



Adsorption study of patent blue VF using ginger waste material

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Abstract

Ginger waste material (GWM) has been utilized as adsorbent for removal of hazardous Patent Blue VF (PBVF) dye from aqueous solution. Batch adsorption experiments were performed as a function of pH, contact time, dye concentration, adsorbent dose and temperature. The optimum pH required for the maximum adsorption was found to be 2. The experimental equilibrium adsorption data were tested using Langmuir and Freundlich isotherm equations and maximum monolayer adsorption capacity was found to be 9.56 mg/g. Adsorption kinetics data were modeled using the pseudo first order and pseudo second order kinetic equations and intraparticle diffusion model. Results indicate that pseudo second order model best describe adsorption kinetics data.

Keywords: Adsorption, Ginger waste material, Thermodynamics, Kinetics, Isotherms

1. Introduction

Dyes are one of the major constituents of the wastewater produced from dyestuff manufacture and some similar industries, which poses a severe threat to the surrounding ecosystem because many of the dyes are extremely toxic [1]. Patent Blue VF is widely used as a colouring agent and even on small consumption it have many adverse effects to the environment and human such as allergic, skin and eye irritation, irritating to mucous membranes and upper respiratory tract etc. Due to the large degree of organics present in these molecules and the stability of modern dyes, conventional physicochemical and biological treatment methods are ineffective for their removal [2, 3]. This led to the study for other effective methods. Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency in the removal of pollutants. Adsorption can produce high quality products while also being a process that is economically feasible [4]. Activated carbon is the most widely used adsorbent but commercially available activated carbons are very expensive [5, 6]. Nowadays, a large number of low cost agricultural waste adsorbents have been investigated for the dyes removal like cotton [7] coconut shell [8, 9], palm shell [10, 11], almond shell [12] olive seed waste [13, 14], pine waste [15], pine wood [16] and wood char [17].

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India is the largest producer of ginger (*Zingiber Officinale*) in the world. The production of ginger is greater than 275,000 million tones per year in India. Due to large amount of ginger waste material it can be used as an effective adsorbent. In the present work, ginger waste material (GWM) has been used as the adsorbent for the removal of Patent Blue VF in batch process. The equilibrium was attained within 120 min. The optimum pH required for the maximum adsorption was found to be 2. The adsorption process has been found endothermic and spontaneous in nature.

2. Experimental

2.1. Adsorbate

Patent Blue VF (C.I. = 42045, molecular formula = $C_{27}H_{31}N_2NaO_6S_2$, $\lambda_{max} = 635$ nm, molecular weight = 566.66) was obtained from CDH New Delhi, India. Dye solutions were prepared by dissolving appropriate amount in double distilled water. The structure of PBVF is given in Fig.1.

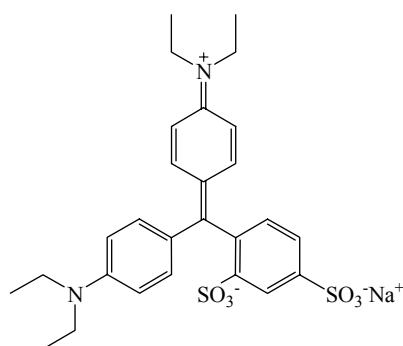


Fig. 1 Structure of Patent Blue VF

2.2. Preparation and characterization of adsorbent

The GWM was collected from a local market. It was washed with hot distilled water to remove impurities, dried at 60 °C and the material was finally sieved into 100 mesh BSS particle size. Powered adsorbent was washed again with distilled water and dried in oven at 60 °C for adsorption studies. The surface morphology of GWM was characterized by scanning electron microscopy (SEM). SEM images clearly showing the irregular and porous surface (Fig.2).

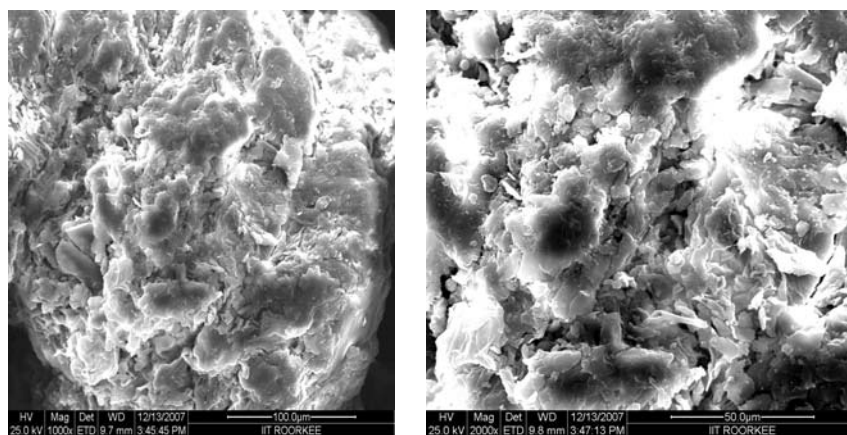


Fig. 2 SEM images of ginger waste material before adsorption at different magnification (a) 1000x (b) 2000x

2.3. Batch adsorption studies

Adsorption studies were performed in 250 ml flasks, where solutions of dye (50 ml) with different initial concentrations (5-20 mg L⁻¹) were placed. Equal mass of 0.05 g of GWM were added to dye solution and each sample was kept in shaker for 180 min to reach equilibrium. The flasks were then removed from the shaker and the final concentration of dye in the solution was analyzed by the double beam UV-Vis spectrophotometer (Elico SL 164, India) at 635 nm. The adsorption capacity at equilibrium, q_e (mg g⁻¹), was calculated by:

$$q_e = (C_0 - C_e) \frac{V}{M} \quad (1)$$

where C_0 and C_e (mg L⁻¹) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (l) and W is the mass of dry adsorbent used (g).

3. Result and discussion

3.1. Effect of concentration and contact time

Adsorption capacity of GWM increases from 3-6.6 mg g⁻¹ with the increasing dye concentration from 5 to 20 mg L⁻¹ because large number of dye molecules comes in the contact of adsorbent surface at higher concentration. The influence of contact time on dye uptake from aqueous phase is shown in Fig. 3. A large fraction of the PBVF was removed within 120 min of the contact time. It is evident from the figure that the rate of PBVF removal was rapid initially and then gradually slowed down until equilibrium was achieved. Beyond which there was no significant increase in the rate of PBVF removal. The initial rapid adsorption may be attributed to large number of adsorbent sites were available for dye molecules.

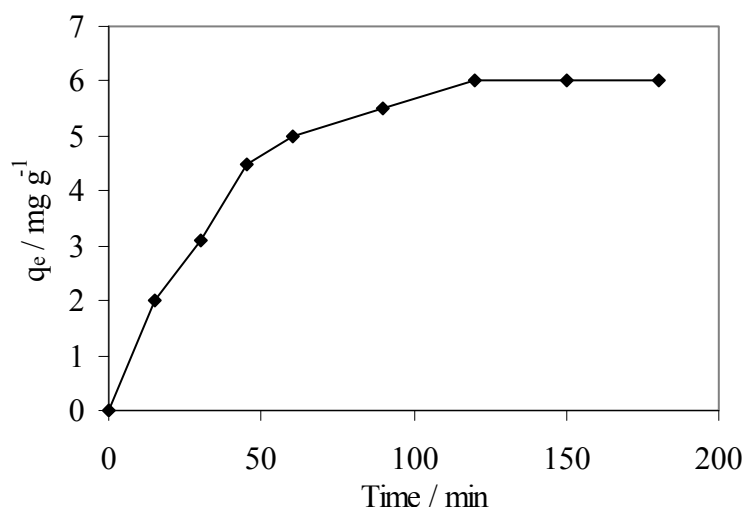


Fig. 3 Effect of contact time for the adsorption of PBVF

3.2. Variation in adsorbent dose

As the adsorbent dose increases, available sites for the dye molecules also increase and consequently better adsorption takes place. In the present study, the adsorbent dosages were varied from 0.025 to 0.2 g in 10 mg L⁻¹ dye solution. As shown in Fig. 4, the maximum adsorption was 95 % at 0.2 g adsorbent mass. However, it was observed that the efficiency did not increase linearly with the increase in the adsorbent dosage [18] because number of adsorbent sites increase but concentration of solution remain constant so adsorbent site remain vacant.

3.3. Effect of pH

The effect of solution pH on equilibrium adsorption capacity of GWM was studied at 10 mg L⁻¹ initial PBVF concentration at 30 °C. It was observed that the solution pH affects the amount of dye adsorbed. As Fig. 5 shows, the adsorption of PBVF was optimum at the pH 2. At lower pH, the GWM may become positively charged, which enhances the adsorption of negatively charged dye molecules through electrostatic forces of attraction.

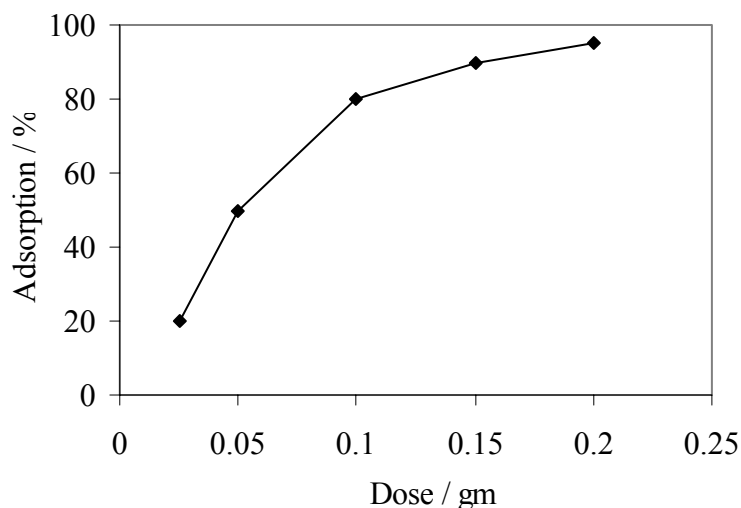


Fig. 4 Effect of adsorbent dose for the adsorption of PBVF

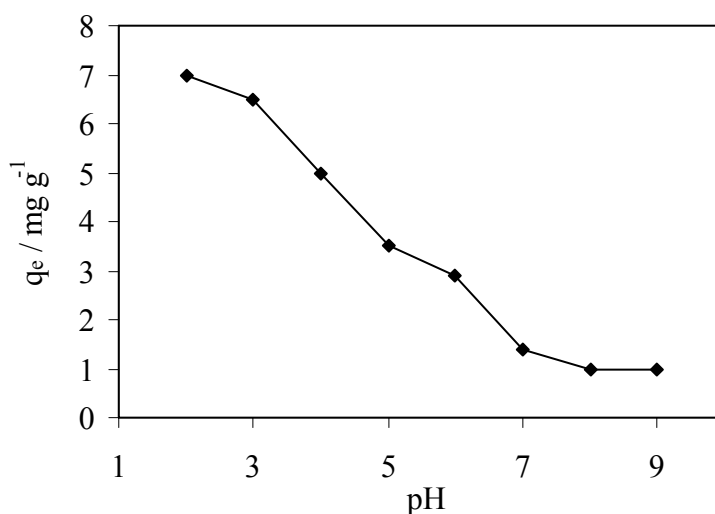


Fig. 5 Effect of pH for the adsorption of PBVF

3.4. Effect of temperature

To determine the effect of the temperature, adsorption studies of PBVF were performed at three different temperatures, i.e., 30, 40, and 50 °C. The result shows (Fig. 6) that adsorption capacity increases with increasing temperature, indicating endothermic nature of adsorption process. The increase of adsorption with temperature may be due to the increased mobility of the dye molecules with the rising temperature, and increasing temperature produces a swelling effect within the internal structure of the GWM enabling large dye molecules to penetrate further [19].

3.5. Adsorption thermodynamics

Thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined by using the following equations

$$K_c = C_{Ae} / C_e \quad (2)$$

where C_{Ae} (mg L^{-1}) is the amount adsorbed on solid at equilibrium and C_e (mg L^{-1}) is the equilibrium concentration and K_c is the distribution coefficient. ΔG° can be calculated using the relation given below:

$$\Delta G^\circ = -RT \ln K_c \quad (3)$$

$$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / RT \quad (4)$$

where R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the universal gas constant, T (K) is the absolute solution temperature. By plotting a graph of $\ln K_c$ vs. $1/T$, the values of ΔH° and ΔS° can be estimated from the slope and intercept (Table 1).

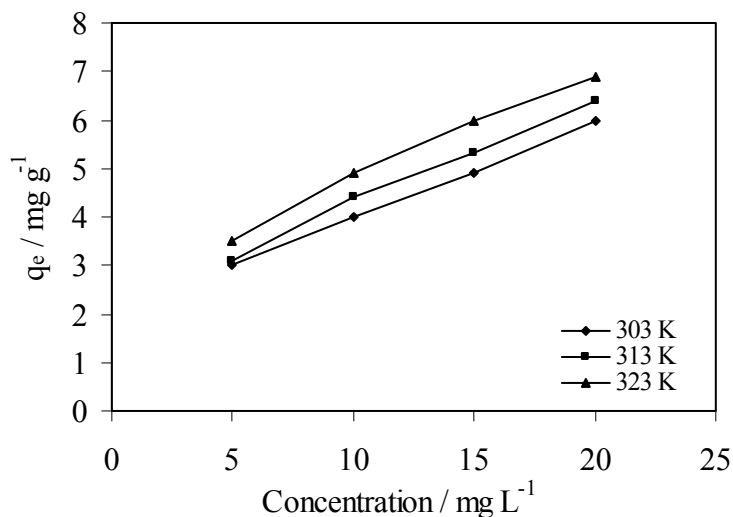


Fig. 6 Effect of temperature for the adsorption of PBVF at different concentration

Table 1

Values of thermodynamic parameters for the adsorption of PBVF on GWM

Temperature ($^\circ\text{C}$)	$-\Delta G^\circ$ (KJ mol^{-1})	ΔH° (KJ mol^{-1})	ΔS° ($\text{KJ mol}^{-1} \text{ K}^{-1}$)	R^2
30	0.896			
40	1.007	2.46	0.011	0.973
50	1.062			

The negative values of ΔG° indicated the feasibility of the process and the spontaneous nature of the adsorption. The positive value of ΔH° indicated the endothermic nature of the adsorption process. The positive value of ΔS° showed the affinity of the GWM for PBVF and the increasing randomness at the solid–solution interface during the adsorption process.

3.6. Adsorption isotherm

Adsorption isotherm is important to describe how solutes interact with adsorbent. The applicability of the Langmuir and Freundlich isotherm models were studied to describe the adsorption process. Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface [20]. The linear form of Langmuir isotherm equation is given as:

$$1/q_e = 1/qbC_e + 1/q \tag{5}$$

where C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}), q and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The constants can be evaluated from the intercept and the slope of the linear plots of $1/q_e$ vs. $1/C_e$ (Fig. 7). The Figure shows a straight line with a good correlation coefficient (R^2) indicating the applicability of the model for TGW-PBVF adsorption (Table 2).

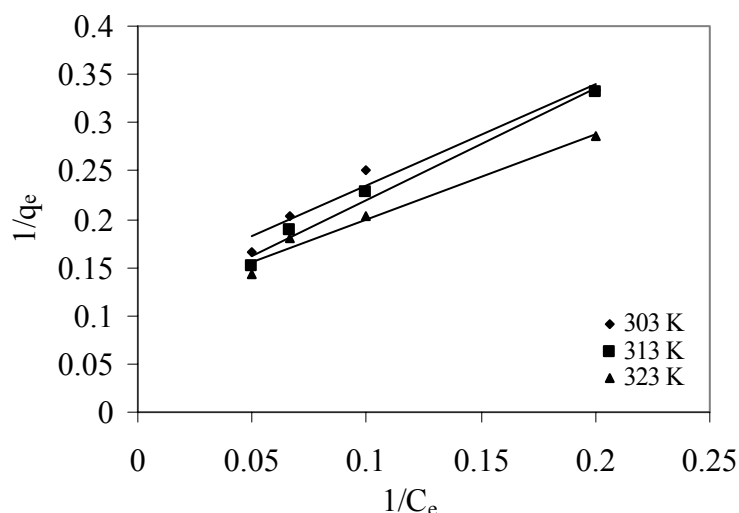


Fig. 7 Langmuir adsorption isotherm

Table 2

Langmuir and Freundlich isotherm model for adsorption of PBVF on GWM

T (°C)	Langmuir isotherm model				Freundlich isotherm model		
	q (mg g^{-1})	b (l mg^{-1})	R_L	R^2	K_F (mg g^{-1})	n (l mg^{-1})	R^2
30	7.751	0.123	0.289	0.963	1.339	2.048	0.987
40	9.560	0.097	0.340	0.986	1.308	1.694	0.997
50	8.888	0.128	0.280	0.973	1.651	2.155	0.980

The essential characteristics of the Langmuir isotherm can be expressed in terms of either a dimensionless constant separation factor or equilibrium parameter, R_L

$$R_L = 1 / (1 + b C_0) \tag{6}$$

where R_L is a dimensionless separation factor, C_0 the initial concentration of dye solution (mg L^{-1}) and b is the Langmuir constant. The parameter R_L indicates the shape of the isotherm accordingly

$R_L > 1$ unfavorable

$R_L = 1$ linear

$R_L = 0$ irreversible
 $0 < R_L < 1$ favorable

Freundlich adsorption isotherm is often used for heterogeneous surface energy systems. The Freundlich equation in linear form is given as:

$$\log q_e = \log K_F + 1/n \log C_e \quad (7)$$

where K_F is the Freundlich constant and n the Freundlich exponent. K_F and n can be determined from the linear plot of $\log q_e$ vs. $\log C_e$ (Fig. 8). The values of n (Table 2) are greater than unit in all case with good correlation coefficient indicating the applicability of Langmuir model [21].

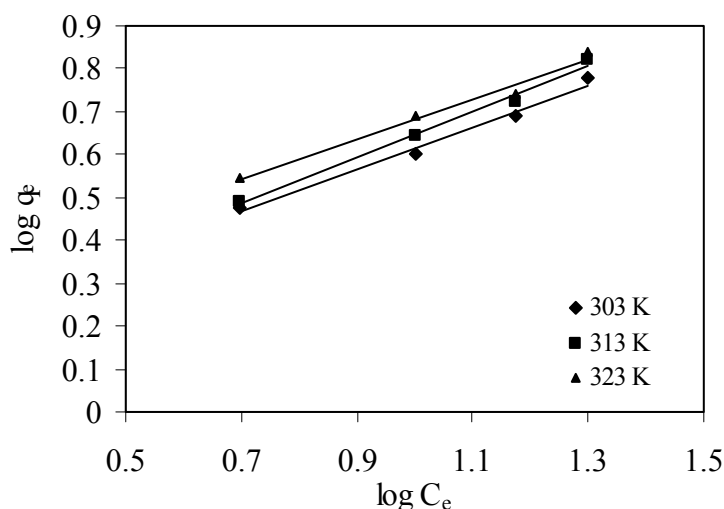


Fig. 8 Freundlich adsorption isotherm

3.7. Kinetic studies

In order to examine the mechanism of adsorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the rate data.

3.7.1. Pseudo first order kinetics model

The adsorption kinetics may be described by a pseudo first order equation:

$$dq_t/dt = K_1 (q_e - q_t) \quad (8)$$

where q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t (mg g^{-1}), respectively, and k_1 is the equilibrium rate constant of pseudo first order adsorption (l min^{-1}). Integration of above eq.:

$$\log q_e / (q_e - q_t) = k_1 t / 2.303 \quad (9)$$

The linear form of the eq. is

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (10)$$

3.7.2. Pseudo second order kinetic model

A pseudo second order kinetic model may also be described the kinetic of adsorption:

$$dq_t/dt = K_2 (q_e - q_t)^2 \quad (11)$$

where k_2 is pseudo second order rate constant. Integration of above eq.:

$$1/(q_e - q_t) = 1/q_e + k_2 t \quad (12)$$

The linear form of eq. is

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (13)$$

Figs. 9 and 10 show linear plots of pseudo first and pseudo second order model for PBVF adsorption. As can be seen from Table 3, the calculated value of q_e has close agreement with the experimental q_e data and good correlation coefficient for pseudo second order. It can be said that PBVF adsorption system followed pseudo second order kinetic model.

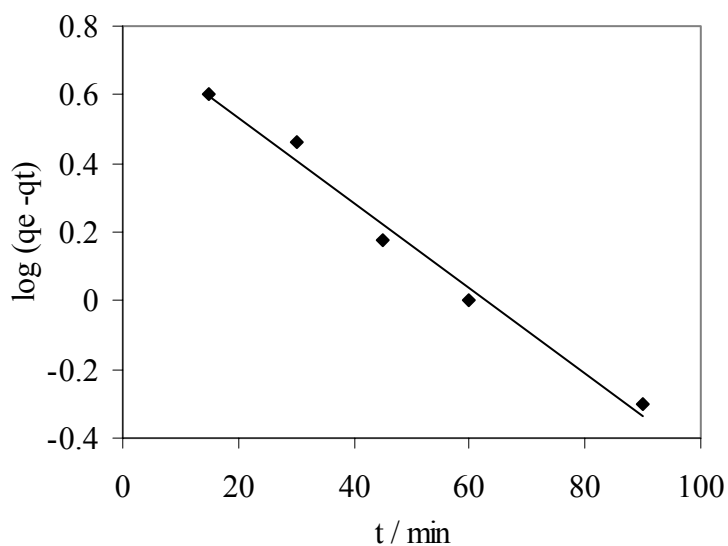


Fig. 9 Pseudo first order kinetics

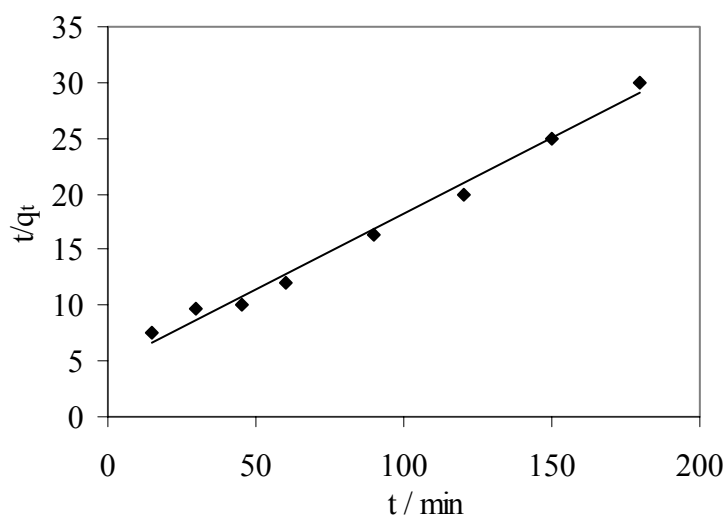


Fig. 10 Pseudo second order kinetics

Table 3

Values of kinetic parameters for the PBVF adsorption on GWM

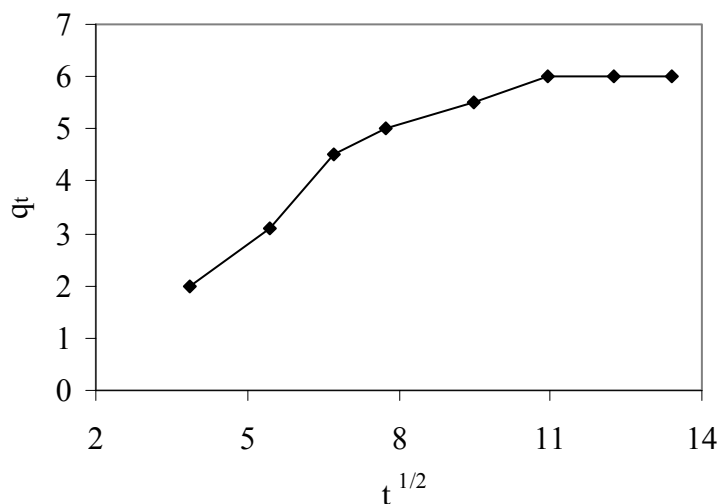
Concn. (mg L ⁻¹)	q _e (Exp.) (mg g ⁻¹)	Pseudo first order			Pseudo second order		
		q _e (Cal.) (mg g ⁻¹)	k ₁ (min ⁻¹)	R ²	q _e (Cal.) (mg g ⁻¹)	K ₂ (g mg ⁻¹ min ⁻¹)	R ²
10	6	14.32	0.555	0.924	7.3	0.005	0.989

3.7.3. Intra-particle diffusion

In a solid–liquid adsorption process, the transfer of the adsorbate is controlled by either boundary layer diffusion or intra-particle diffusion, or by both. It has been noticed in many studies that boundary layer diffusion is dominant during the initial adsorbate uptake, and then gradually the adsorption rate becomes controlled by intra-particle diffusion after the adsorbent's external surface is loaded with the adsorbate. The intra-particle diffusion parameter, k_{id} is defined by the following equation [22]:

$$q_t = k_{id} t^{0.5} + c \quad (10)$$

where q_t is the amount of PBVF adsorbed (mg g⁻¹) at time t , k_{id} is intra-particle diffusion constant (mg g⁻¹ min^{0.5}), and c is the intercept. k_{id} was determined from the slope of the plot q_t vs. $t^{0.5}$ (Fig. 11). The calculated value of k_{id} is 0.421 mg g⁻¹ min^{0.5} and c is 1.164. The double nature of plot may be explained by the fact that the initial curved portion is boundary layer diffusion effect while final linear portion is the result of intra-particle diffusion. [23].

**Fig. 11** Intra-particle diffusion for the adsorption of PBVF

4. Conclusions

The present study shows that GWM is an effective adsorbent for the removal of PBVF from aqueous solution. The optimum pH for adsorption was found to be 2. The performance of the as an adsorbent to remove PBVF has been investigated under different experimental conditions in the batch mode. The Effect of contact time shows that equilibrium was attained within 120 min. The adsorption isotherm of PBVF onto GWM was fitted by Langmuir and Freundlich models. Kinetics result showed both bulk and intra-particle are effective adsorption mechanism.

References

- [1] W. Yang, D. Wu, R. Fu, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 312 (2008) 118.
- [2] G. Mc Kay, *J. Chem. Technol. Biotechnol.* 32 (1982) 759.
- [3] G. Mc Kay, *Am Dyestuff Rep.* 68 (1979) 29.
- [4] S.J. Allen, Q. Gan, R. Matthews, P.A. Johnson, *Ind. Eng. Chem. Res.* 44 (2005) 1942.
- [5] B.K. Singh, N.S. Rawat, *J. Chem. Technol. Biotechnol.* 61 (1994) 307.
- [6] S.K. Khare, K.K. Panday, R.M. Srivastava, V.N. Singh, *J. Chem. Technol. Biotechnol.* 38 (1987) 99.
- [7] S. Tunc, O. Duman, *J. Food Engineering* 81 (2007) 133.
- [8] P.M.S. Sai, J. Ahmed, K. Krishnaiah, *Ind. Eng. Chem. Res.* 36 (1997) 3625.
- [9] W.M.A.W. Daud, W.S.W. Ali, *Bioresour. Technol.* 93 (2004) 63.
- [10] W.M.A.W. Daud, W.S.W. Ali, M.Z. Sulaiman, *J. Chem. Technol. Biotechnol.* 78 (2003) 1.
- [11] J.S. Tan, F.N. Ani, *Carbon* 41 (2003) 840.
- [12] C.A. Toles, W.E. Marshall, L.H. Wartelle, A. Mc Aloon, *Bioresour. Technol.* 75 (2000) 97.
- [13] T.T. Al-Khalid, N.M. Haimour, S.A. Sayed, B.A. Akash, *Fuel Process. Technol.* 57 (1998) 55.
- [14] F. Rodriguez-Reinoso, M. Molina-Sabio, M.T. Gonzalez, *Carbon* 33 (1995) 15.
- [15] A. Garcia-Garcia, A. Gregorio, C. Franco, F. Pinto, D. Boavida, I. Gulyurtlu, *Bioresour. Technol.* 88 (2003) 27.
- [16] R.L. Tseng, F.C. Wu, R.S. Juang, *Carbon* 41 (2003) 487.
- [17] M.F. Tennant, D.W. Mazyck, *Carbon* 41 (2003) 2195.
- [18] E. Demirbas, M. Kobya, E. Senturk, T. Ozkan, *Water SA* 30 (2004) 533.
- [19] B. Acemioglu, *J. Colloid. Interface Sci.* 274 (2004) 371.
- [20] T.W. Weber, R.K. Chakravorti, *AIChE J.* 20 (1974) 228.
- [21] C. Namasivayam, R. Jeyakumar, R.T. Yamuna, *Waste Manage.* 14 (1994) 643.
- [22] W.J.W. Jr., J.C. Morris, *J. Sanitary, Eng. Div. Proceed. Am. Soc. Civil Eng.* 89 (1963) 31.
- [23] G. Mc Kay, G. Ramprasad, P. Mowli, *Water Research* 21 (1987) 375.