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Adsorption of Victoria blue by carbon/Ba/alginate beads: Kinetics, thermodynamics and isotherm studies

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ABSTRACT

The kinetic, thermodynamic and isotherm modeling studies were carried out on adsorptive removal of Victoria blue (VB) dye using activated carbon, Ba/alginate and modified carbon/Ba/alginate polymer beads. The feasibility of sorption process was determined by varying the experimental parameters viz., dye concentration (4–20 mg L^{-1}), contact time (10–90 min), pH (3–10), adsorbent dose (0.5–2.5 g) and temperature (303–343 K). Freundlich and Langmuir isotherms were determined and ascertained with the dimensionless separation factor (R_L). Lagergren's pseudo-first order, pseudo-second order and intra-particle diffusion model equations were used to analyze the kinetics of the adsorption process. The thermodynamic consistency of adsorption was found with Gibbs free energy (ΔG°), changes in enthalpy (ΔH°) and entropy (ΔS°) were calculated using the Van't Hoff plot. The polymer beads were characterized using Fourier Transform Infrared Spectroscopy (FTIR) and their morphology was determined by scanning electron microscopy (SEM).

1. Introduction

Over the past two centuries the human population and the economic wealth of the world have grown tremendously. For sustainable life style, each and every country has increased productivity of all materials by industrializing their economies, which has led to the accumulation of large quantity of industrial wastes. Approximately, 80% of the industrial effluents are responsible for the environmental pollution. The effluents that are discharged into the aquatic bodies and affect either directly or indirectly, the quality of water and the aquatic living organisms and in turn the human health. Dye industries contribute and play a vital role in contaminating the environment. It is commonly known that dyes are extensively used in textile, paper, pulp, rubber, pharmaceuticals and leather industries (Crini, 2006; Pearce, Lloyd, & Guthrie, 2003; Tan, Hameed, & Ahmad, 2007). Dyes are synthetic organic compounds that are capable of producing active materials which are nonbiodegradable in nature (Raffainer & Rudolf von Rohr, 2001). Even a trace quantity of dye present in the water may produce color in the bulk and make it unusable.

The nonbiodegradable dye compounds present in the water bodies may also cause some mutagenic and carcinogenic problems. Further they cause severe damage to living things like altering the normal functions of organs such as kidneys, reproductive system, liver, brain and central nervous system (Vanhulle et al., 2008). To avoid these kinds of hazardous health problems, it has thus become essential to remove the dye molecules from the water bodies. Several physical, chemical and biological methods are available for the removal of dyes from wastewater such as; flocculation and coagulation (Ogutveren, Gonen, & Koparal, 1992; Riera Torres, Guti_errez-Bouz_an, & Crespi, 2010), biosorption (Sarma, Sarma, & Bhattacharyya, 2008), precipitation (Tan, Teng, & Mohd Omar, 2000), membrane filtration (Koyuncu, Topacik, & Yuksel, 2004), electrochemical techniques (Edip & Erol, 2010), microbial decolorization (Hatchinson & Robinson, 1990) and photodegradation (Xu & Langford, 2001). Numerous materials are also used for the degradation or removal of dyes such as; zeolite (Dogan, Akgul, et al., 2007), perlite (Vijayakumar, Tamilarasan, & Dharmendirakumar, 2012), sepiolite (Ozcan, Oncu, & Ozcan, 2006), fly ash (Khare, Panday, Srivastava, & Singh, 1987), plant materials (Vaughan, Seo, & Marshall, 2001), coir pith (Namasivayam et al., 2001), metal alloys (Tang & Chen, 1996), hydrogen peroxide (Kamble, Sawant, Schouten, & Pangarkar, 2003; Mehrdad & Hashemzadeh, 2010) and metal electrodes (Mohan, Balasubramanian, & Basha, 2007).

All the methods mentioned above are not able to effectively remove the dyes and posses some drawbacks like; incomplete removal, toxic products, tedious processing conditions, difficulty in regeneration and consume more time. In contrast to the techniques mentioned earlier, adsorption is a most versatile and convenient method for the removal of dyes without the production of any hazardous products. Adsorption has also gained favor due to its proven efficiency in the removal of pollutants from effluents compared to

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other methods (Danis, Gurses, & Canpolat, 1999). Since the amount of dye adsorbed on the adsorbents is not high enough, researches are conducted to improve their adsorption performance. Natural carbohydrate materials have a considerable attention for the removal of dyes since these materials are eco-friendly and do not produce any harmful effect to the environment.

Sodium alginate (SA) is a natural non-toxic polysaccharide which contains sodium salt of alginic acid as a polyelectrolyte that is found in several natural carbohydrates. Sodium alginate is manufactured from the brown algae of some bacteria. Alginate contains β-D-mannuronic acid (M) and α-L-guluronic acid (G) and these produce a variety of sequential 1,4-linkages with other materials. Alginate beads are hydrophilic in nature, due to the presence of carboxylic groups and possess high mechanical strength that is of natural origin and has good stability in high operational conditions. Alginates are extensively used in pharmaceutical industries for the preparation of timed release enteric coated tablets and are capable of giving very good gel formation when in contact with the metal solution that produces completely enclosed polymeric beads.

In the present work, the polymeric bead was prepared by the ionic polymerization route. In this study: (i) activated carbon, Ba/alginate and modified carbon/Ba/alginate polymer composite beads were used; (ii) alginate was chosen as the natural carbohydrate; (iii) various parameters were used for the adsorption studies; (iv) Freundlich and Langmuir isotherm equations were used for the equilibrium studies; (v) kinetic equations were used as the pseudo-first order and pseudo-second order equations; (vi) various thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated using Van't Hoff plot; and (vii) adsorbent characterization was done using Fourier Transform Infrared Spectroscopy (FTIR) and the morphology of the polymer beads was determined by using scanning electron microscopy (SEM).

Prosopis juliflora is a tropical tree that is widely grown in the dry lands, arid regions and other parts of India. It is one of the most tolerant species for saline, alkaline soils and is also capable of growing in water logged areas. The *Prosopis juliflora* bark carbon (PJBC) has not yet been tried as an adsorbent for the removal of dyes; hence this material was taken for the adsorption study. The adsorbent material was prepared using sodium alginate, barium chloride and *Prosopis juliflora* bark activated carbon.

2. Materials and methods

2.1. Preparation of activated carbon

The activated carbon preparation method was presented in the previous research paper (Kumar & Tamilarasan, 2013).

2.2. Adsorbate

The dye stock solution of the adsorbate was prepared from an exact and pre-weighed quantity of Victoria blue dye (4-[[4-anilino-1-naphthyl][4(dimethylamino)-phenyl]-methylene]-cyclohexa-2,5-dien-1-ylidene] dimethylammonium chloride) having a molecular formula of $C_{33}H_{32}ClN_3$ and a formula weight of 506.10 that was dissolved in 1000 ml of double distilled water and used throughout the experiment.

2.3. Preparation of activated carbon/Ba/alginate beads

The polymer composite bead preparation method was presented in the previous research work (Kumar & Tamilarasan, 2013). In this study the metal solution of $BaCl_2$ was chosen for the preparation of polymer composite beads (Ba/alginate polymer beads). The activated carbon used polymer composite beads were represented as activated carbon/Ba/alginate polymer composite beads.

2.4. Adsorption studies

Adsorption studies were carried out on each adsorbent by varying the dye concentration, pH, temperature, dose of adsorbent and agitation time. The concentration of the dye solution was varied from 4 to 20 mg L^{-1} with an increment of 4 mg L^{-1}. The pH was varied from 3 to 10 using 0.1 N HCl and 0.1 N NaOH. The adsorbent dose was varied from 0.5, 1.0, 1.5, 2.0 and 2.5 g with wet beads. Agitation time was varied from 10 to 90 min with 10 min increments. The adsorption experiment was carried out by varying the temperature from 303 to 343 K in increments of 10 K. The variation of temperature is intended to calculate the thermodynamic parameters. The amount of sorption q_t (mg g^{-1}), at time t, was calculated using the following equation

$$q_t = \frac{(C_0 - C_t)V}{M} \quad (1)$$

where C_0 is initial concentration of dye, C_t is the concentration at any given time t, V is the volume of the dye solution in L and M is weight of activated carbon in g. All the adsorption experiments were carried out using double distilled water in a thermostatic controlled shaker with Erlenmeyer flasks using 25 ml of the dye solution.

2.5. Analytical studies

The adsorbent morphology of Ba/alginate and activated carbon/Ba/alginate polymer beads was analyzed by using scanning electron microscopy (SEM). The surface functional groups of the polymer composite beads were studied using Fourier Transform Infrared spectroscopy (FTIR) before and after the adsorption of dye. The FTIR spectra of the samples were recorded in the frequency range from 4000 and 400 cm^{-1}.

2.6. Determination of pH_{zpc}

The zero point charge (pH_{zpc}) of Ba/alginate and activated carbon/Ba/alginate polymer composite beads was calculated by the titration method. 25 ml of NaCl solution was taken in a series of six stoppered 250 ml Erlenmeyer flask and its pH adjusted in the range of 2–12 by adding 0.1 M HCl or 0.1 M NaOH solution. 1 g of adsorbent was then added to each flask and the flasks were shaken well with an optimum time and the contents were allowed to attain equilibrium in 48 h. The pH of the solution in each flask was checked and recorded. The zero point charge (pH_{zpc}) value was then obtained by plotting a graph between pH_{final} vs. $pH_{initial}$ and the point at which the plots intersect was taken as pH_{pzc} of the surface of PJBC.

3. Results and discussion

3.1. Characterization of the adsorbent

The adsorption process is mainly influenced by the presence of functional groups in the surface of the adsorbent material. If the surface of the adsorbent attains positive charge then that adsorbent adsorbs anionic dyes; whereas, if the surface of the adsorbent attains negative charge, then it adsorbs cationic dyes. This phenomenon of adsorption mainly depends on the presence of surface charges of an adsorbent. The presence of various functional groups in the adsorbent material was identified with Fourier Transform Infrared Spectroscopy (FTIR) in the range of 4000–400 cm^{-1}. The FTIR spectrum of Ba/alginate polymer beads and VB dye loaded beads is shown in Fig. 1a. Fig. 1a

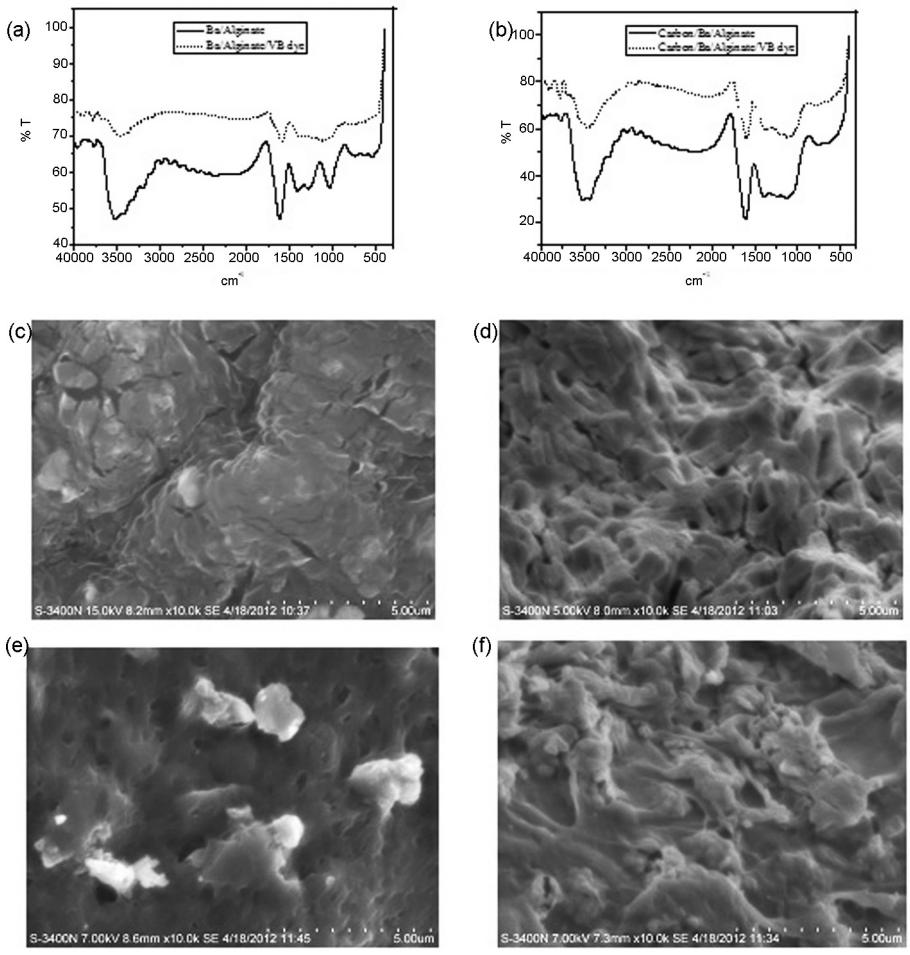

Fig. 1. (a) The FTIR spectrum of Ba/alginate and Ba/alginate/VB dye, (b) The FTIR spectrum of activated carbon/Ba/alginate and activated carbon/Ba/alginate/VB dye, (c) SEM image of Ba/alginate, (d) SEM image of activated carbon/Ba/alginate, (e) SEM image of Ba/alginate/VB dye and (f) SEM image of activated carbon/Ba/alginate/VB dye.

shows peaks at 3500 cm^{-1}, 2750 cm^{-1}, 1535 cm^{-1}, 1475 cm^{-1} and 1050 cm^{-1}. The VB dye loaded beads shows peaks at 3478 cm^{-1}, 1510 cm^{-1}, 1434 cm^{-1} and 1010 cm^{-1}. In Fig. 1a, the peaks positions are found to have shifted and reduced implying that the VB dye was adsorbed on the surface of the Ba/alginate polymer beads. Fig. 1b shows the resolved peaks at the following positions; 3963 cm^{-1}, 3770 cm^{-1}, 3511 cm^{-1}, 2992 cm^{-1}, 2884 cm^{-1}, 2173 cm^{-1}, 1609 cm^{-1}, 1392 cm^{-1}, 1124 cm^{-1} and 748 cm^{-1}. The peak obtained in the range of 4000–3500 cm^{-1} implies that the presence of OH groups are either due to moisture or other compounds and the peaks at 2992 cm^{-1} and 2884 cm^{-1} reveal the presence of aliphatic C—H of symmetric or asymmetric vibrations (Guo, Li, Liu, Ma, & Zhang, 2011; Sreelatha, Kushwaha, Rao, & Padmaja, 2010). The peak positions at 2173 cm^{-1}, 1609 cm^{-1}, 1392 cm^{-1}, 1124 cm^{-1} and 748 cm^{-1} indicate the presence of N—H stretching, C—H bending, C=O of esters or aromatic C=C stretching and C=O of aromatic stretching respectively. The VB dye loaded alginate polymer bead (Fig. 1b) shows a shift and reduction in the peak positions that are observed at 3900 cm^{-1}, 3780 cm^{-1}, 3459 cm^{-1}, 2096 cm^{-1}, 1596 cm^{-1}, 1104 cm^{-1} and 794 cm^{-1}, implying that the VB dye is chemically adsorbed on the surface of the alginate polymer bead.

3.2. Scanning electron microscope (SEM) studies

The scanning electron microscopic studies of the polymer beads are presented in Fig. 1c–f. Fig. 1c and e shows bright cavities and a porous structure on the surface of the adsorbents. In the case of the VB dye (Fig. 1d and f) loaded alginate polymer bead and activated carbon/Ba/alginate polymer beads the porous nature of the adsorbent was thought to be fully occupied with the VB dye material since the brightness of the surface was not seen.

3.3. Effect of pH

The pH of the solution always affects the nature and surface binding property of the adsorbent and is responsible for the interaction of the dye molecules with the adsorbent material may be due to protonated or deprotonated surface charges in solution at different pH values (Alkan, Dogan, Turhan, Demirbas, & Turan, 2008). Generally in aqueous medium, the ionization of basic dyes acquires a net positive charge and the adsorbents containing organic functional groups on their surfaces also develop charges on their own surfaces since they are pH dependent making it necessary to find the optimum pH of the working solution. In this study, the pH values of activated carbon, Ba/alginate and activated carbon/Ba/alginate polymeric beads were found out experimentally. From various pH values, the pH value of 5 shows a higher percentage of removal of the dye (93%) in activated carbon, while Ba/alginate has a value of 5 and activated carbon/Ba/alginate has a value of 4 as optimum pHs for the adsorption of VB dye onto polymeric beads (figure not shown).

3.4. Zero point charge (pH_{zpc})

The zero point charge of pH (pH_{zpc}) of the polymer composite bead adsorbent was determined by plotting the $pH_{initial}$ vs. pH_{final} for the removal of VB. The value of zero point charge (pH_{zpc}) of Ba/alginate and activated carbon/Ba/alginate polymer composite beads was found as 4.9 and 5.2 respectively (figure not shown).

3.5. Effect of equilibrium time and dye concentration

The present study was carried out to determine the optimum equilibrium time and initial dye concentration that are necessary for the removal of VB using various polymer composite beads. The equilibrium time was varied from 10 to 90 min and the dye concentration was varied from 4 to 12 mg L^{-1}. In the case of activated carbon, the dye removal peaked at 96 % with a contact time of 40 min as compared to other contact times and at 12 mg L^{-1} dye concentration, Ba/alginate shows 89% of dye removal in a contact time of 50 min as compared to other contact times and at a 12 mg L^{-1} of dye concentration and the activated carbon/Ba/alginate shows 98% dye removal in a contact time of 50 min as compared to other contact times at a 12 mg L^{-1} of dye concentration (figures not shown). Hence, the optimum conditions of the adsorption process were chosen as 40, 50 and 50 min (equilibrium time) and 12 mg L^{-1} (dye concentration) in activated carbon, Ba/alginate and activated carbon/Ba/alginate respectively. The percentage of dye removal in the solution was calculated using the following equation,

$$\text{Removal}\ \ (\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}$$

where C_0 is the initial concentration of dye and C_t is the concentration of dye at time t.

3.6. Adsorption isotherm studies

Adsorption isotherm studies were helpful to predict the interaction between the dye molecule and the surface of the adsorbent material. Though several types of adsorption isotherms are available for the determination of the adsorption process, the adsorption isotherm used in this study are the standard and widely used isotherms like Langmuir and Freundlich isotherms. In Langmuir adsorption isotherm, based on the assumption of uniform distribution of energies for the sorption (physically or chemically) of adsorbate on the surface of the adsorbent, there is no transmigration of sorbate particles in the plane of the surface of adsorbent material. The mathematical expression of the Langmuir isotherm equation (Langmuir, 1916) is given as

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{3}$$

Eq. (3) can be rearranged by a linear equation as

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \tag{4}$$

where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amounts of dye adsorbed per unit mass of sorbent and unadsorbed dye concentration in solution, q_m is the maximum amount of dye adsorbed per unit mass of sorbent at complete monolayer bound on the surface, and K_a(L mg^{-1}) is a constant related to the affinity of the binding sites.

The Freundlich isotherm was used under the assumption that the ratio of the amount of solute adsorbed on a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations. The Freundlich isotherm (Freundlich, 1906) equation is given by the following expression

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

Table 1
Isotherm parameters obtained by using linear method.

Isotherm		Adsorbents		
		AC/VB	Ba/Algi/VB	AC/Ba/Algi/VB
Langmuir 1	q_m (mg g^{-1})	1.9851	1.6526	1.9463
	K_a (L mg^{-1})	2.6497	1.9333	3.1901
	r^2	0.9863	0.9484	0.9990
Langmuir 2	q_m (mg g^{-1})	2.9672	2.8649	3.2138
	K_a (L mg^{-1})	2.4380	3.4616	4.5240
	r^2	0.9259	0.8486	0.9504
Langmuir 3	q_m (mg g^{-1})	2.1273	1.1446	1.4003
	K_a (L mg^{-1})	0.7265	0.9235	1.0217
	r^2	0.9488	0.8978	0.9779
Langmuir 4	q_m (mg g^{-1})	2.2178	1.2397	1.4532
	K_a (L mg^{-1})	0.7075	0.8911	1.0028
	r^2	0.9488	0.8978	0.9779
Freundlich	$1/n$	0.2326	0.4476	0.2371
	K_F (mg g^{-1}) (L g^{-1})	1.1337	1.2325	0.9700
	r^2	0.9799	0.9193	0.9825

AC/VB, activated carbon/Victoria blue; Ba/Algi/VB, barium/alginate/Victoria blue; AC/Ba/Algi/VB, activated carbon/barium/alginate/Victoria blue.

Eq. (5) can be rearranged by a linear form as

$$\log(q_e) = \log(K_F) + \frac{1}{nF}\log(C_e) \tag{6}$$

where K_F(mg g^{-1}) (L g^{-1}) is an indicator of the adsorption capacity, $1/n$ is the adsorption intensity. The magnitude of the exponent $1/n$ shows the favorability of adsorption with the $1/n$ value having $n < 1$ representing the favorable adsorption condition. The Langmuir isotherm equation was tested with various forms of linear equations. The obtained experimental results are presented in Table 1. From the results, the Langmuir isotherm-1 (Fig. 2a) of activated carbon/Ba/alginate beads shows a closer proximity to unity of the correlation coefficient value ($r^2 = 0.9990$) while activated carbon shows a value of $r^2 = 0.9863$ and Ba/alginate shows $r^2 = 0.9484$. This indicates that the Langmuir-1 isotherm was the best fit for the absorption of VB onto polymer composite beads. The other forms show correlation coefficient values of activated carbon/Ba/alginate adsorbent as $r^2 = 0.9504, 0.9779, 0.9779$ and 0.9825 for Langmuir-2 (Fig. 2b), Langmuir-3 (Fig. 2c), Langmuir-4 (Fig. 2d) and Freundlich (Fig. 3a) isotherms respectively. In activated carbon alone, the correlation coefficient values are $r^2 = 0.9259$, 0.9488, 0.9488 and 0.9799 and Ba/alginate has the values as $r^2 = 0.8486$, 0.8978, 0.8978 and 0.9193 for Langmuir-2 (Fig. 2b), Langmuir-3 (Fig. 2c), Langmuir-4 (Fig. 2d) and Freundlich (Fig. 3a) isotherms respectively. The similar research work was reported by Ai, Li, and Li (2011), the article gives an information about the correlation coefficient values of the Langmuir isotherm ($r^2 = 0.973$) and Freundlich isotherm ($r^2 = 0.979$) the results supports that both isotherms were favorable for the adsorption process. Aravindhan, Fathima, Rao, and Nair (2007) presented an equilibrium data of Langmuir isotherm and Freundlich isotherm. The results of the data confirms that the monolayer adsorption process of the cationic dye onto the alginate beads. The same results were also reported by Zhanga, Gaoa, Guoa, Li, and Liu (2011) and Sui et al. (2012). The correlation coefficient value of Langmuir isotherm-1 ($r^2 = 0.9990$) of our research work significantly enhance the rate of adsorption as well as the removal capacity of dye on activated carbon/Ba/alginate beads when compared with other adsorbent materials. All the research evidences were strongly support that the dye removal efficiency of the polymer composite beads.

The characteristic of the adsorption process was checked using the equilibrium parameter as a dimensionless separation factor (R_L). The value of R_L gives the information about the favorability

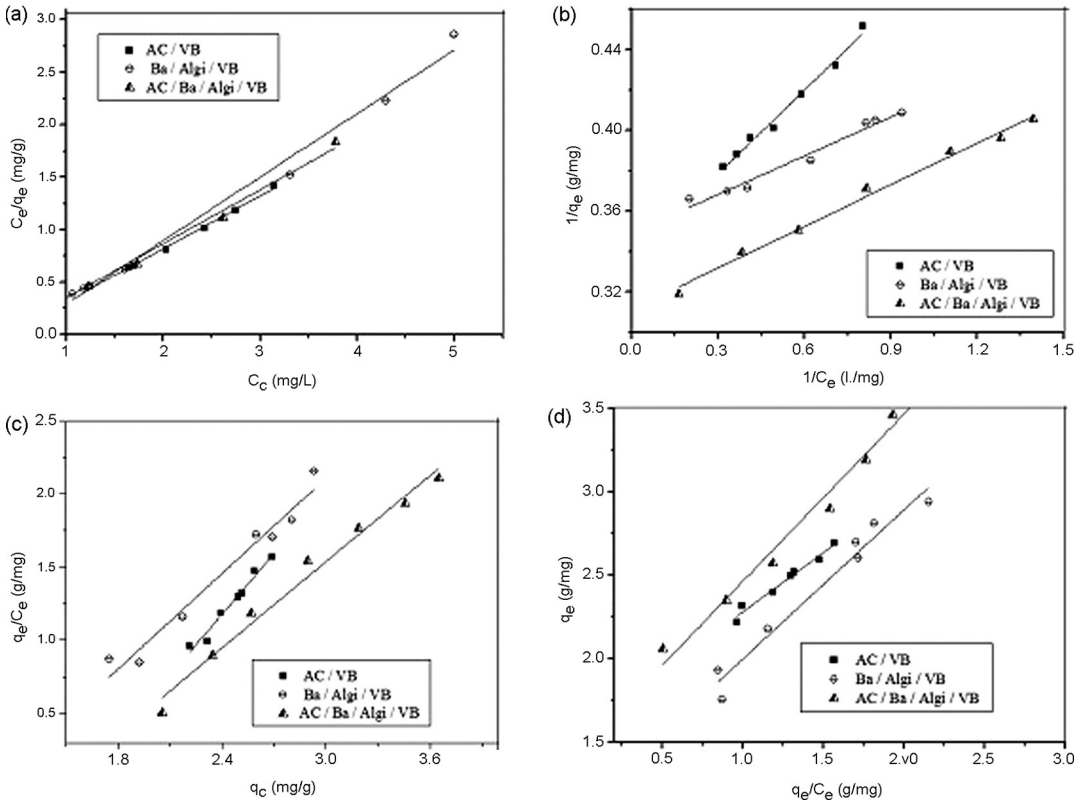

Fig. 2. (a) Langmuir-1 plot for the adsorption of VB dye, (b) Langmuir-2 plot for the adsorption of VB dye, (c) Langmuir-3 plot for the adsorption of VB dye and (d) Langmuir-4 plot for the adsorption of VB dye.

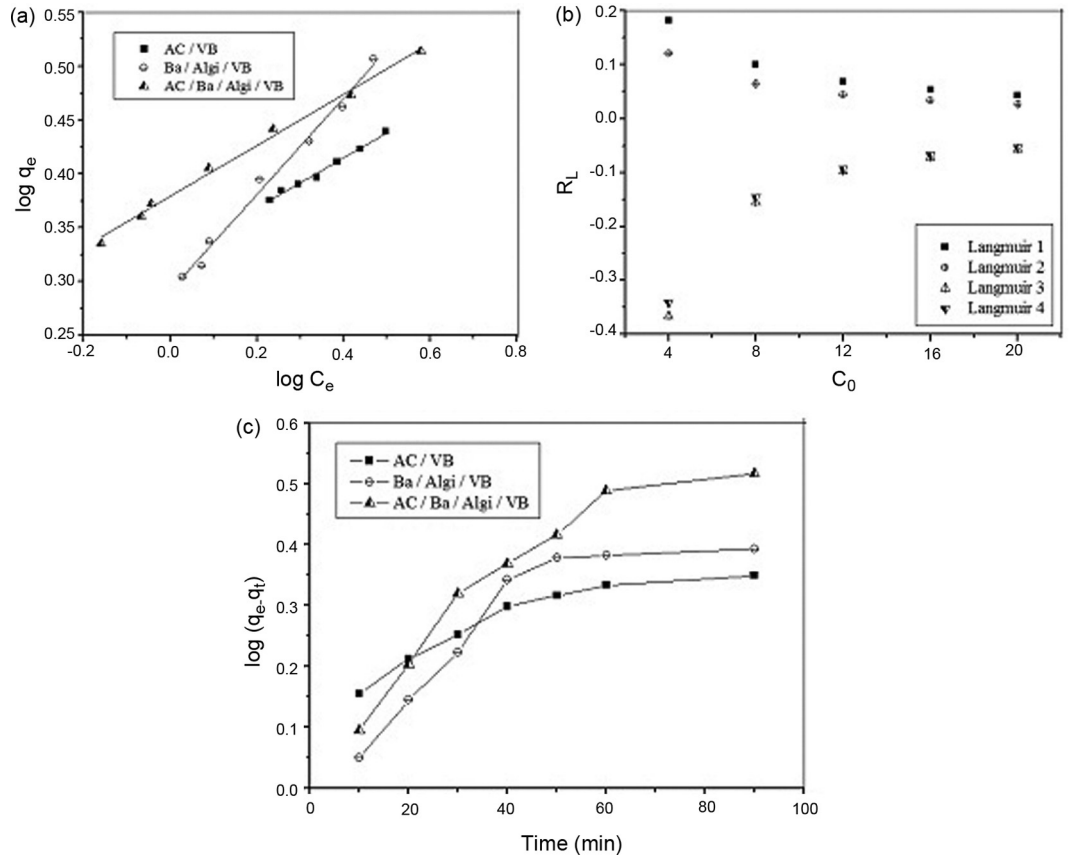

Fig. 3. (a) Freundlich plot for the adsorption of VB dye, (b) dimensionless separation factor (R_L) for the adsorption of VB dye and (c) pseudo-first order plot for the adsorption of VB dye.

of adsorption and feasibility of the adsorption process using the equation

$$R_L = \frac{1}{1 + bC_0} \tag{7}$$

The R_L values indicate the type of isotherm to be either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$) (Wu, Liu, Chu, & Suen, 2008; Wu, Wu, & Fu, 2007). Fig. 3b reveals that the obtained experimental results of R_L values lie in the range of 0–1 for activated carbon, Ba/alginate and activated carbon/Ba/alginate adsorbents. Thereby the adsorption of VB dye on to each adsorbent material was considered to be a favorable adsorption process.

3.7. Kinetic studies

Adsorption kinetics relates the adsorption capacity and process time. The kinetic studies of the adsorption process were checked with the Lagergren's pseudo-first order and Ho's pseudo-second order equations. The first order equation was used under the assumption that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and the amount of solid uptake with time (Khaled, Nemr, El Sikaily, & Abdelwahab, 2009). The pseudo-first order equation of Lagergren (Lagergren, 1898) is generally expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{8}$$

where q_e is sorption capacity at equilibrium, q_t is the sorption capacity at equilibrium at time t ($mg\,g^{-1}$) and k_1 is the rate constant of pseudo-first order sorption ($L\,min^{-1}$). Integrating Eq. (8) by applying the boundary conditions as $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. (8) becomes

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{9}$$

where k_1 is the pseudo first order adsorption rate constant, q_e is the amount of dye adsorbed at equilibrium ($mg\,g^{-1}$), q_t is the amount of dye adsorbed at any time t ($mg\,g^{-1}$). Pseudo-first order rate constant obtained by plotting a graph between $\log(q_e - q_t)$ vs. t should be a straight line. The equation was applied with the experimental results; where it gives a deviation from the true first order equation (Aharoni & Sparks, 1991). Another model for the analysis of sorption kinetics is pseudo-second-order (Azizian, 2004). The rate law for this equation is expressed as

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

Integrating Eq. (10), for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, gives

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{11}$$

where k_2 is the pseudo-second-order rate constant of sorption. Eq. (11), can be rearranged to obtain a linear form,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{12}$$

The plot of t/q_t vs. $1/q_e$. The amount of solute sorbed on the sorbent surface at equilibrium (q_e) and sorption rate constant (k_2) could be evaluated from the slope and intercept respectively. The pseudo-second order model was recently applied for the analysis of sorption kinetics from liquid solutions by Ho and McKay (1999) and various forms of Lagergren's kinetic (Dogan, Yunus, Mustafa, & Mustafa, 2007) equations were used for the prediction of kinetic parameters. From the application of the various kinetic models, the experimentally obtained kinetic parameters of pseudo-first order values are presented in Table 2a. The result of the kinetic parameters shows that the adsorption process follows the pseudo-second order kinetic model (Table 2b) in each adsorbent material. The pseudo second-order kinetic model was the rate controlling step in three adsorbent materials for the removal of VB dye onto polymer composite bead and was checked using the pseudo-first order and the various forms of pseudo-second order kinetic equations. The pseudo-first order kinetic (Fig. 3c) data gave the correlation coefficient values of 0.7971, 0.6976 and 0.8334 for activated carbon, Ba/alginate and activated carbon/Ba/alginate respectively. While the pseudo-second order-1 (Fig. 4a) kinetic data gives the values as 0.9880, 0.9445 and 0.9943 for activated carbon, Ba/alginate and activated carbon/Ba/alginate respectively. From the data it could be seen the pseudo-first order kinetic model was not well fitted with the adsorption process. Whereas the other forms of pseudo-second order kinetic models provide the r^2 values of 0.5780, 0.9587 and 0.9584 (activated carbon), 0.5666, 0.9140 and 0.9140 (Ba/alginate) and 0.6222, 0.9688 and 0.9688 (activated carbon/Ba/alginate) for pseudo-second order-2 (Fig. 4b), pseudo-second order-3 (Fig. 4c) and pseudo-second order-4 (Fig. 4d) respectively.

3.8. Intraparticle diffusion model

The prediction of the mechanism for an adsorption process viz., the intraparticle diffusion based mechanism has been studied

Table 2
(a) Pseudo-first order kinetic data for the adsorption of VB onto polymer bead and (b) pseudo-second order kinetic data for the adsorption of VB onto polymer bead.

(a)

Adsorbent	Pseudo-first order		
	K_1 (min^{-1})	q_e ($mg\,g^{-1}$)	r^2
AC/VB	0.0055	0.77	0.7971
Ba/Algi/VB	0.0100	1.07	0.6976
AC/Ba/Algi/VB	0.0121	0.93	0.8334

(b)

Adsorbent	Pseudo second order – I				Pseudo second order – II			Pseudo second order – III			Pseudo second order – IV		
	q_e·exp	K_2	q_e·cal	r^2	K_2	q_e·cal	r^2	K_2	q_e·cal	r^2	K_2	q_e·cal	r^2
AC/VB	0.85	0.63	0.35	0.9880	0.18	0.68	0.5780	4.49	1.17	0.9587	30.62	0.22	0.9584
Ba/Algi/VB	1.75	0.17	0.56	0.9445	0.05	0.80	0.5666	3.82	1.15	0.9140	9.00	1.45	0.9140
AC/Ba/Algi/VB	2.82	0.61	0.19	0.9943	0.06	0.61	0.6222	4.22	1.16	0.9688	22.5	1.81	0.9688

AC/VB, activated carbon/Victoria blue; Ba/Algi/VB, barium/alginate/Victoria blue; AC/Ba/Algi/VB, activated carbon/barium/alginate/Victoria blue.

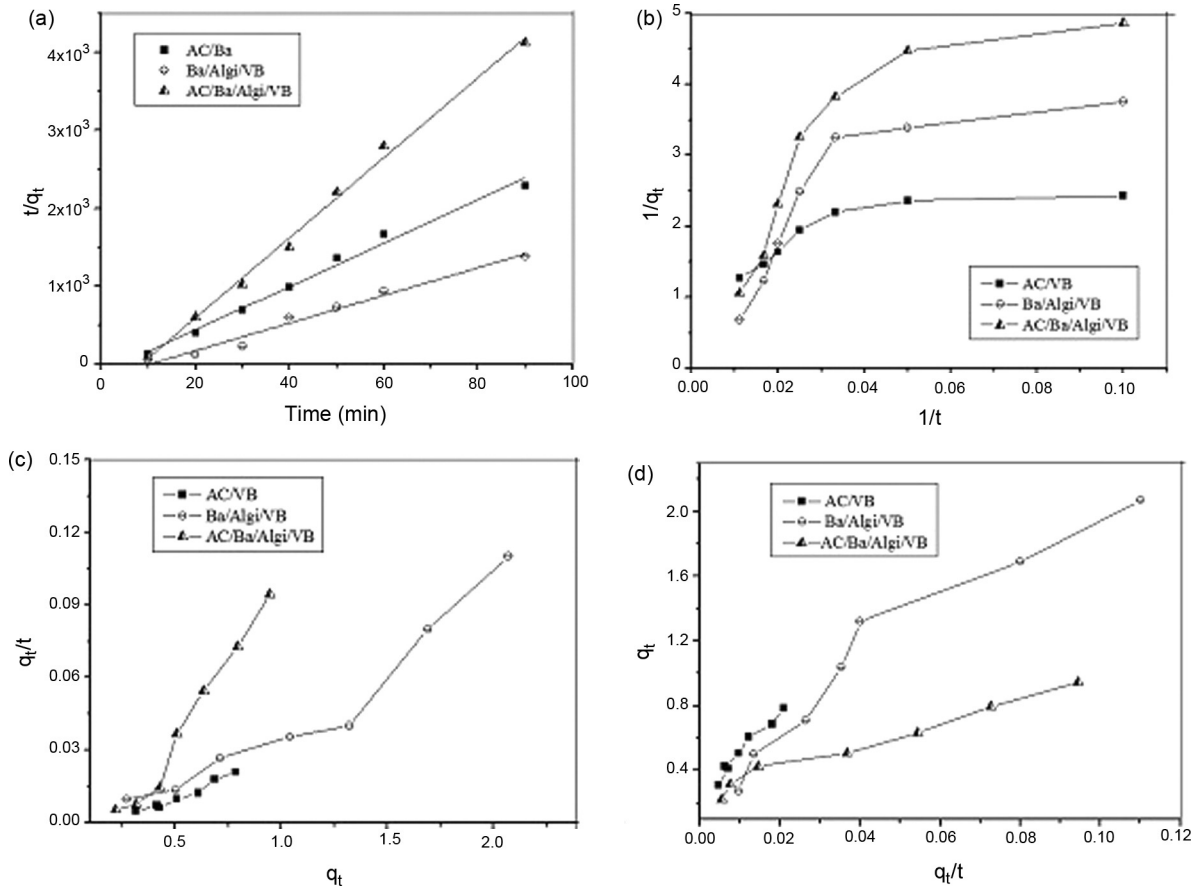

Fig. 4. (a) Pseudo-second order-1 plot for the adsorption of VB dye, (b) pseudo-second order-2 plot for the adsorption of VB dye, (c) pseudo-second order-3 plot for the adsorption of VB dye and (d) pseudo-second order-4 plot for the adsorption of VB dye.

(Cheung, Szeto, & McKay, 2007). The mathematical expression for the intraparticle diffusion equation is

$$q_t = K_{id}\, t^{1/2} + C \tag{13}$$

where k_{id} is the intraparticle diffusion rate constant (mg g^{-1} min$^{1/2}$) and C is the intercept.

Based on the experimental values and the plot of $t^{1/2}$ vs. $q_t$that the two parts are found to be straight lines (Fig. 5a) and obtained in three adsorbent materials. The first portion indicates that the diffusion of dye happens through an external surface of the adsorbent, or the diffusion of solute molecules on the boundary layer is involved gradually and in which the intraparticle diffusion process was rate limiting. The second portion of the line indicates that the adsorption process equilibrium reaches the end-stage, where the intraparticle diffusion process starts in a slow manner due to the low concentration of dye in the solution. Table 3a shows the calculated intraparticle diffusion parameters for the adsorption of VB onto alginate bead process.

3.9. Thermodynamic studies

The understanding and prediction of thermodynamic parameters are the most suited conditions for the evaluation of an

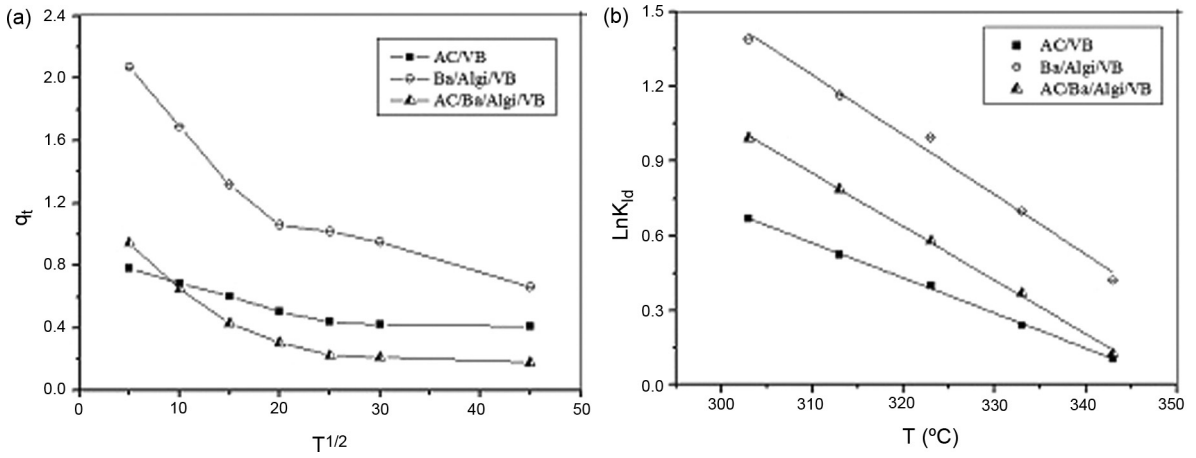

Fig. 5. (a) Intraparticle diffusion for the adsorption of VB dye and (b) Van't Hoff plot for the adsorption of VB dye.

Table 3
(a) Intraparticle diffusion parameters for the adsorption of VB onto polymer bead and (b) thermodynamic parameters for the adsorption of VB onto polymer bead.

(a)

C_0 (mg g^{-1})	k_i (mg g^{-1} s$^{1/2}$)	C (mg g^{-1})	r^2
AC/VB	0.0096	0.7579	0.7611
Ba/Algi/VB	0.0330	1.9607	0.6212
AC/Ba/Algi/VB	0.0178	0.8039	0.8584

(b)

Adsorbents	T (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
AC/VB	303	−0.22	0.03	40.95
	313	−0.22		
	323	−0.29		
	333	−0.34		
	343	−0.41		
Ba/Algi/VB	303	−0.35	0.04	62.09
	313	−0.39		
	323	−0.41		
	333	−0.35		
	343	−0.25		
AC/Ba/Algi/VB	303	−0.25	0.06	72.86
	313	−0.31		
	323	−0.35		
	333	−0.39		
	343	−0.41		

AC/VB, activated carbon/Victoria blue; Ba/Algi/VB, barium/alginate/Victoria blue; AC/Ba/Algi/VB, activated carbon/barium/alginate/Victoria blue.

adsorption process. The thermodynamic parameters were developed under the assumption that the sorbate molecules are absorbed into a porous adsorbent with a constant void fraction, providing a uniform distribution on the surface (Khan, Riazi, & Al Roomi, 2000). The parameters chosen in this study are; change in enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy change (ΔG°). The experimental values obtained from the following equations inform whether the adsorption process was spontaneous or not.

$$K_d = \frac{q_e}{C_e} \tag{14}$$

$$\Delta G = -RT \ln K_d \tag{15}$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{16}$$

The thermodynamic parameters obtained from the experiments (Fig. 5b) shows the change in enthalpy (ΔH°) gives a positive value (Table 3b) of 0.03, 0.04 and 0.06 for activated carbon, Ba/alginate and activated carbon/Ba/alginate respectively. This indicates that the adsorption process was endothermic in nature and the magnitude of adsorption supports the formation of partial chemical processes that are involved during the removal process. The negative value of the Gibbs free energy change (ΔG°) reveals that the adsorption process was spontaneous in nature (Zou, Li, Bai, Shi, & Han, 2011) and the decreasing value of ΔG° (Table 3b) with increasing temperature shows the spontaneous nature of the adsorption of VB dye. The entropy change ΔS° shows positive values of 40.95, 62.09 and 72.86 in activated carbon, Ba/alginate and activated carbon/Ba/alginate respectively. This confirms that the increasing randomness between the solid–solution interfaces during the adsorption process.

4. Conclusion

It may be concluded from the present study that: (i) the Ba/alginate and activated carbon/Ba/alginate polymer composite bead shows well characterized and reduced peaks in the FTIR spectrum; (ii) the SEM image shows well defined structure variation before and after the adsorption process; (iii) optimum parameters of initial concentration and agitation time of the VB dye are chosen as 12 mg L^{-1} and 50 min; (iv) isotherm parameters of the adsorption process fitted well with the Langmuir isotherm-1 rather than Freundlich and other forms of the Langmuir equations; (v) the dimensionless separation factor (R_L) was found to lie between 0 and 1, revealing that the adsorption process was favorable for the removal of VB dye; (vi) the nature of the adsorption process follows the pseudo-second order kinetic model wherein the rate determining step was governed by the chemical forces of attraction; (vii) the thermodynamic parameters of change in enthalpy (ΔH°) shows a positive value, indicating that the adsorption process was endothermic in nature and the magnitude of adsorption supports the formation of partial chemical process that are involved during the removal process; (viii) the negative value of the Gibbs free energy change (ΔG°) reveals that at various temperatures the adsorption process was spontaneous in nature; and (ix) the positive value of ΔS° confirms the increasing randomness between the solid–solution interface during adsorption and is effectively reflected in the adsorbent for the dye removal process. From these analytical and analytical evidences it could be understood and concluded that the adsorption of Victoria blue onto the activated carbon, Ba/alginate and activated carbon/Ba/alginate polymer composite beads was an effective process with eco-friendly manner.

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