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Modeling studies: Adsorption of aniline blue by using Prosopis Juliflora carbon/Ca/alginate polymer composite beads

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ABSTRACT

The research article describes the experimental and modeling study for the adsorptive removal of aniline blue dye (AB dye) from aqueous matrices using a Prosopis Juliflora modified carbon/Ca/alginate polymer bead as a low cost and eco-friendly adsorbent. The rate of adsorption was investigated under various experimental parameters such as contact time, adsorbent dose, dye concentration, pH and temperature. The kinetics, equilibrium and thermodynamic studies were assessed to find out the efficiency of the adsorption process. The equilibrium uptake capacity of the adsorption process was found with Freundlich and Langmuir adsorption isotherm equations and it was evaluated by dimensionless separation factor (R_L). The dynamics of adsorption was predicted by pseudo-first order, pseudo-second order Lagergren's equation and intra particle diffusion model. Adsorption feasibility was assessed with thermodynamic parameters such as isosteric heat of adsorption (ΔH°), standard entropy (ΔS°) and Gibbs free energy (ΔG°) using VantHoff plot. The alginate bead was characterized with FTIR spectroscopy and Scanning Electron Microscopy (SEM).

1. Introduction

The water bodies contaminated with organic based chemicals have created a serious environmental problem. Industries like textiles, paper, rubber, plastics, leather, cosmetics, food and pharmaceuticals use large quantities of synthetic dyes for coloration of their products and hence, effluents from them contain residues of dyes. It is estimated that more than 10,000 types of dyes and pigments are used and produced annually (Lee, Choi, Thiruvenkatachari, Shim, & Moon, 2006) and among them 10–15% are found in wastewaters (Hai, Yamamoto, & Fukushi, 2007). Synthetic dyes have a complex structure and contain various active functional groups that bind with textile fibers and produce various colors. Dyes are often more stable molecules against sunlight, oxidizing agent and microbial attack and are difficult to degrade (Nigam et al., 2000). The presence of dyes reduces the photosynthetic activity (Ozer, Dursun, & Ozer, 2007) and aesthetic quality of the water sources. The colored wastewaters not only affect the aesthetic acceptability of the receiving waters but also influence aquatic life by hindering light penetration and thereby disturbing the food chain of various organisms leading to an imbalance in the function of ecosystem (Pearce, Lloyd, & Guthric, 2003; Pierce, 1994). Even in very low concentrations, these dyes can cause malfunction and health problems in the vital organs of human beings such as; kidney, reproductive system, liver, brain, central nervous system, allergic dermatitis, skin irritation, cancer and mutation problems in living things (Amin, 2009; Wang & Hu, 2007). In view of the very high toxicity and poor biodegradability of dyes, it becomes imperative to remove them from the industrial wastewaters before the waste waters are discharged into water sources. Various conventional decolorization methods of dyes containing wastewaters involve; the combination of physical, chemical and biological methods such as chemical coagulation/flocculation (Verma, Dash, & Bhunia, 2012), advanced oxidation processes (Bandala, Pelaez, Garcia-Lopez, Salgado, & Moeller, 2008; Gaya & Abdullah, 2008), nanofiltration (Avlonitis, Poulios, Sotiriou, Pappas, & Moutesidis, 2008), chemical precipitation (Zhu, Lee, Wang, & Wang, 2007), ion-exchange (Labanda, Sabaté, & Llorens, 2009), reverse osmosis (Bastaki, 2004), sedimentation (Sostar Turk, Simonic, & Petrinic, 2005), color irradiation (Cheremisinoff, 2002; Ting & Jamaludin, 2008), and ozonation (Malik & Sanyal, 2004; Wu, Doan, & Upreti, 2008) which may be efficient for the removal dye from wastewater. However, the application of the mentioned technologies has some disadvantages like technical and economical constraints (Banat, Nigam, Singh, & Marchant, 1996; Jalil et al., 2010; Pagnanelli et al., 2001).

Adsorption is one of the superior processes compared to other methods that have been successfully used for color removal from wastewater (Tunali, Ozcan, Kaynak, Ozcan, & Akar, 2007). Many new promising adsorbents have been used in the past few years to

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reduce dye concentrations in aqueous solutions (Crini, 2006; Gupta & Suhas, 2009; Hameed, Tan, & Ahmad, 2008; Ho, Chiang, & Hsueh, 2005; Kavitha & Namasivayam, 2007; Mall, Srivastava, Agarwal, & Mishra, 2005; Salleh, Mahmoud, Karim, & Idris, 2011). Activated carbon is studied as an effective adsorptive material for the removal of dye products but has several drawbacks like relatively high price, high operating costs and problems with regeneration hamper in large scale application (Vijayakumar, Tamilarasan, & Dharmendra Kumar, 2012).

Therefore, there is a growing need for finding a low cost, renewable and locally available material that can be used more economically on large scale applications for the removal of dyes. Recently, the modified carbon/metal/alginate composite bead has received great attention because of its relatively high adsorption capacity for some dyes and for its bio-degradable nature. Thus, the main objectives of this paper are: (i) to study the feasibility of activated carbon/Ca/alginate composite bead as an adsorbent for the removal of aniline blue dye, (ii) to determine the physico-chemical characteristics of carbon/Ca/alginate composite bead, (iii) to find the various parameters that affect the adsorption, such as adsorbent dose, initial concentration, contact time, temperature and pH by experimentally, (iv) to evaluate the dynamics of adsorption by using pseudo-first order, pseudo-second order Lagergren equations and intra particle diffusion model, (v) to analyze the equilibrium uptake capacity of the adsorption process from various isotherm models like Freundlich and Langmuir adsorption isotherm equations,(vi) to test the equilibrium uptake capacity with dimensionless separation factor (R_L) and (vii) to determine the adsorption feasibility with the thermodynamic activation parameters such as, standard enthalpy (ΔH°), standard entropy (ΔS°) and Gibbs free energy (ΔG°) using VantHoff plot.

2. Materials and methods

2.1. Preparation of activated carbon

Prosopis Juliflora bark used to prepare the activated carbon that was used in the present study was collected in the premises of Anna University-Pattukottai campus. The collected bark was washed with hot distilled water to remove earthy materials, cut into small pieces and dried in sunlight for three days. It was impregnated with 1:1 sulphuric acid for 24 h for carbonization. The carbonized materials were washed several times using distilled water until the washings of the pH become neutral. The obtained material was placed in a hot air oven at about 120 °C for 24 h and subsequently heat treated in a muffle furnace at 450 °C for complete carbonization of the bark. After the carbonization, the material was ground and sieved (180–300 μm sized carbon). The other reagents used in this study were of analytical grade (Merck, India). Double distilled water was used in all the experiments.

2.2. Adsorbate

The bulk solution of the dye was prepared by dissolving a measured quantity of aniline blue dye (molecular formula is $C_{32}H_{25}N_3Na_2O_9S_3$ and formula weight is 737.74) in 1 L of double distilled water.

2.3. Preparation of the activated carbon/Ca/alginate beads.

The polymer bead was prepared by ionic polymerization route, wherein 100 mL of double distilled water was taken in a 500 mL beaker and boiled to 80 °C. To this heated water, 1.2 g of sodium alginate powder was added and stirred well for 45 min till the solution turns clear and viscous. To this 1.2 g of carbon was added and stirred for 30 min. This aqueous solution consisting of alginate and carbon was then added drop wise into 0.2 mol kg^{-1} of $CaCl_2$ solution. The aqueous drops become gelled into polymeric beads on contact with the $CaCl_2$ solution. Finally, the polymeric beads were washed several times with distilled water for removing excess $CaCl_2$.

3. Result and discussion

3.1. Characterization of the carbon/Ca/alginate polymer bead

The presence of functional groups in the modified Prosopis Juliflora carbon/Ca/alginate polymer bead was identified using the Fourier Transform Infrared Spectroscopy (FTIR). The morphology of the adsorbent was found using Scanning Electron Microscope (SEM).

3.1.1. FTIR studies

The FTIR spectrum of Prosopis Juliflora carbon/Ca/alginate polymer beads is given in Fig. 1a and b. Fig. 1a shows various peaks at 3931 cm^{-1}, 3807 cm^{-1}, 3384 cm^{-1}, 1626 cm^{-1} and 1134 cm^{-1}. The peaks obtained at 3931 cm^{-1} and 3807 cm^{-1} reveals the presence of OH group and or moisture and a peak at 3384 cm^{-1} confirms the presence of intermolecular hydrogen bond with OH group (Ozcan & Ozcan, 2004). The peak positions at 1626 cm^{-1}, 1134 cm^{-1} and 606 cm^{-1} indicate the presence of aromatic and other substituted compounds (Silverstein & Webster, 2011). Fig. 1b shows the dye loaded Prosopis Juliflora carbon/Ca/alginate polymer bead. The reduction of peak height and shifted peak positions at 3890 cm^{-1}, 3784 cm^{-1}, 3368 cm^{-1}, 2296 cm^{-1}, 1594 cm^{-1}, 1230 cm^{-1} and 802 cm^{-1} confirms that the adsorption of AB dye onto the carbon/Ca/alginate polymer bead is either by physical or chemical sorption.

3.1.2. SEM studies

The Scanning Electron Microscope (SEM) images of the carbon/Ca/alginate polymer bead are shown in Fig. 1c and d. In Fig. 1c, the carbon/Ca/alginate polymer bead shows a very bright, porous structure on the adsorbent surface. In Fig. 1d, dye loaded polymer beads appears very dark and all the pores of the surface are found covered due to the occupation of AB dye molecule. These different morphological images are evident for the dye molecule that has strongly adsorbed onto the surface of the polymer beads.

3.2. Adsorption studies

Adsorption studies were carried out by varying the operational parameters like; dye concentration, contact time, temperature, pH and adsorbent dose. The pH of the solution is an important parameter to validate the feasibility and rate of the adsorption process, since it determines the interaction between the adsorbate and adsorbent surface. This interaction phenomenon implies which type of species (anions or cations) are liberated or surrounded on the surface of adsorbent during the adsorption. The liberation of species is mainly dependent on the value of pH of the solution (Alkan, Dogan, Turhan, Demirbas, & Turan, 2008). In this study, the pH was varied in the range of 3–10. From the various values of pH, the pH with a value of 6 shows a higher percentage removal compared to other values (Fig. 2a). The concentration of dye was varied from 10 to 70 mg L^{-1} with an increment of 10 mg L^{-1}. The percentage removal of dye was calculated by

$$\text{Removal}\,(\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

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

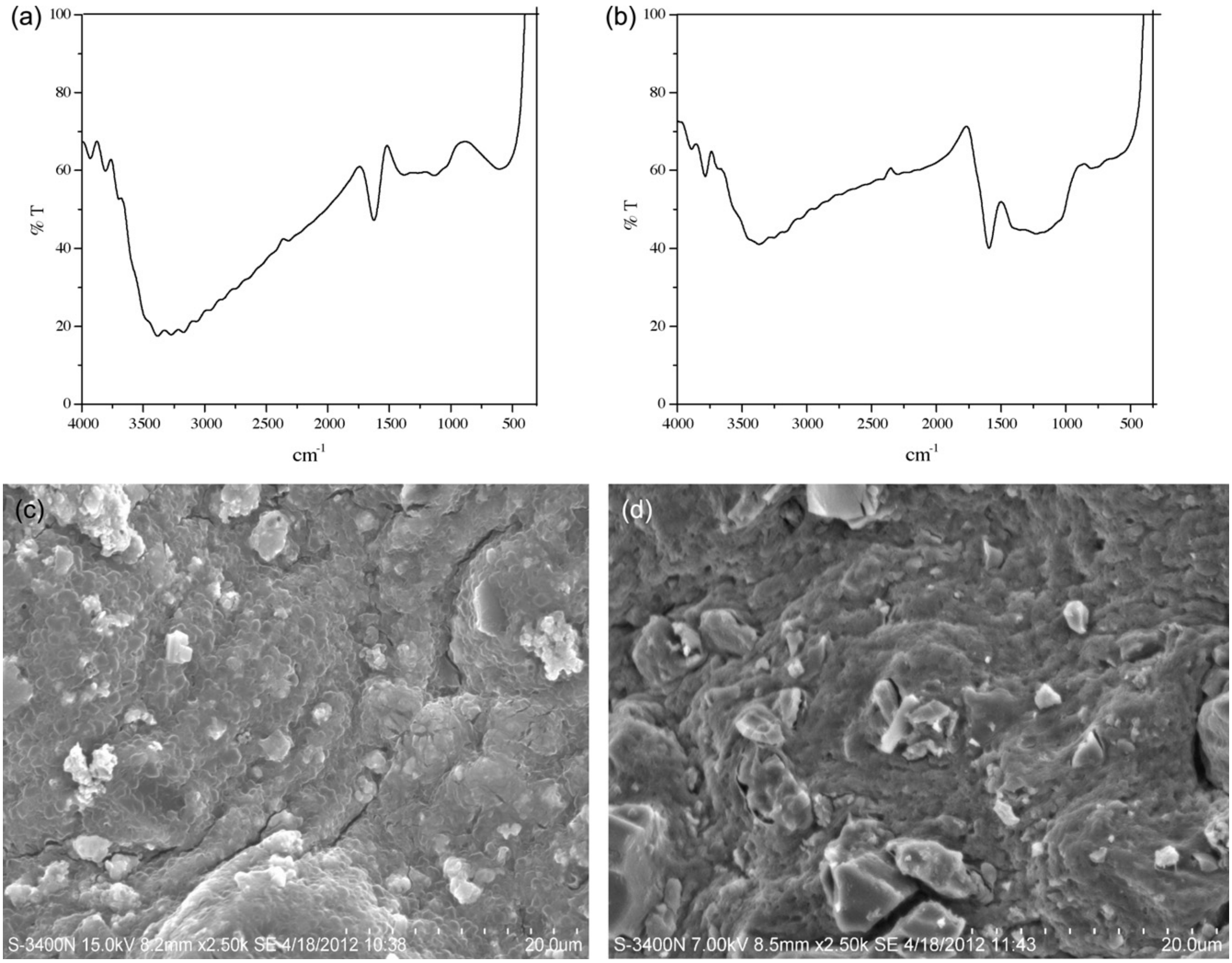

Fig. 1. (a) FTIR-spectrum of carbon/Ca/alginate bead, (b) FTIR-spectrum of carbon/Ca/alginate with dye loaded bead, (c) SEM-image of carbon/Ca/alginate bead, and (d) SEM-image of carbon/Ca/alginate with dye loaded bead.

From among the various concentrations of dye used, it was observed that 60 mg L^{-1} of dye concentration shows a higher percentage (98.61%) of removal (Fig. 2b). The contact time of the adsorption process was varied from 10 to 90 min with 10 min intervals. On comparison with the contact time, 60 min of contact time shows an excellent removal percentage (98.61%) of AB dye (Fig. 2b). The dose of adsorbent is a main factor that determines the efficiency of an adsorption process. Whenever the dose of adsorbent get increases, the efficiency of adsorbent also gradually increases; this is due to the increase of the number of available sites on the adsorbent surface. In this study, the dose of adsorbent was varied as 0.5 g, 1.0 g, 1.5 g, 2.0 g and 2.5 g with wet beads. The AB dye removal was significantly enhanced with the increasing dosage of adsorbent but after reaching an equilibrium dosage of adsorption, the percentage removal of the adsorbate was found to be not as rapid as in the initial stages but increasing with minor variation (Fig. 2c). An adsorbent dose of 1 g shows 98.6% of dye removal as compared to other dosage values. It was also observed when the temperature was varied in the range of 30–70 °C; the rate of adsorption was increasing slowly. At room temperature, the effective removal of adsorbed dye was observed as 98.2% (Fig. 2d).

3.3. Isotherm studies

The most important and widely used isotherms such as Freundlich and Langmuir adsorption isotherm equations are used to predict, whether the process of adsorption involved is a monolayer or multilayer process. Freundlich isotherm assumes that the adsorption process depends on the concentration of the adsorbate molecule. If the adsorbate concentration is high then the adsorbent adsorbs more adsorbate molecules on the surface of adsorbent. The adsorption process significantly increases due to the availability of large number of adsorbate molecules. Therefore multilayer adsorption on the surface of an adsorbent may be possible (Allen, Mckay, & Porter, 2004; Freundlich, 1906). The mathematical form of Freundlich equation is,

$$q_e = K_F C_e^{1/nf} \qquad (2)$$

Eq. (2) is rearranged into linear form as

$$\log(q_e) = \log(K_F) + \frac{1}{nF}\log(C_e) \qquad (3)$$

where, K_F (mg g^{-1}) (L g^{-1}) is the Freundlich adsorption capacity co-efficient, $1/n$ is the adsorption intensity. The value of $1/n$ determines the magnitude of adsorption in Freundlich isotherm. If $1/n$ value is greater than 1, then the adsorption is not favorable, whereas if the value becomes $1/n$ is less than 1, then it represents a favorable adsorption. The Langmuir isotherm assumes that the adsorbate molecules are adsorbed on the surface of adsorbent in monolayer only. Moreover, when the adsorbent attains an equilibrium saturation point no further adsorption takes place even with an interaction of more number of adsorbate molecules on the

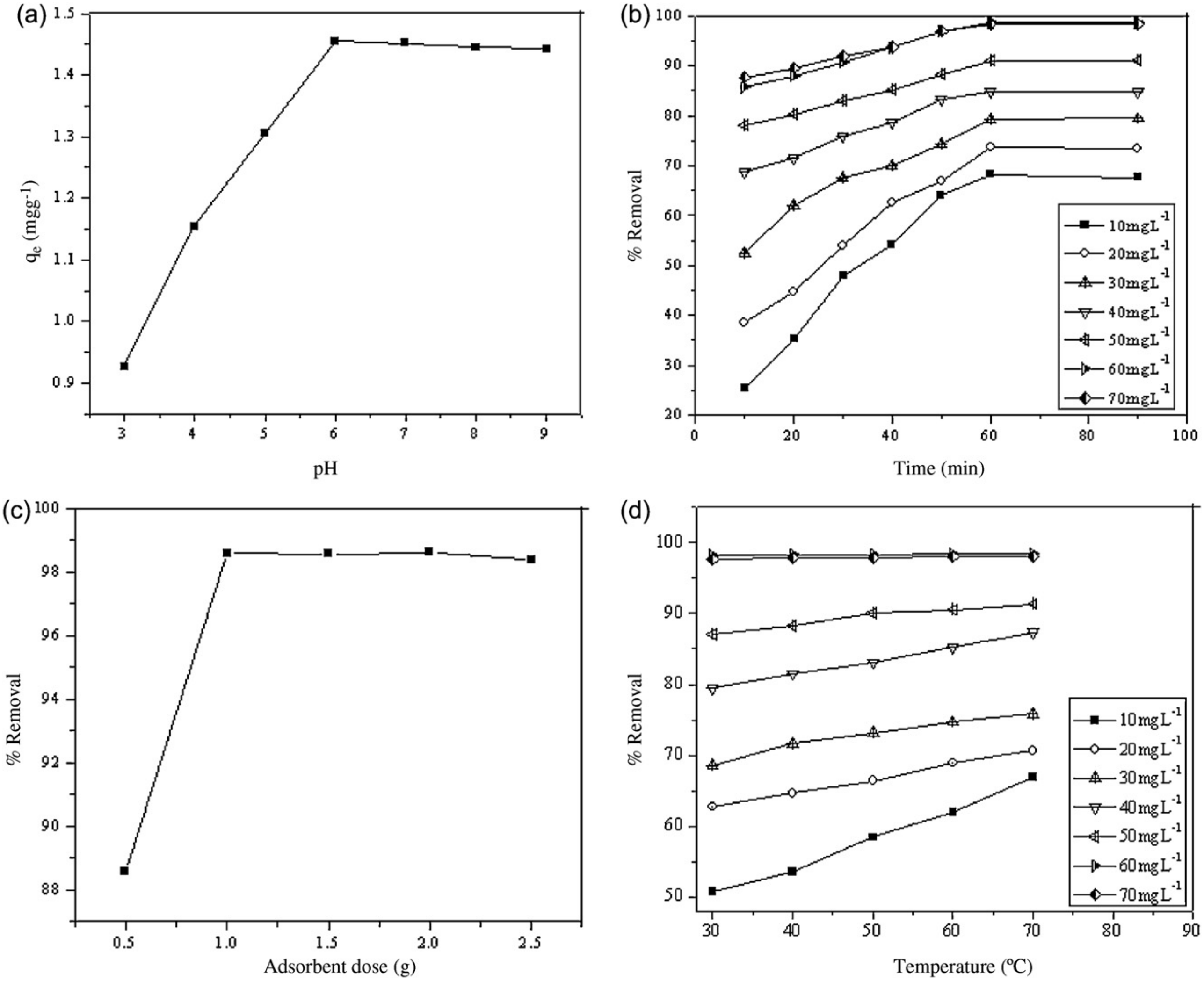

Fig. 2. (a) Effect of pH for the adsorption of AB dye onto polymer bead, (b) effect of concentration and contact time for the adsorption of AB dye onto polymer bead, (c) effect of adsorbent dose for the adsorption of AB dye onto polymer bead, and (d) effect of temperature for the adsorption of AB dye onto polymer bead.

surface of adsorbent material (Langmuir, 1918). The mathematical expression of the Langmuir isotherm is,

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

Eq. (4) is rearranged into linear form as

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m} \tag{5}$$

where, q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amounts of dye adsorbed per unit mass of the sorbent and unadsorbed dye concentration in the solution, q_m is the maximum amount of dye adsorbed per unit mass of the sorbent at complete monolayer on the surface and K_a (L mg^{-1}) is a constant related to the affinity of the binding sites. By rearranging Eq. (5), various linearized forms of Langmuir equations are obtained such as Langmuir-2, Langmuir-3 and Langmuir-4 isotherm and the mathematical expressions of the various forms are presented in Table 1. The experimental results are correlated with the different forms of linear regression Langmuir isotherm equations. The predicted results show that Langmuir-1 was the best suited model as compared with other Langmuir isotherm equations (Fig. 3a). This was evident by the correlation coefficient (r^2) value of Langmuir-1 (0.9988 ($r^2$1)) when compared with (r^2 = 0.9333), (r^2 = 0.9679) and (r^2 = 0.9813) as in Langmuir-2 (Fig. 3b), Langmuir-3 (Fig. 3c) and Langmuir-4 (Fig. 3d), respectively (Table 2). The Freundlich equation provides a correlation coefficient (r^2) value of 0.9824 (Fig. 4a), implying that the adsorption process follows Langmuir isotherm (monolayer) rather than Freundlich isotherm (multilayer). This indicates that the adsorption process is favorable for the removal of AB dye using carbon/Ca/alginate polymer bead. The adsorption isotherm process favorability was also checked using the dimensionless separation factor (R_L) and the values were calculated using the following equation,

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

The values of R_L determine the favorability of adsorption process. If the value of R_L lies between 0 and 1 ($0 < R_L < 1$), the adsorption process is favorable. If the value of R_L lies beyond one ($1 < R_L$), the adsorption process is not favorable. Whereas if the R_L value equals unity (*i.e.*, $R_L = 1$), then the process is linear and if R_L attains a value of zero ($R_L = 0$) then the adsorption process is irreversible in nature (Xiong et al., 2010). Fig. 6a shows the calculated value of R_L lying between 0 and 1. The experimental and calculated results of the adsorption process are the evidences supporting the isotherm condition and hence it could be concluded that the adsorption of AB dye onto carbon/Ca/alginate polymer bead is very favorable. In addition, the lower values of R_L indicate that the interaction between dye

Table 1
Isotherm equations and their forms.

Isotherms	Non-linear	Linear	Plot	Reference
Freundlich	$q_e = K_F C_e^{1/nF}$	$\log(q_e) = \log(K_F) + \frac{1}{nF}\log(C_e)$	$\log(q_e)\ vs.\ \log(C_e)$	Freundlich (1906)
Langmuir-1		$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{q_e}\ vs.\ C_e$	Langmuir (1918)
Langmuir-2	$q_e = \frac{q_m K_a C_e}{1+K_a C_e}$	$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}\ vs.\ \frac{1}{C_e}$	
Langmuir-3		$q_e = q_m - \left(\frac{1}{K_a}\right)\frac{q_e}{C_e}$	$q_e\ vs.\ \frac{q_e}{C_e}$	
Langmuir-4		$\frac{q_e}{C_e} = K_a q_m - K_a q_e$	$\frac{q_e}{C_e}\ vs.\ q_e$	

molecules and the polymer bead may be due to relatively strong chemical forces of attraction (Weber & Chakravorti, 1974).

3.4. Adsorption dynamic studies

The dynamics of adsorption process was tested with the Lagergren's pseudo-first order and pseudo-second order equations. The pseudo-first order equation is applicable in the initial stage of the process involving the physical exchange of atoms or molecules.

The pseudo-first order equation is expressed (Lagergren, 1898) as

$$\frac{d_q}{d_t} = k_1(q_e - q_t) \tag{7}$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the quantities of dye adsorbed at equilibrium and at time t, respectively, and k_1 (min^{-1}) is the rate constant of the first order equation. The linear form of Eq. (7) is written as

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{8}$$

From Fig. 4b, the value of the correlation coefficient (r^2) for the pseudo-first order equation was found to be 0.8311.

The pseudo-second order equation is used with the assumption that the interaction between the adsorbate and adsorbent material is due to the chemical forces of attraction. The pseudo-second order equation could be considered as a rate limiting step in all

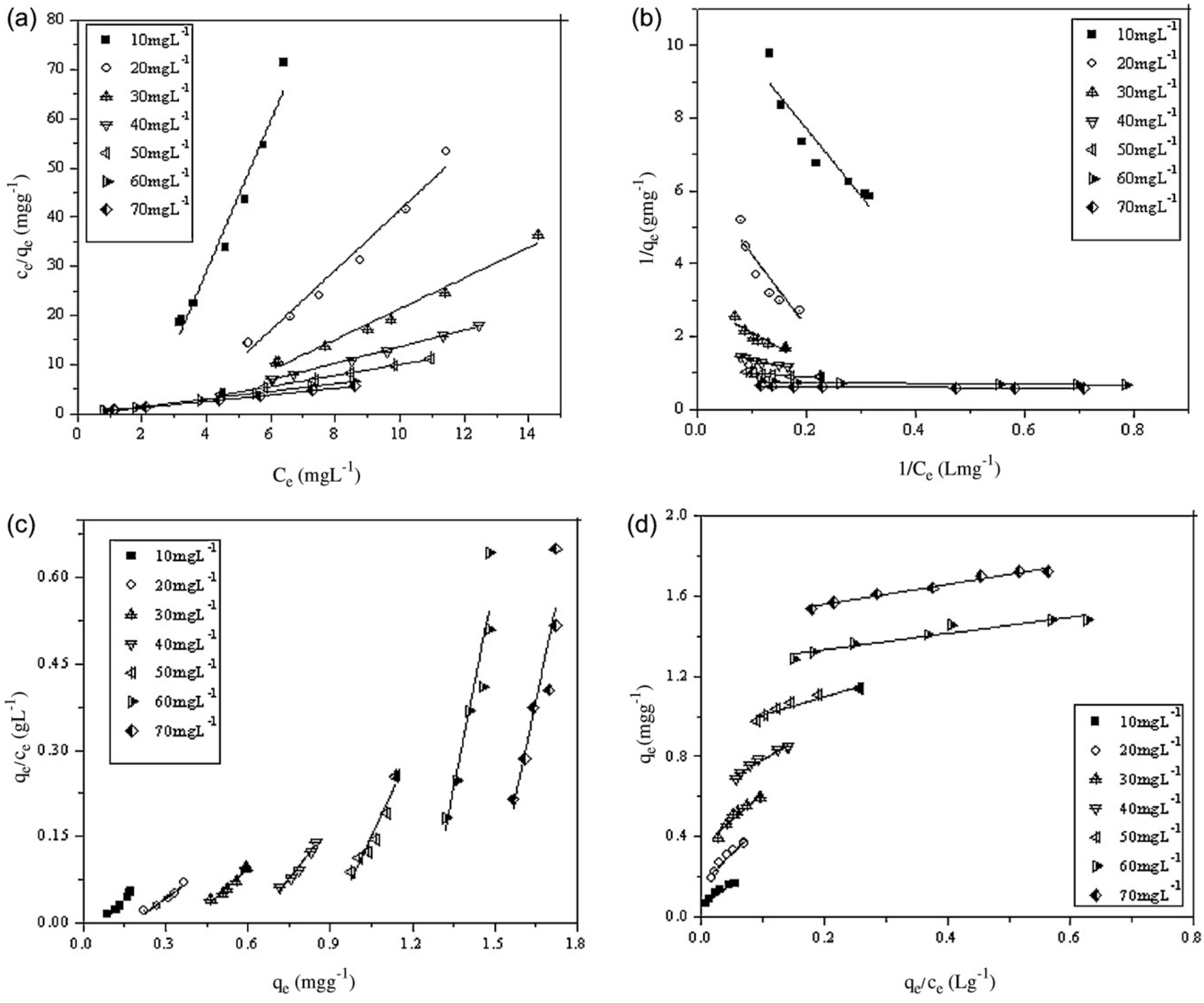

Fig. 3. (a) Langmuir-1 isotherm for the adsorption of AB dye onto polymer bead, (b) Langmuir-2 isotherm for the adsorption of AB dye onto polymer bead, (c) Langmuir-3 isotherm for the adsorption of AB dye onto polymer bead, and (d) Langmuir-4 isotherm for the adsorption of AB dye onto polymer bead.

Table 2
Freundlich and Langmuir isotherm parameters for adsorption process.

Isotherm	Parameter	Concentration ($mg\,L^{-1}$)						
		10	20	30	40	50	60	70
Langmuir-1	q_m ($mg\,g^{-1}$)	0.0651	0.1639	0.3200	0.5934	0.8986	1.2805	1.5234
	K_a ($L\,mg^{-1}$)	0.4726	0.3111	0.3138	0.5215	0.9777	5.1765	5.1586
	r_2	0.9633	0.9721	0.9791	0.9962	0.9978	0.9983	0.9988
Langmuir-2	q_m ($mg\,g^{-1}$)	0.0876	0.1601	0.3430	0.6055	0.9162	1.2993	1.5430
	K_a ($L\,mg^{-1}$)	0.6171	0.3148	0.3598	0.5597	1.1028	5.7415	5.9099
	r_2	0.8567	0.8250	0.8283	0.9333	0.9103	0.8268	0.8305
Langmuir-3	q_m ($mg\,g^{-1}$)	0.0337	0.0625	0.1689	0.3758	0.9313	2.9927	3.3370
	K_a ($L\,mg^{-1}$)	2.0099	2.8595	2.2696	1.6558	0.9710	0.4183	0.4432
	r_2	0.9547	0.9452	0.9633	0.9679	0.9297	0.8500	0.8078
Langmuir-4	q_m ($mg\,g^{-1}$)	0.1302	0.3434	1.2359	3.0902	2.7546	0.0263	0.05443
	K_a ($L\,mg^{-1}$)	2.6846	1.7689	1.0188	0.4047	0.5123	2.2135	3.0530
	r_2	0.9214	0.9602	0.9813	0.8998	0.9624	0.9406	0.9390
Freundlich	$1/n$	0.0700	0.7277	0.4702	0.2791	0.1643	0.0543	0.0516
	K_F ($mg\,g^{-1}$) ($L\,g^{-1}$)	2.3154	2.2250	1.8531	1.8980	1.7983	1.7735	1.4203
	r_2	0.9288	0.9534	0.9534	0.9824	0.9759	0.8988	0.9229

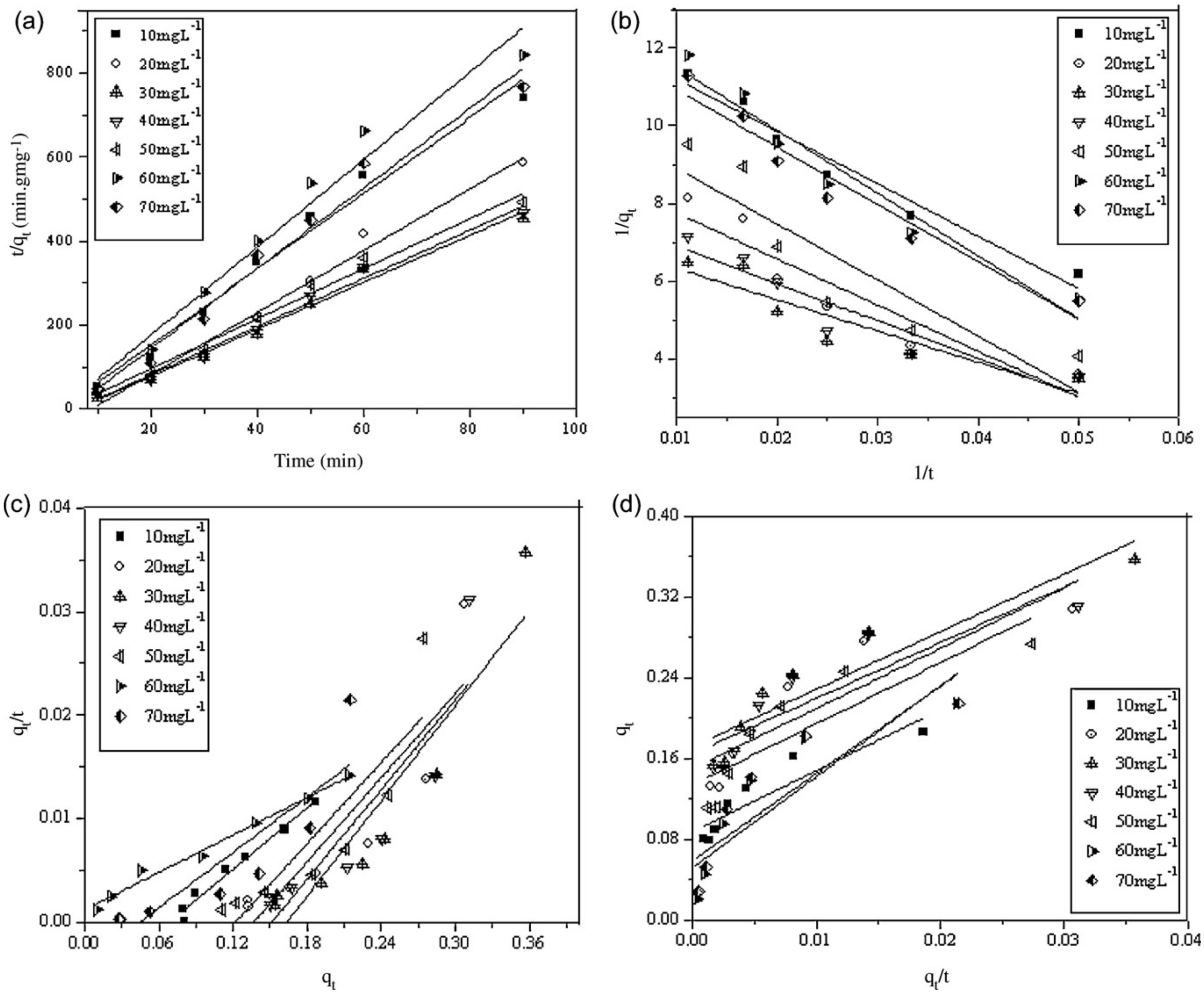

Fig. 4. (a) Pseudo-second order-1 equation for the adsorption of AB dye onto polymer bead, (b) pseudo-second order-2 equation for the adsorption of AB dye onto polymer bead, (c) pseudo-second order-3 equation for the adsorption of AB dye onto polymer bead, and (d) pseudo-second order-4 equation for the adsorption of AB dye onto polymer bead.

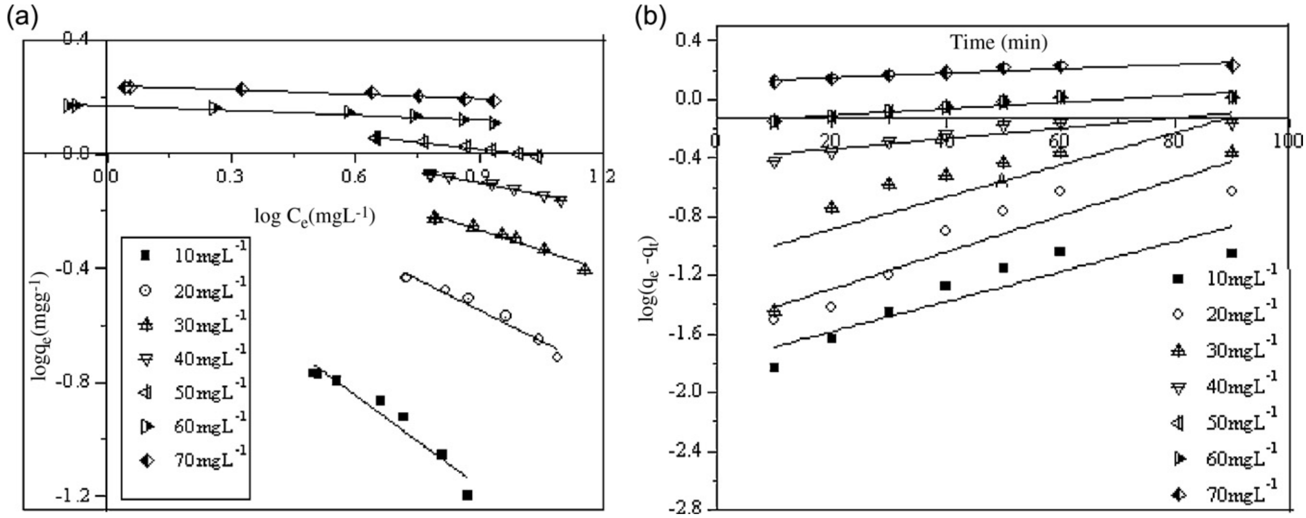

Fig. 5. (a) Freundlich isotherm for the adsorption of AB dye onto polymer bead and (b) pseudo-first order equation for the adsorption of AB dye onto polymer bead.

kinds of adsorption processes. The pseudo-second order equation is expressed as

$$\frac{d_q}{d_t} = k_2(q_e - q_t)^2 \tag{9}$$

where, k is a rate constant of the second-order model (g mg min^{-1}) and q_e (mg g^{-1}) is the amount of dye uptake at equilibrium. The linear form (Ho, 2006) of Eq. (9) is written as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

On rearranging Eq. (10), different forms of pseudo-second order equations like pseudo-second order-2, pseudo-second order-3 and pseudo-second order-4 could be obtained. The various forms of the mentioned kinetic equations are presented in Table 3. The resultant parameter values are used to plot the graphs between t/q_t *vs* . t, $1/q_t$ *vs* . $1/t$, q_t *vs* . q_t/t and q_t/t *vs* . q_t for the prediction of the kinetic constants. The experimental results were applied to various forms of linear regression pseudo-second order equations. The results show that the correlation coefficient (r^2) value of 0.9874 ($r^2$1) of the pseudo-second order-1 equation fits well (Fig. 5a) with the adsorption process. The other values of the calculated pseudo-second order equations (r^2) are; 0.9571 (Fig. 5b), 0.9756 (Fig. 5c) and 0.8456 (Fig. 5d) respectively for pseudo-second order-2, pseudo-second order-3 and pseudo-second order-4 (Table 4). It is revealed that an interaction between the adsorbent and an adsorbate molecule may be by chemical forces of attraction. Thus, by comparing the correlation coefficient values of the pseudo-first order and pseudo-second order equations showing that the adsorption process follows pseudo-second order kinetic equation rather than the pseudo-first order equation.

For the prediction of the mechanism of adsorption process an intra particle diffusion based mechanism has been used (Cheung, Szeto, & McKay, 2007). From the experimental values and by plotting $t^{1/2}$ *vs* . q_t, two parts of straight lines (Fig. 6c) were obtained. The first portion indicates that the diffusion of dye happens through an external surface of the adsorbent, or the gradual involvement of diffusion of solute molecules on the boundary layer where the intraparticle diffusion process was rate limiting. The second portion of the line indicates that the adsorption process has attained equilibrium in the end stage and where the intraparticle diffusion process starts in a slow manner due to the low concentration of dye molecules available in the solution. The calculated results of the intraparticle diffusion parameters are presented in Table 5a.

3.5. *Thermodynamic parameters studies*

The frequently used thermodynamic parameters assessed in this study are; change in Gibbs free energy (ΔG°), isosteric heat of adsorption (ΔH°) and the change in entropy (ΔS°) using Van-tHoff plot (Fig. 6b). The parameters are assessed using the equations (Ramesh, Lee, & Wong, 2005),

$$K_d = \frac{q_e}{C_e} \tag{11}$$

$$\Delta G^\circ = -RT \ln K_d \tag{12}$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{13}$$

The experimental value of the Gibbs free energy (ΔG°) shows a negative sign (Table 5b), intimating that the process is spontaneous in nature. The increase in negative values denotes that equilibrium increases with temperature. The positive value (Table 5b) of isosteric heat of adsorption (ΔH°) reveals that the adsorption process is endothermic in nature and the competition between the solute and the solvent particle involves a complex phenomenon on the solid surface. Moreover the process of adsorption and desorption takes place simultaneously. The positive value (Table 5b) of the ΔS°

Table 3
Kinetic equations and their forms.

Type	Non-linear	Linear	Plot	Reference
Pseudo-first order	$q = q_e(1 - e^{-K_1 t})$	$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}$	$\log(q_e - q_t)$ *vs* . t	Lagergren (1898)
Pseudo-second order-1	$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	$\frac{t}{q_t}$ *vs*. t	Ho (2006)
Pseudo-second order -2		$\frac{1}{q_t} = \left(\frac{1}{k q_e^2}\right) \frac{1}{t} + \frac{1}{q_e}$	$\frac{1}{qt}$ *vs*. $\frac{1}{t}$	
Pseudo-second order-3		$q_t = q_e - \frac{1}{q_e} \frac{q_t}{t}$	q_t *vs*. $\frac{q_t}{t}$	
Pseudo-second order-4		$\frac{q_t}{t} k q_e^2 - k q_e q t$	$\frac{q_t}{t}$ *vs*. q_t	

Table 4
Kinetic parameters for the adsorption process.

Type	Parameter	C_0 (mg L^{-1})						
		10	20	30	40	50	60	70
Pseudo-first	K_1	0.0051	0.0033	0.0234	0.0285	0.0252	0.0081	0.0051
	q_e	0.0926	0.09176	0.0789	0.0654	0.0788	0.0545	0.0654
	r^2	0.83111	0.81067	0.77194	0.79447	0.50714	0.76705	0.83111
Pseudo-second-1	q_e exp	0.17	0.37	0.59	0.85	1.14	1.48	1.72
	K_2	0.9821	1.4808	3.2782	1.9163	2.8972	0.8355	0.9087
	q_e cal	0.1739	0.1674	0.0956	0.1046	0.1107	0.1357	0.1784
	r^2	0.9873	0.9850	0.9680	0.9738	0.9792	0.9840	0.9854
Pseudo-second-2	K_2	1.1677	0.6732	0.6311	0.6408	0.742	1.0636	1.0417
	q_e cal	0.0797	0.1119	0.1404	0.1272	0.0967	0.0763	0.0807
	r^2	0.9517	0.8336	0.7896	0.8443	0.7460	0.9373	0.9329
Pseudo-second-3	K_2	0.7904	3.2914	2.6147	3.1762	4.8032	0.91341	0.83015
	q_e cal	0.0127	0.0185	0.0249	0.0218	0.0159	0.0122	0.0135
	r^2	0.9756	0.7673	0.8456	0.7529	0.7276	0.7364	0.7204
Pseudo-second-4	K_2	4.1425	2.3681	1.8850	1.8394	2.7066	1.5514	1.2672
	q_e cal	0.0145	0.0251	0.0302	0.0299	0.0221	0.0057	0.0068
	r^2	0.806	0.7673	0.8456	0.7529	0.7139	0.7314	0.7199

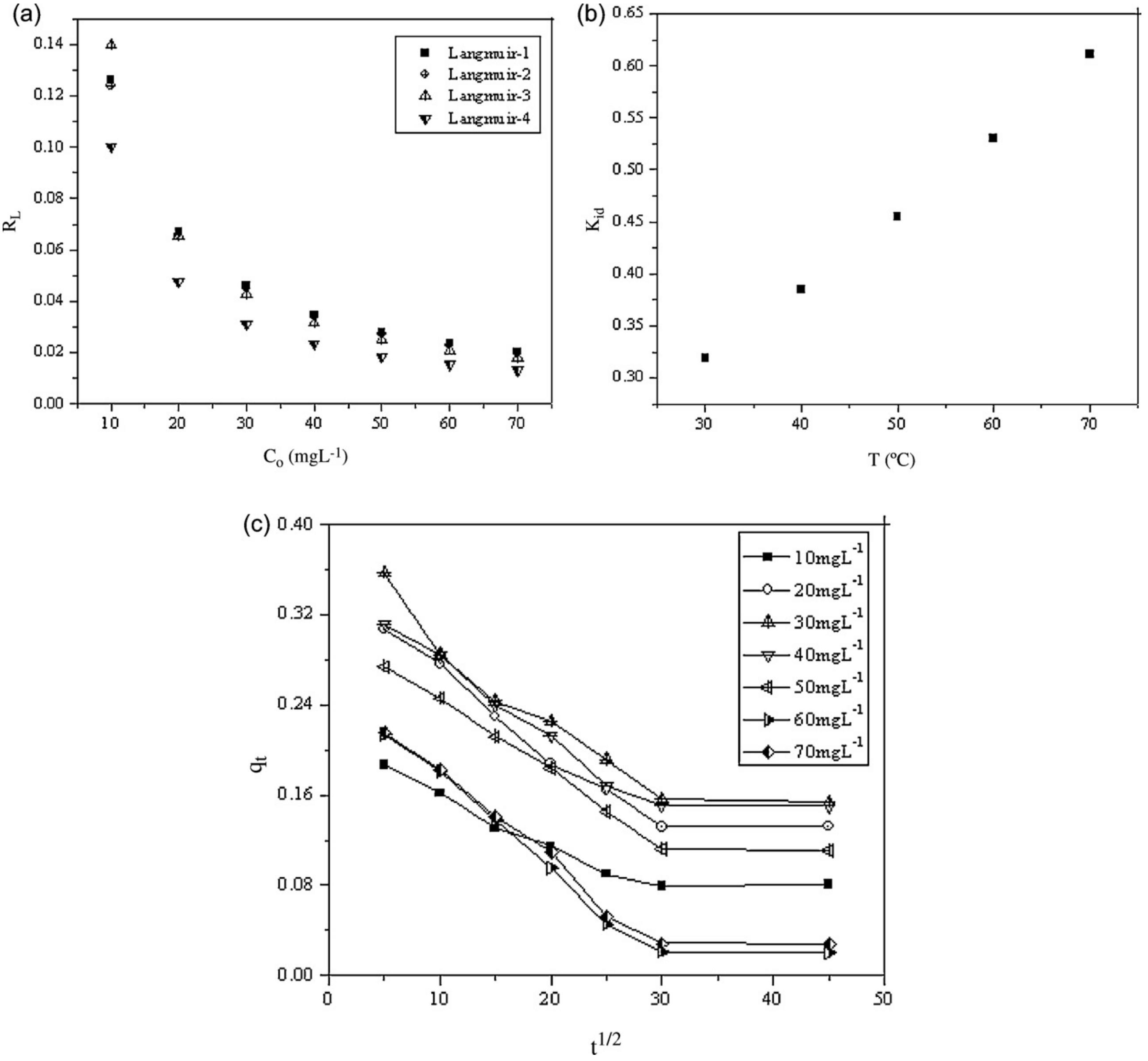

Fig. 6. a) Dimensionless separation factor (R_L) for the adsorption of AB dye onto polymer bead, (b) VantHoff plot for the adsorption of AB dye onto polymer bead, and (c) intraparticle diffusion parameters for the adsorption of AB dye onto polymer bead.

Table 5a
Intra particle diffusion parameters for the adsorption process.

C_0 (mg g^{-1})	k_{id} (mg g^{-1} s$^{1/2}$)	C (mg g^{-1})	r^2
10	0.0027	0.1798	0.7594
20	0.0047	0.3051	0.8046
30	0.0049	0.3360	0.7881
40	0.0044	0.3107	0.8002
50	0.0045	0.2788	0.8478
60	0.0053	0.2164	0.8126
70	0.0052	0.2185	0.8206

Table 5b
Thermodynamic parameters for the adsorption process.

Temperature (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1}K^{-1})
30	−0.08	0.17	7.90
40	−0.13		
50	−0.19		
60	−0.26		
70	−0.36		

implies that the increment of an orderliness between the adsorbate and the adsorbent molecules.

4. Conclusion

From the studies it may concluded that, Prosopis Juliflora carbon/Ca/alginate polymer bead is eco-friendly and a cheap material that could be used as a potential adsorbent for the removal of aniline blue dye from aqueous solution and polluted water. The adsorption of dye depends on the pH of the solution. Based on these results, the optimum contact time is considered to be 60 min and the adsorbent dosage as 1 g. For the application of Langmuir and Freundlich equations, the experimental result shows that the Langmuir-1 was the best suited model as compared to other Langmuir and Freundlich isotherm equations. The result of dimensionless separation factor implies that the adsorption process was favorable and the value of R_L lies between 0 and 1. The kinetic data tends to fit very well in the pseudo-second-order kinetics model, indicating that the chemisorption of the dyes occur on the modified beads. The negative value of ΔG° shows that the process was spontaneous in nature and progression of more negative value indicates that equilibrium increases with temperature. The positive value of ΔH° reveals that the adsorption process was endothermic in nature and the competition between solute and the solvent particle involves a complex phenomenon on the solid surface. Moreover the process of adsorption and desorption takes place simultaneously. The positive value of ΔS° implies that the increment of an orderliness between the adsorbate and the adsorbent molecules. The FTIR spectrum shows a good reduction in peak height and peak shifting before and after adsorption of AB dye. SEM images shows well defined and characterized morphological images that are evident for the strong adsorption of the dye molecule on the surface of the polymer beads.

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