin, & Tzeng, 2009), fibers (Kavitha & Namasivayam, 2007), peels (Hameed, 2009), seeds (Hameed & Ahmad, 2009) and waste materials from forest industries such as sawdust (Hamdaoui, 2006) etc. have been used as adsorbents for the purifications and removing of dyes and pigments.

Water soluble sodium alginate, is linear polysaccharide, natural occurring polymer composed of α-guluronate and β-mannuronate residues. Alginate has some unique properties such as, its hydrophilicity, biocompatibility and it is considered to be non-toxic substance (Liu, Chen, Zhong, & Wu, 2009). The gelation properties of sodium alginate is mainly affected by the confirmed exchange

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http://dx.doi.org/10.1016/j.carbpol.2013.10.104

of sodium ions from the guluronic acid residues with different divalent cations such as Ca^{2+}, Sr^{2+}, Ba^{2+}, etc. All divalent cations connect to the α-L-guluronic acid blocks between two different chains resulting in 3D network (Sarmento et al., 2006). Calcium alginate is widely used in immobilization of activated carbon (Kim, Jin, Park, Kim, & Cho, 2008), carbon nanotubes (Li et al., 2010), titanian nanoparticles (Mahmoodi, Hayati, Arami, & Bahrami, 2011) and magnetite nanoparticles (Rocher, Siaugue, Cabuil, & Bee, 2008) to create different adsorbents in order to remove wastes like dyes, pigments and metals from aqueous solutions.

The main objectives of this research work are: (i) preparation of NaOH-activated carbon from coconut shells, calcium alginate beads from sodium alginate solution, and calcium alginate/activated carbon composite beads, (ii) textural and chemical characterization of the prepared adsorbents using N_2 adsorption at −196 °C, SEM, FTIR and pH_{PZC} (iii) adsorption of methylene blue from all solutions, which are previously prepared by the solid adsorbents, taking into account the kinetic and thermodynamic parameters, (iv) comparative studies between the three adsorbents toward organic pollutants.

2. Materials and methods

2.1. Materials

Calcium chloride, sodium hydroxide, methylene blue, sodium alginate, hydrochloric acid, sodium chloride were all purchased from Sigma–Aldrich (USA) and Loba Chemie Pvt. Ltd. (India). All other chemicals were used without any further purification. Deionized water was used for the preparation of all the required solution.

2.2. Preparation of adsorbents

2.2.1. Preparation of NaOH-activated carbon (C)

Coconut shells collected from coconut are obtained from Egyptian local markets and were used as precursor. Firstly, they were washed with distilled water to remove any adhering impurities, and then dried at 110 °C for 24 h followed by grinding and sieving in order to use a particles size ranged between 1 mm and 2 mm. NaOH/activated carbon sample (C) was prepared via two steps: carbonization of dried precursor at 600 °C for 4 h in absence of air using a stainless steel reactor (600 mm × 40 mm) at a rate of 10 °C/min up to 600 °C. The carbonized sample was cooled and soaked with certain weight of NaOH (40 g of carbonized sample with 120 g of solid NaOH) in 50 ml distilled water for 48 h at room temperature, followed by drying at 110 °C and finally activated at 750 °C for 4 h. Prepared sample was washed several times with distilled water till neutral filtrate and then dried at 110 °C to constant weight and finally stored in a clean dry glass bottle.

2.2.2. Preparation of calcium alginate beads (AB)

A solution of 1% sodium alginate and 3% calcium chloride were prepared separately in deionized water. For preparation of AB beads, 1% sodium alginate solution was added drop wise to calcium chloride solution. The water-soluble sodium alginate was converted to water-insoluble calcium alginate beads. All beads were then washed with deionized water several times to remove the excess of unbounded calcium chloride from the bead surfaces. The washed beads were then dried at 70 °C for 24 h and stored in a clean dry glass bottle.

2.2.3. Preparation of calcium alginate/activated carbon composite beads (ACB)

Calcium alginate/activated carbon composite beads (ACB) were prepared by ionic gelation method (Bée, Talbot, Abramson, & Dupuis, 2011; Fiol, Poch, & Villaescusa, 2004). Two grams of powdered activated carbon (C) was dispersed in 100 mL deionized water and mixed with clear viscous 200 mL (1%, w/v) solution of sodium alginate. The mixture was stirred for 2 h. Once the mixture was homogenous, 50 ml of this solution is added to calcium chloride solution and the resulting black composite beads were collected and treated as the above prepared AB beads.

2.2.4. Adsorption procedure

The adsorption of adsorbate (methylene blue) was conducted in a static batch experiment. Aqueous solution of certain concentration of adsorbate was shaken in Stoppard Pyrex bottles of 100 mL capacity with 0.1 g of adsorbent (C, AB, or ACB) for 24 h. The supernatant liquid was filtered out, where the equilibrium concentration of the dye was determined using UV–vis spectra (Unicam 5625 UV/VIS spectrophotometer) at 662 nm. The adsorbed amount at equilibrium, q_e (mg/g) was calculated by:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e are the initial and equilibrium concentration (mg/L) of adsorbate solution, respectively; V is the volume of working solution (L) and W is the weight (g) of adsorbent used.

The effect of adsorbent dosage on the uptake was determined by shaking 1, 2, 3, 4, 5, 7, and 10 g/L of adsorbent with 75 mL of 1000 mg/L of methylene blue. All mixtures were shaken at 20 °C and at pH 7.5. The reduction in adsorbate concentrations was measured.

Effect of pH was measured by carrying out the adsorption process at different pH values ranged between 2 and 12. Effect of time was carried out by contacting 0.1 g of adsorbent with 100 ml bottles of definite concentration of adsorbate (1000 mg/L of methylene blue). The concentration of adsorbate after recorded time intervals is determined; the adsorption capacity at time t, q_t (mg/g) was calculated using:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

where C_t (mg/L) is the liquid-phase concentration of adsorbate at time t. Effect of temperature was examined at 20 and 40 °C and constant pH of 7.5. In these experiments, 0.1 g of adsorbents with 100 mL of 1000 mg/L of methylene blue was employed. After shaking, the adsorbed amount was measured; mg/g.

2.3. Characterization of solid adsorbents (C, AB, and ACB)

Fourier transform infrared spectra (FT-IR) were recorded on a Mattson 5000 FTIR spectrometer in the range between 4000 cm^{-1} and 450 cm^{-1}. Point of zero charge (pH_{PZC}) of solid adsorbents was carried out by: initially; 50 mL of 0.01 M NaCl solutions were put into several closed Erlenmeyer flasks. The pH within each flask was adjusted to a value between 2 and 12 by adding HCl (0.1 M) or NaOH (0.1 M) solutions, then a portion of the sample (0.15 g) was added to each flask, the flasks were agitated for 48 h and the final pH was then measured. The pH_{PZC} is the point where $pH_{final} = pH_{initial}$ (Hameed & Ahmad, 2009).

The morphological structure of the investigated samples was examined by scanning electron microscopy (SEM) using SEM model Quanta 250 FEG (Field Emission Gun) attached with EDX unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 kV, magnification 14× up to 1,000,000 and resolution for Gun. Specific surface area (S_{BET}, m^2/g), total pore volume (V_T, mL/g), and average pore radius (r^-, nm) were determined via nitrogen adsorption at −196 °C (outgassing was carried out at room temperature) using NOVA2000 gas sorption analyzer (Quantachrome Corporation, USA) system.

Table 1A
Textural properties and pH_{PZC} for sodium hydroxide activated carbon based coconut shells (C), calcium alginate beads (AB) and calcium alginate/activated carbon composite beads (ACB).

Adsorbents	S_{BET} (m^2/g)	V_T (mL/g)	r^- (nm)	PZC
C	1620.0	1.070000	1.320	7.8
AB	32.7	0.017205	1.053	6.0
ACB	733.8	0.380680	1.038	7.1

3. Results and discussion

3.1. Characterization of textural structure and surface chemistry of all adsorbents

Textural characteristics for the three adsorbents C, AB, and ACB are shown in Table 1A. Sodium hydroxide activated carbon (C) shows the highest surface area compared with the other two solid adsorbents which could be related to the effect of sodium hydroxide as activating agent at 750 °C. It was expected to make drastic changes in the texture and porous surface development. Reaction of NaOH with carbon atoms resulted in loss of carbon content and an increase in porosity according to the following equation:

$$4NaOH + C \rightarrow Na_2O + Na_2CO_3 + 2H_2 \quad (3)$$

Some reactions may be established due to decomposition of NaOH as follows:

$$2NaOH \rightarrow Na_2O + H_2O \quad (4)$$

$$C + H_2O \rightarrow H_2 + CO \quad (5)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \quad (6)$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3 \quad (7)$$

$$Na_2O + H_2 \rightarrow 2Na + H_2O \quad (8)$$

$$Na_2O + C \rightarrow 2Na + CO \quad (9)$$

$$Na_2CO_3 + 2C \rightarrow 2Na + 3CO \quad (10)$$

It was reported that, the decomposition of NaOH, the reduction of carbon framework, the evolution of hydrogen in reaction (3) and the evolution of carbon dioxide and steam as oxidizing gases in other reactions could stand behind the production of new pores and could also lead to the erosion of pore walls (Guo et al., 2002).

Upon inspection of Table 1A (i) surface area for alginate beads sample (AB) is very low compared with that of sodium hydroxide activated sample (represent about 2% only of the total surface area of sodium hydroxide activated sample) and surface area of calcium alginate/activated carbon composite beads (ACB) recorded about 733 m^2/g which is lower than that recorded with C sample (represent about 45% of the total surface area of sodium hydroxide activated sample) which could be related to the decrease in porosity of activated carbon sample by the effect of alginate polymer deposition which is confirmed by the sharp decrease in total pore volume of C from 1.07000 mL/g to 0.38068 mL/g for ACB.

(ii) Average pore radius could be calculated from the equation,

$$r^-(\text{nm}) = \frac{2V_T(\text{mL/g})}{S_{BET}(\text{m}^2/\text{g})} \times 10^3 \quad (11)$$

where V_T is the adsorbed volume near saturation point, i.e. at $p/p^o \approx 0.95$, multiplied by the factor 15.5×10^{-4}. It was found that the average pore radius ranged between 1.3200 nm and 1.0530 nm. The decrease in average pore radius of sodium hydroxide activated carbon when mixed with alginate polymer form ACB sample indicates pore bio capsulation by alginate polymer.

SEM photographs shown in Fig. 1 were taken at 1200× magnification to observe the surface morphologies of C, AB, and ACB. The surface of AB had a uniform morphology while the surface of C with irregular porosity which explains the effect of sodium hydroxide as activating agent at 750 °C. The surface of ACB with porosity less than in pure activated carbon sample (C).

Table 1B
Langmuir constants for adsorption of methylene blue onto sodium hydroxide activated carbon based coconut shells (C), calcium alginate beads (AB) and calcium alginate/activated carbon composite beads (ACB), at two different temperatures; 20 and 40 °C.

Adsorbents	20 °C			40 °C		
	q_m (mg/g)	b (L/mg)	R^2	q_m (mg/g)	b (L/mg)	R^2
C	1030	0.21577	0.99721	961	0.26375	0.99699
AB	800	0.16035	0.99596	406	0.17188	0.99827
ACB	892	0.15678	0.99778	730	0.18113	0.9984

Table 1C
Pseudo-first order and pseudo-second order kinetic model parameters for adsorption of methylene blue onto sodium hydroxide activated carbon based coconut shells (C), calcium alginate beads (AB) and calcium alginate/activated carbon composite beads (ACB).

Adsorbents	q_m (mg/g)	Pseudo-first order			Pseudo-second order		
		R^2	q_e (mg/g)	K_1 (h^{-1})	R^2	q_e (mg/g)	K_2 (g/mg h^{-1})
C	1030	0.9804	773	0.26515	0.99248	1055	5.72×10^{-4}
AB	800	0.81616	299.5	0.43169	0.94880	776	9.04×10^{-4}
ACB	892	0.96624	635.7	0.35733	0.95857	961.5	3.41×10^{-4}

Table 1D
Thermodynamic parameters for adsorption of methylene blue onto sodium hydroxide activated carbon based coconut shells (C), calcium alginate beads (AB) and calcium alginate/activated carbon composite beads (ACB), at 20 and 40 °C.

Adsorbents	K_o		$-\Delta G^\circ$ (kJ mol^{-1})		ΔS (kJ mol^{-1} K^{-1})		ΔH° (kJ mol^{-1})
	293 K	313 K	293 K	313 K	293 K	313 K	
C	31.30	29.10	8.388	8.172	0.0025	0.0036	7.656
AB	18.81	8.29	7.148	5.504	0.0150	0.0091	2.647
ACB	24.16	16.28	7.758	7.260	0.0077	0.0056	5.505

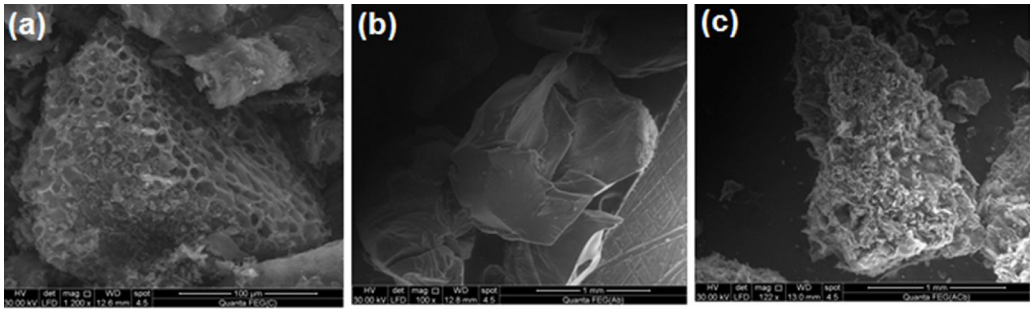

Fig. 1. SEM of: (a) sodium hydroxide activated carbon based coconut shells (C), (b) calcium alginate beads (AB), and (c) calcium alginate/activated carbon composite beads (ACB).

Besides the physical structure, activated carbons have a chemical structure that also affect as well. The adsorption capacity of activated carbons is determined by their physical or porous structure but is also influenced by the chemical structure of their surfaces. Activated carbon can chemisorbs oxygen even on more exposure to air or oxygen (Guo et al., 2002) preferably at 400–500 °C. The oxygen is fixed firmly and comes off; only oxides of carbon on high-temperature evacuated. Infrared spectroscopy has been one of the most frequently used instrumental analysis tools to characterize the surface functionalities in activated carbons (Yang & Lua, 2003). FT-IR spectra for the three adsorbents are shown in Fig. 2. The band at about 3440 cm^{-1} is attributed to O—H (stretching) due to phenolic groups. The band around 3423 cm^{-1} can be assigned to O—H vibrations suggesting the presence of phenol groups. Other observable peaks were detected around 2922 cm^{-1} which could be related to aliphatic C—H vibrations. The band at 2855 cm^{-1} are attributed to —O—CH_3 or two bands for aldehyde group (Ahmad, Loh, & Aziz, 2007). Peaks located around 1624 and 1032 cm^{-1} could be related to C=C stretching for unsaturated aliphatic structures and alcoholic (Bandosz, 2006) groups, respectively.

The PZC can be affected by the pH. The PZC is also considered as an indicator for the oxidation of carbon surfaces, since it points out the increase in surface acidity/basicity after treatment. PZC was 7.8, 6.0 and 7.1 for C, AB and ACB, respectively.

3.2. Adsorption of methylene blue

3.2.1. Effect of adsorbent mass

Fig. 3A shows the plot between removal percent of methylene blue against the adsorbent dosage (g/L). From the figure, the removal percent increased from 67.5% to 95% with an increase in the adsorbent dosage of C from 2 to 10 g/L. There is a very fast superficial sorption onto adsorbent surface that produces a lower solute concentration in the solution, this happened only when the adsorbent to dye ratio is very low. This is because; adsorbent can only adsorb a certain amount of methylene blue. Therefore, the more adsorbent dosage, the larger the volume of effluent that a fixed mass of adsorbent can remove (Kumar & Kumaran, 2005). For AB and ACB the same trend was observed but the increase in removal % with the increase in adsorbent dosage is higher in case of C > ACB > AB which could be related to the surface areas and porosity where C > ACB > AB.

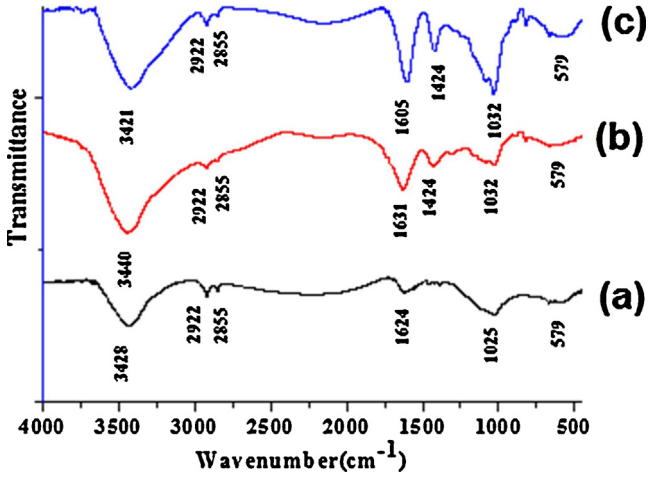

Fig. 2. FTIR spectrum of: (a) sodium hydroxide activated carbon based coconut shells (C), (b) calcium alginate beads (AB), and (c) calcium alginate/activated carbon composite beads (ACB).

3.2.2. Effect of pH

The degree of adsorption of ionic dyes onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which is affected by the pH of the solution. It is seen from Fig. 3B that the maximum removal % of methylene blue takes place at pH > 6. The decrease in methylene blue removal at lower pH values may be related to the protons competition with methylene blue for the available adsorption sites. Equilibrium pH attained at pH > PZC (Bestani, Benderdouche, Benstaali, Belhakem, & Addou, 2008). The three adsorbents (C, AB and ACB) approximately show the same trend where their PZC are closer to each other.

3.2.3. Adsorption isotherm

It describes the relationship between the amount adsorbed by the adsorbent and the adsorbate concentration remaining in the solution. The adsorptions isotherms of methylene blue are studied on the samples prepared (C, AB and ACB) at 20 and 40 °C and are presented in Fig. 3C. It can be observed that, at the same temperature the highest value for the adsorbed amounts was obtained for C followed by ACB, while the lowest value was those for AB. The linear form of Langmuir equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (12)$$

where b (L/mg) is Langmuir constant, C_e (mg/L) is the equilibrium concentration, q_e (mg/g) is the amount adsorbed at equilibrium, and q_m (mg/g) represents the monolayer capacity. A plot of C_e/q_e versus C_e gives a straight line of slope $1/q_m$ and intercept $1/bq_m$. The constants calculated from the linear form of Langmuir equation are given in Table 1B. Upon inspection of Table 1B (i) q_m for C adsorbent more than the others which related to the higher surface area for C and the presence of microporosity as indicated by SEM image. (ii) Correlation coefficient (R^2) in all cases ranged between 0.99840 and 0.99596 indicating the applicability of Langmuir

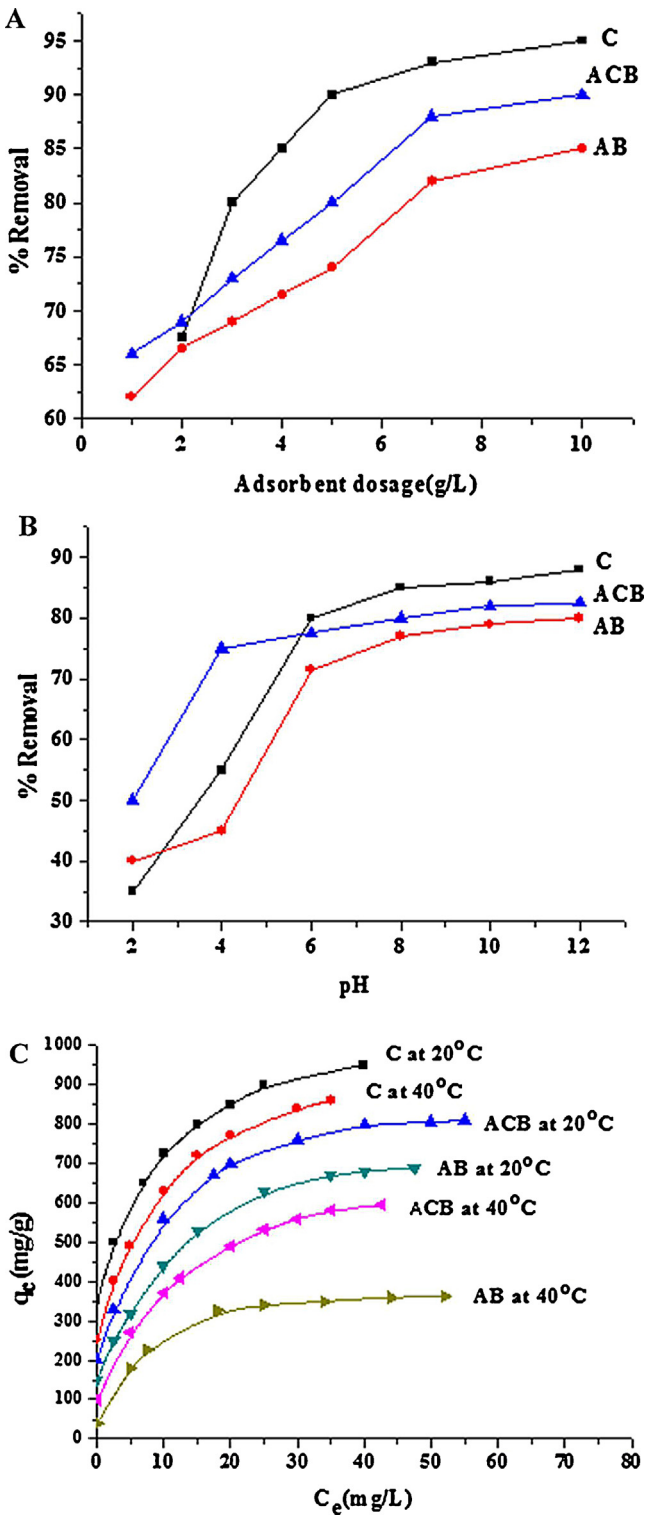

Fig. 3. (A) Effect of adsorbent dosage on adsorption of methylene blue onto sodium hydroxide activated carbon based coconut shells (C), calcium alginate beads (AB) and calcium alginate/activated carbon composite beads (ACB). (B) Effect of pH on adsorption of methylene blue onto sodium hydroxide activated carbon based coconut shells (C), calcium alginate beads (AB) and calcium alginate/activated carbon composite beads (ACB). (C) Adsorption of methylene blue fitted with Langmuir isotherm onto sodium hydroxide activated carbon based coconut shells (C), calcium alginate beads (AB) and calcium alginate/activated carbon composite beads (ACB) at two different temperatures; 20 and 40 °C.

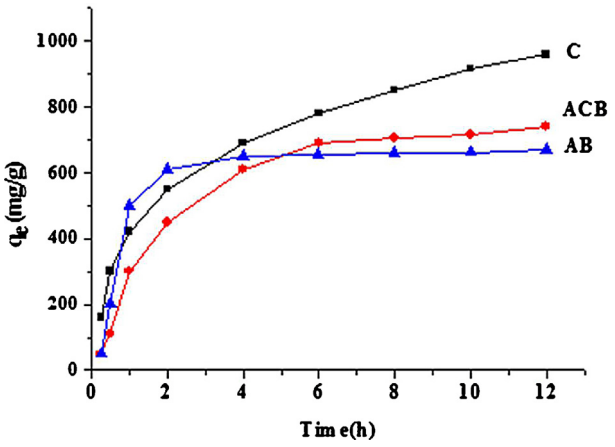

Fig. 4. Effect of time on the adsorption of methylene blue onto sodium hydroxide activated carbon based coconut shells (C), calcium alginate beads (AB) and calcium alginate/activated carbon composite beads (ACB).

equation. Dimension separation factor R_L (Sun, Zhang, Wu, & Liu, 2010) which is defined as:

$$R_L = \frac{1}{1 + bC_0} \tag{13}$$

where b (L/mg) is the Langmuir constant and C_o (mg/L) is the initial methylene blue concentration. The value of R_L indicates the type of isotherm to be unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L values for methylene blue adsorption onto C, AB and ACB were less than one and more than zero indicating favorable adsorption.

3.2.4. *Effect of contact time and adsorption kinetics*

A series of contact time experiments for methylene blue have been carried out using 800 mg/L as an initial concentration for the dye and at pH of 7. Fig. 4 shows that, equilibrium time required for adsorption not less than 8 h in case of C and ACB as adsorbents but equilibrium time for AB about 2 h which may be related to the fact that, activated carbon is composed of porous structure with large internal surface area (C = 1620 and ACB = 733 m^2/g). Three consecutive mass transport steps are associated with the adsorption from solution by porous adsorbent. First, film diffusion, followed by solute movement from particle surface into interior site by pore diffusion and finally the adsorbate is absorbed into the active sites at the interior of the adsorbed particle. This process takes relatively long contact time (Hameed, Din, & Ahmad, 2007). Pseudo-first order equation (PFO) and pseudo-second order equation (PSO) were applied to express the mechanism of adsorption onto the adsorbent. A linear form of PFO model is:

$$\ln(q_e - q_t) = \ln(q_e) - (k_1 t) \tag{14}$$

where q_e and q_t are the amounts of methylene blue adsorbed (mg/g) at equilibrium and at time t (h), respectively and k_1 the rate constant adsorption (h^{-1}). Values of k_1 were calculated from the plots of $\ln(q_e - q_t)$ versus t (Fig. 5) and q_e calculated from the intercept. Table 1C shows characteristic constants for PFO. It indicates that adsorption of methylene blue onto C, AB and ACB are not follow PFO due to, either the calculated correlation coefficient is lower as in case of AB, $R^2 = 0.81616$, or the large difference between calculated q_e (mg/g) from PFO model and that calculated from Langmuir equation, q_m (mg/g) as in case of C and ACB. On the other hand, a linear form of PSO model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{15}$$

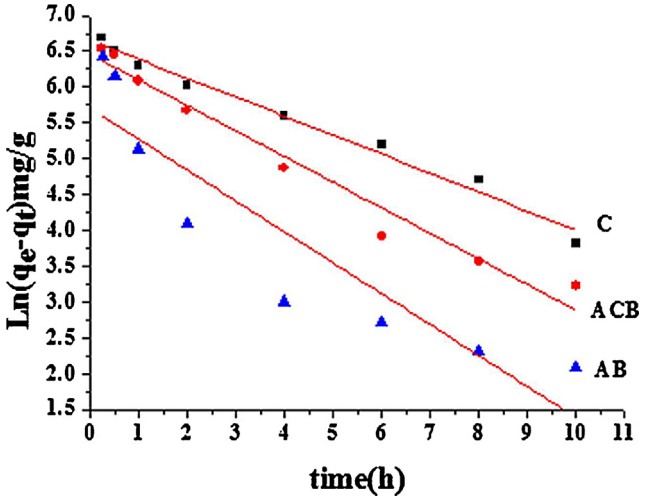

Fig. 5. Pseudo-first-order kinetics for adsorption of methylene blue onto sodium hydroxide activated carbon based coconut shells (C), calcium alginate beads (AB) and calcium alginate/activated carbon composite beads (ACB).

where K_2 (g/mg h^{-1}) is the rate constant of second-order adsorption. Linear plot of t versus t/q_t in Fig. 6 and the calculated PSO characteristics model are shown in Table 1C. Correlation coefficient values ranged between 0.994880 and 0.94880 indicating good linear plots. q_e values calculated from PSO model close to those calculated from Langmuir equation indicating the applicability of PSO mechanism for the adsorption of methylene blue onto C, AB and ACB.

3.2.5. Adsorption thermodynamic

Thermodynamic parameters of MB adsorption on C, AB, and ACB were determined at 20 and 40 °C. Thermodynamic parameters, namely thermodynamic equilibrium constant K_o, Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated using the following equations:

$$K_0 = \frac{C_s}{C_e} \tag{16}$$

where C_s is the surface concentration of MB and C_e the equilibrium concentration.

$$\Delta G^\circ = -RT \ln K_0 \tag{17}$$

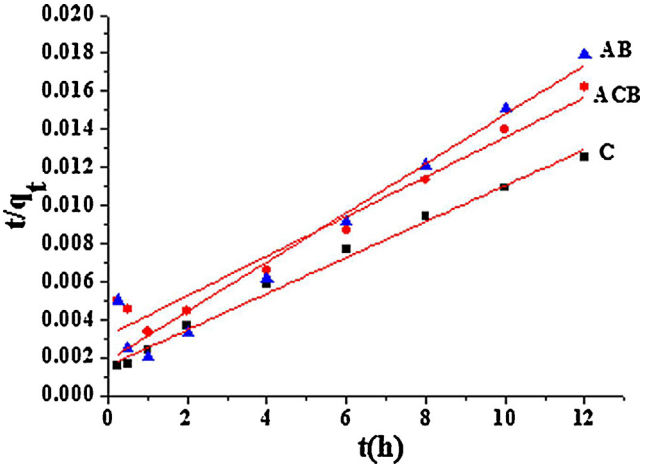

Fig. 6. Pseudo-second-order kinetics for adsorption of methylene blue onto sodium hydroxide activated carbon based coconut shells (C), calcium alginate beads (AB) and calcium alginate/activated carbon composite beads (ACB).

where R is the universal gas constant (8.314×10^{-3} kJ K^{-1} mol^{-1})

$$\Delta H^\circ = R\left(\frac{T_1 T_2}{T_2 - T_1}\right) 2.303 \log \frac{b_2}{b_1} \tag{18}$$

where b_1 and b_2 are the Langmuir constants at 20 and 40 °C, respectively.

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{19}$$

The values of K_o for C > ACB > AB indicating the increase in adsorption capacity which could be related to the increase in specific surface area and to the total pore volume of adsorbent. Based on the obtained values of thermodynamic parameters (Table 1D), the negative values of ΔG° indicate the spontaneous adsorption of MB on adsorbent samples. Adsorption of MB can be considered as physisorption when the change in free energy for adsorption of MB on samples ranges between −8.388 kJ mol^{-1} and −5.504 kJ mol^{-1}. It is known that, the absolute magnitude of the change in free energy for physisorption is between −20 kJ mol^{-1} and 0 kJ mol^{-1} and that chemisorption occurs between −80 kJ mol^{-1} and −400 kJ mol^{-1} (Yu, Zhuang, & Wang, 2001). The positive values of entropy change reflect the increased randomness at solid/solution surface. This is a direct consequence of enhancement of the mobility and extent of penetration within the activated carbon pores and overcoming the activation energy barrier and enhancing the rate of intra-particle diffusion as well. The positive values of ΔH° (ranged between 2.647 kJ mol^{-1} and 7.656 kJ mol^{-1}) confirm the endothermic nature of the overall adsorption process.

4. Conclusion

Textural characterization of all prepared samples indicate that, the porosity, S_{BET} and total pore volume of C > ACB > AB. Carbon oxygen function groups for AB > ACB > C. The adsorption of methylene blue onto C, AB and ACB was observed at pH > PZC to avoid the competition with H^+. The amount of dye adsorbed increase as the adsorbent dosage increase. C shows the higher adsorption capacity than ACB and AB. The adsorption of methylene blue follow PSO model. The adsorption was observed to be spontaneous and endothermic in nature as explained and recorded by the thermodynamic parameters.

Acknowledgements

This paper was in-part financially supported by the research sector of Damanhour University. The authors would like to extend their sincere appreciation to the Deanship of Scientific Research at King Saud University for its funding of this research through the research group project no. RGP-VPP-201.

The work was financially supported by the project "CEITEC - Central European Institute of Technology – excellent teams (CZ.1.07/2.3.00/30.0005) financed from European Social Fund.

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