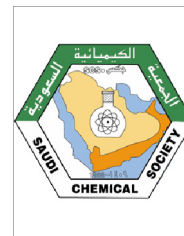




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ORIGINAL ARTICLE

Kinetics, equilibrium data and modeling studies for the sorption of chromium by *Prosopis juliflora* bark carbon

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KEYWORDS

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Abstract In this study, the activated carbon was prepared from *Prosopis juliflora* bark as a novel adsorbent. Removal of chromium (Cr) was assessed by varying the parameters like metal concentration, temperature, pH, adsorbent dose and contact time. The feasibility of the sorption was studied using Freundlich and Langmuir isotherms including linear and non-linear regression methods. In Langmuir, various forms of linearized equations were evaluated. The isotherm parameter of dimensionless separation factor (R_L) was also studied. The kinetics of adsorption was studied by using Lagergren's pseudo-first order and pseudo-second order equations and the results have shown that the adsorption process follows pseudo-second order kinetics and the adsorption process depends on both time and concentration. The mechanistic pathway of the adsorption process was evaluated with intraparticle diffusion model. The effect of heat of adsorption of the adsorbate onto the adsorbent material was determined using the thermodynamic parameters and the reusability of the adsorbent materials was ascertained with desorption studies. The adsorbent material characterization was done by using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD) method and morphology of the surface of adsorbent was identified with Scanning Electron Microscope (SEM).

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1. Introduction

Chromium possesses 21st place in the abundance of the earth's crusts and sixth place in the abundance of transition metal. Hence the utilization of chromium is essential in all kind of

metallic industries. Chromium compounds are widely used in industries like metal plating, paints, leather, tanning, textile, dyeing, printing inks and wood preservation. These industries discharge an enormous quantity of non biodegradable waste products and they are diverted into the environment. Chromium can exist in water either as Cr(III) or Cr(VI) (Costa, 1997) and Cr(VI) will be eventually reduced to Cr(III) by the presence of organic matters.

Chromium has some advantages and disadvantages to mankind. A trace element of trivalent chromium is used for the metabolism process by various living organisms (Kimrough et al., 1999). The human body contains approximately 0.03 ppm of chromium and the daily intake strongly depends

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on feed level that is approximately 15–200 μg . The recommended level of chromium in potable water is only 0.05 mg L^{-1} (Mohana and Pittman, 2006). Hexavalent chromium is very toxic to flora and fauna. Acute exposure of Cr(VI) in human body causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage, respiratory track problems and bone cancer (Lakshmipathiraj et al., 2008). Inhalation may cause irritation and ulceration of the nasal septum and respiratory sensitization (asthma) (Di Bona et al., 2011). Chromium(VI) compounds come under the water hazard class III (Raji and Anirudhan, 1992). Therefore it is essential to remove Cr(VI) from wastewater prior to discharge into the environment.

Many of the conventional methods such as reduction, precipitation (Esmaceli et al., 2005), ion exchange (iqbal et al., 2009), electrolysis, reverse osmosis, solvent extraction (Selvaraj et al., 2003), adsorption (Huang and Wu, 1975) and electrochemical precipitation (Kongsricharean and Palprasert, 1991) are available for the removal of chromium in water. Among these, adsorption is the most versatile technique for the removal of metals from wastewater. A variety of adsorbents like saw dust (Adouby et al., 2007), coconut husk (Olayinka et al., 2009), rubber tyres (Hamadi et al., 2001), soya cake (Daneshvar et al., 2002), activated alumina (Mor et al., 2007), Coconut coir (Gonzalez et al., 2008) and bagasse (Demiral et al., 2008) are used to remove the toxic metals present in the water resources.

The objectives of the present study are (i) Find out the efficiency of activated carbon for the removal of chromium by *Prosopis juliflora* bark carbon using various parameters, (ii) The prediction of isotherm parameters, Freundlich and Langmuir equations were used for equilibrium studies, (iii) Lagergren's equations like Pseudo-first order and pseudo-second order equations were used for the prediction of kinetic parameters, (iv) The effect of heat on the adsorption process was evaluated by using various thermodynamic parameters such as Gibbs free energy (ΔG^0), Enthalpy change (ΔH^0) and Entropy change (ΔS^0) were calculated using Van't Hoff plot, (v) The surface functional group characterization of the adsorbent material was done using Fourier Transform Infrared Spectroscopy (FTIR) and the morphology of the adsorbent material was identified with Scanning Electron Microscopy (SEM) and (vi) The force of attraction involved between the adsorbate and adsorbent material was identified with X-ray Diffraction analysis.

In this study *Prosopis juliflora* bark was chosen for the preparation of activated carbon and it was named as *Prosopis juliflora* bark carbon (PJBC). In India *Prosopis juliflora* was used for the production of carbon which was utilized by household and small industries as timber and fuel.

2. Materials and methods

2.1. Preparation of activated carbon

Prosopis juliflora Bark Carbon (PJBC) was prepared from *Prosopis juliflora* bark. It was collected in Anna University, Pattukottai premises and the bark was dried without sunlight for 7 days and carbonized with 1:1 sulfuric acid. Carbon was washed with distilled water until neutral pH and dried in hot air oven at 393 K for 24 h then treated into a muffle furnace

at 723 K for complete carbonization. Carbon was powdered in a ball mill to get the desired size of an activated carbon.

2.2. Preparation of metal solution

Stock solution of 1000 (mg L^{-1}) of metal solution was prepared by dissolving 5.6579 g of $\text{K}_2\text{Cr}_2\text{O}_7$ (Merck, India limited, analytical grade (assay 99.8%)) into 1 L of distilled water. Fresh dilutions of desired metal solution concentrations were made at each experiment.

2.3. Sorption studies

Batch adsorption studies of Cr onto PJBC were determined by various parameters such as pH, metal concentration, adsorbent dose, temperature and contact time. The optimum concentration of metal solution was evaluated using 20 to 200 mg L^{-1} with 20 mg L^{-1} variation using 50 mL of metal solution. For the determination of the effect of pH of the sorption process, the pH values were adjusted from 2 to 10 using 0.1 M NaOH and 0.1 M HCl with a systronics pH meter. The adsorbent dosage was varied from 0.05 g to 1 g with 0.05 g variation. The effect of temperature of sorption process was estimated by using various temperatures as 303 K, 313 K, 323 K, 333 K and 343 K. The contact time of the process was predicted by varying the contact time as 10–90 min with 10 min variation. The metal solution concentration of supernatant liquids was determined by using UV-Vis spectrophotometer (λ_{max} : 370 nm).

2.4. Isotherm and kinetic studies

The isotherm equations used in this study are Freundlich and Langmuir isotherm equations of linear and non-linear regression methods. In Langmuir isotherm various forms of linearized equations were examined. The amount of sorption at equilibrium q_e (mg g^{-1}), calculated by the following equation,

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

where, C_0 and C_e (mg L^{-1}) are the liquid phase concentration of Cr at initial and equilibrium respectively.

Kinetic study helps for the prediction of type of mechanisms involved during the sorption process. In order to obtain kinetic data of the adsorption process Lagergren's pseudo-first order and pseudo-second order kinetic equations were used.

2.5. Characterization of the adsorbent

The *Prosopis juliflora* bark carbon was characterized by using Fourier Transform Infrared Spectroscopy. The FTIR provides the information about the type of functional groups present on the surface of the adsorbent material. The surface morphology of the adsorbent material was determined using a Scanning Electron Microscope. SEM image shows that changes occur on the surface of the adsorbent before and after adsorption of the adsorbate molecule. The Characteristics adsorption of Cr metal onto the adsorbent material was determined by using XRD analysis.

2.6. Desorption studies

The desorption study of the adsorbed chromium(VI) was carried out with 25 ml of 120 mg L⁻¹ of chromium solution taken in a series, 100 mg of adsorbent material used for adsorption was then separated from the solution by centrifugation. The adsorbent was filtered using a Whatman filter paper and washed gently with water to remove the unadsorbed chromium(VI). A series of 25 ml of distilled water were taken and their pH values were adjusted in the range 2–12 by addition of 0.5 M HCl or 0.5 M NaOH solution using a pH meter. The spent adsorbent was mixed with pH adjusted distilled water using the estimated time intervals of longer than the equilibrium time. The desorbed chromium(VI) was estimated as before.

3. Results and discussion

3.1. Analytical studies

3.1.1. FTIR studies

FTIR studies are used for prediction of different types of functional groups present in the adsorbent material. The

FTIR spectrum of carbon and Cr loaded carbon is presented in Fig. 1a. The carbon spectrum shows the peaks in the positions of 3432 cm⁻¹, 2161 cm⁻¹, 1591 cm⁻¹, 1359 cm⁻¹ and 1146 cm⁻¹. The peak position of 3432 cm⁻¹ indicates that the presence of stretching vibration of the OH group involves in the intermolecular or intramolecular hydrogen bonding or moisture present either in carbon or KBr. The peaks in the positions of 2161 cm⁻¹, 1591 cm⁻¹, 1359 cm⁻¹ and 1146 cm⁻¹ shows that the presence of alkyl group or due to the presence of tannin, C=C bond in aromatic conjugation, C-N peptide bond and S=O interaction respectively. The Cr loaded spectrum of FTIR shows that there is no change in their position of the peaks but there is a reduction in peak heights and intensity of the peaks shown at 3419 cm⁻¹, 2203 cm⁻¹, 1599 cm⁻¹, 1353 cm⁻¹ and 1224 cm⁻¹. This confirms that the Cr was strongly adsorbed onto the *Prosopis juliflora* bark carbon.

3.1.2. XRD studies

Fig. 1b highlights the XRD powder patterns of PJBC before and after the adsorption of chromium. Fig. 1b, the carbon shows a high intensity XRD peak at 26 Å and a small peak

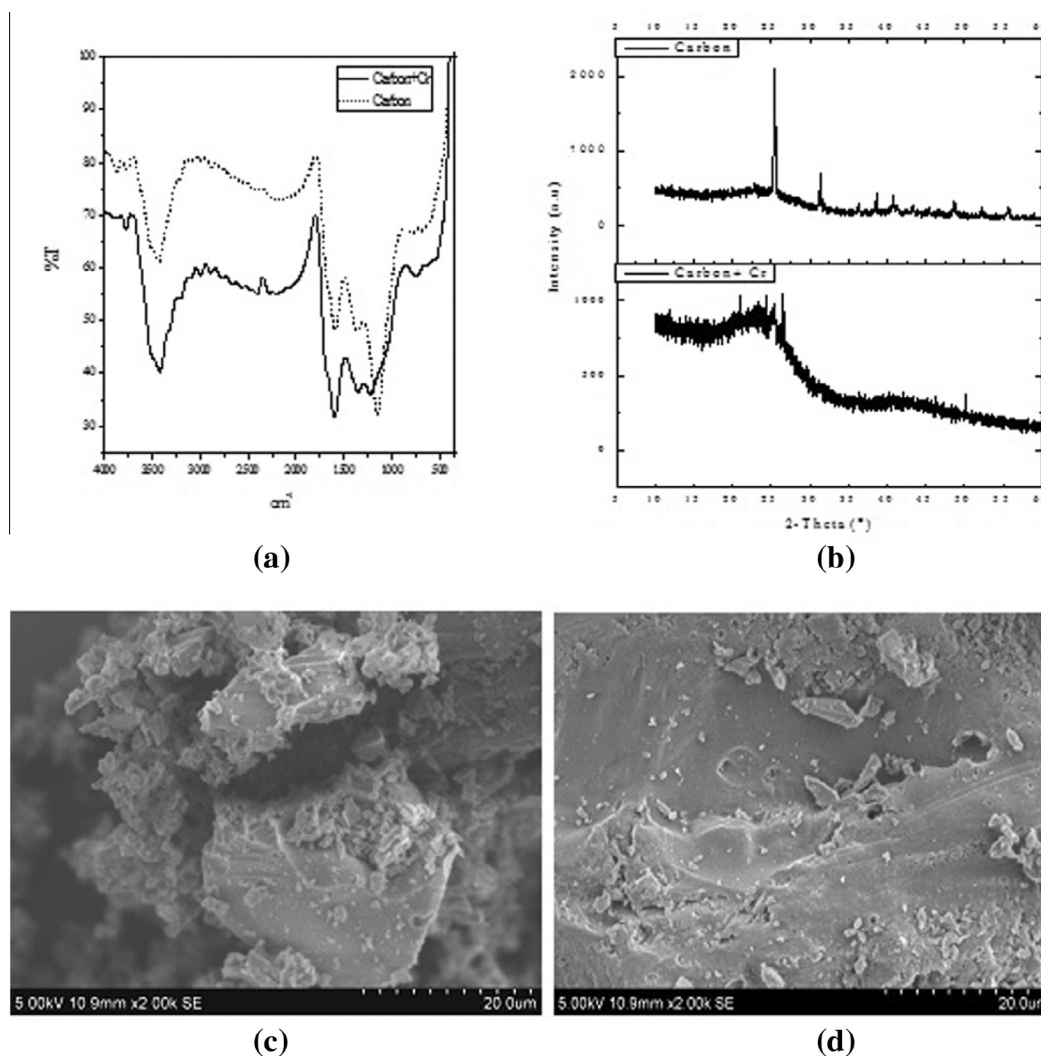


Figure 1 (a) FTIR spectrum of carbon and Cr loaded carbon, (b) XRD spectrum of carbon and Cr loaded carbon, (c) SEM image of Carbon and (d) SEM image of chromium loaded carbon.

at 31 Å indicated the presence of crystalline nature but in the case of carbon + Cr does not show any characteristic intensity peaks. This reveals that the crystalline nature of Cr was distorted due to the strong adsorption of Cr onto the activated carbon surface (Arulkumar et al., 2012). This shows the weak physical force or binding between the adsorbent and adsorbate but a strong chemical force of attraction was found.

3.1.3. SEM studies

The Scanning Electron Microscope (SEM) shows morphology of the adsorbent before and after adsorbed state. Fig. 1c and d shows the morphology of the activated carbon and Cr loaded activated carbon. Fig. 1c shows unoccupied pores on the carbon and layered structure also appears. But in the case of Fig. 1d the outer pores are covered by Cr metal and the layered structure is not seen. This is evident for the adsorption of Cr metal on the surface of adsorbent material.

3.2. Sorption studies

Initial metal concentration is an important factor that affects the adsorption process. The increase of initial concentration of chromium results in the increased uptake capacity, further enhancement leads to a decreased percent removal since number of moles of chromium available on surface area of the adsorbent is high at higher concentrations (Philipot et al., 1984). Adsorption of chromium was studied at different metal

concentrations from 20 mg L⁻¹ to 140 mg L⁻¹ with 20mg L⁻¹ variation. Among all concentrations 120mg L⁻¹ shows the maximum adsorption rate for the removal of Cr at 50 min contact time.

$$\% \text{Removal} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

where, C_i and C_f are initial and final concentration of metal, before and after sorption process.

Solution pH is an important factor that affects the rate of adsorption process. Chromium exists mostly in two oxidation states which are Cr(VI) and Cr(III) and the stability of these forms is dependent on the pH of the system (Jorgenson, 1979; Patterson, 1878; Namasivayam and Sureshkumar, 2008; Cimino et al., 2000). It was postulated that at low pH Cr(VI) could be reduced to Cr(III) in the presence of activated carbon under acidic conditions. Cr(VI) in H₂O system, at low pH, acid chromate ions (HCrO₄⁻) are the dominant species (Selomulya et al., 1999) than chromate ions. In this study at low pH values such as 2 to 5 there was a slow enhancement of the adsorption capacity of Cr. When the pH is further increased, a sharp decrease in uptake capacity of adsorption was observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent and ultimately lead to the reduction in sorption capacity. Fig. 2a, the pH value 6 shows a higher adsorption rate of chromium. Hence, the optimum pH for the adsorption of chromium onto PJBC has been chosen as

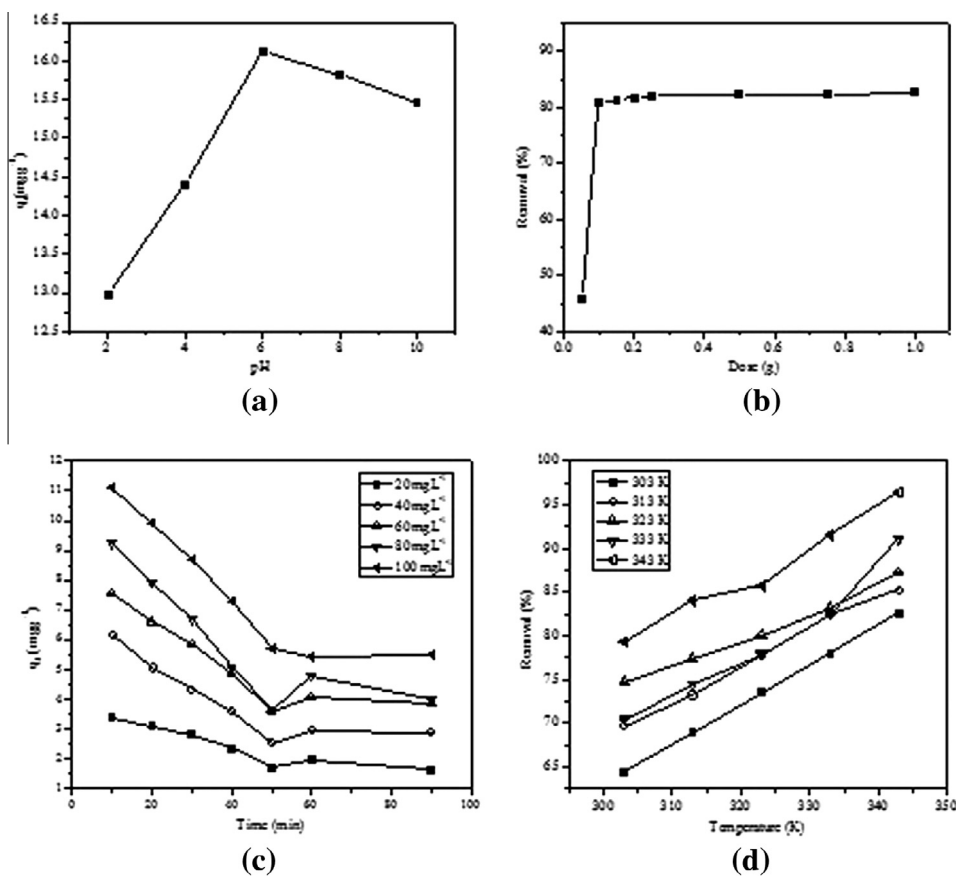


Figure 2 (a) Effect of pH for the removal of Cr onto PJBC, (b) Effect of Dose for the removal of Cr onto PJBC, (c) Effect of contact time and Cr concentration for the removal of Cr onto PJBC and (d) Effect of temperature for the removal of Cr onto PJBC.

pH value of 6.0. It is clear that pH determines the extent of Cr(VI) removal and provides a favorable adsorption onto PJBC.

The effect of adsorption capacity of chromium was found with the variation of dosage of adsorbent material. The dose of adsorbent varied from 0.05 g to 1.0 g L⁻¹. From Fig. 2, the effect of adsorbent dose on percent adsorption of chromium was found with a dose of 0.1 g adsorbent showing higher Cr removal when compared with other dosages. As the adsorbent dose increased, the percent removal of chromium slightly increased due to the availability of more surface area of the adsorbent. Increase in adsorbent dose also increased the reduction of Cr(VI) to Cr(III) (Park et al., 2006) (see Fig. 3).

Effect of temperature plays a vital role in any kind of adsorption processes. Whenever temperature increases the adsorption process slightly increases. The adsorption test was carried out with five different temperature ranges 303 K, 313 K, 323 K, 333 K and 343 K to study about the effect of temperature on adsorption. These experiments were carried out in the pH 5.5–6.0 with 120 mg L⁻¹ of metal solution on PJBC. The experimental observation showed that Cr(VI) adsorption capacity of PJBC surface increased with increasing temperature. As the temperature increased from 303 K to 343 K the adsorption capacity increased from 82.6 mg g⁻¹ to 96.4 mg g⁻¹. The adsorption process does not favor for the change of temperature and it shows only a slight increment.

3.3. Isotherm studies

The adsorption data were analyzed with two adsorption isotherm models, namely Freundlich and Langmuir. Various forms of Langmuir and Freundlich were tested in their linear and non-linear forms (Langmuir, 1916; Longhinotti et al., 1998; Sharma and Forster, 1994b). The Langmuir adsorption model was based on the assumption that the adsorption process was monolayer of the solute molecules on the adsorbent surface. The Langmuir isotherm is expressed as

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (3)$$

where q_e (mg g⁻¹) and C_e (mg L⁻¹) are the amount of dye adsorbed per unit mass of sorbent and unadsorbed dye concentration in solution. q_m – maximum amount of dye adsorbed per unit mass of sorbent at complete monolayer on surface bound, and K_a (L mg⁻¹) is a constant related to the affinity of the binding sites. Various forms of Langmuir and Freundlich isotherms of linear and non-linear are presented in Table 1.

The Freundlich isotherm equation is expressed as

$$q_e = K_F C_e^{1/n_F} \quad (4)$$

where K_F (mg g⁻¹) (L g⁻¹) is an indicator of the adsorption capacity, $1/n$ is the adsorption intensity.

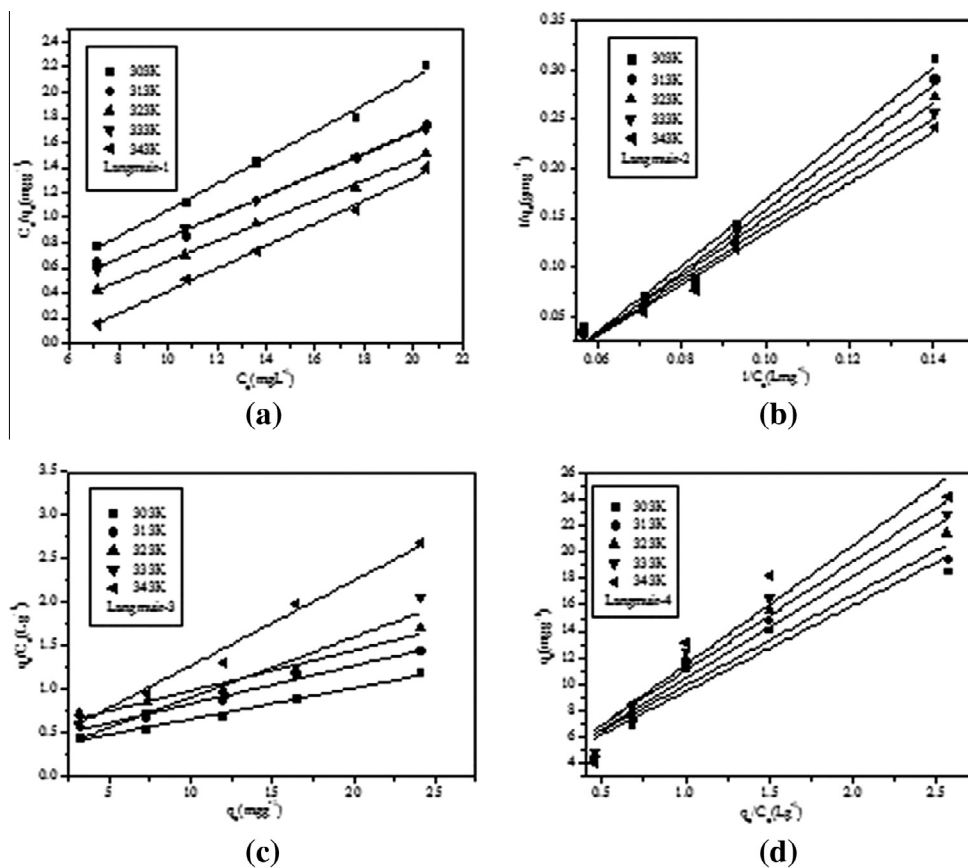


Figure 3 (a) Langmuir isotherm-1 for the adsorption of Cr onto PJBC, (b) Langmuir isotherm-2 for the adsorption of Cr onto PJBC, (c) Langmuir isotherm-3 for the adsorption of Cr onto PJBC and (d) Langmuir isotherm-4 for the adsorption of Cr onto PJBC.

The magnitude of the exponent $1/n$, shows the favorability of adsorption, $1/n$ value $n < 1$ represents favorable adsorption condition (Freundlich, 1906; Sharma and Forster, 1994a).

For the searching of the best suited isotherm model of Freundlich and four Langmuir isotherms shown the calculated q_m , K_a and coefficient of determination r^2 are presented in Table 2. The q_m and K_a values predicted using the parameters of $1/q_e$ vs. $1/C_e$, q_e vs. q_e/C_e and q_e/C_e vs. q_e by plotting graphs and the graphs are termed as Langmuir-2, Langmuir-3 and Langmuir-4, respectively. From Table 2, it was observed that the various forms of Langmuir constants are varied with different forms of linear equations and that depends on the way isotherm equations has linearized (Donmez et al., 1999; Aksu, 2005). Langmuir 1 shows a better correlation coefficient (r^2) value compared to the other Langmuir and Freundlich forms. The higher q_m value of Langmuir-1 confirms that the maximum quantity of adsorption at 303 K. The equilibrium data were further analyzed using the linearized form of Freundlich equation using the same set of experimental data, by plotting $\log(q_e)$ vs. $\log(C_e)$. From Table 2, it was observed that at all solution temperatures, the r^2 values were found to be relatively less than the best fit linearized Langmuir isotherm. This suggests that the Langmuir isotherm is the most appropriate isotherm than Freundlich isotherm for the present system.

Fig. 5 shows experimental data and the predicted equilibrium curve using non-linear method for the two-equilibrium isotherms Freundlich and Langmuir at 303 K, 313 K, 323 K, 333 K and 343 K, respectively. From Table 3, it was observed that at the five solution temperatures of 303 K, 313 K, 323 K, 333 K and 343 K and the various estimated isotherm parameters 303 K was found to be more suitable condition. But in the

case of other temperatures there was a deviation in 313 K, 323 K, 333 K and 343 K, respectively. The results are shown that non-linear method was the best suitable method for prediction of isotherm data compared to the linear method.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The calculated R_L values at different initial concentrations of MB are presented in Fig. 4a and b. The values of R_L lie between $0 < R_L < 1$, thereby confirming that the adsorption is a favorable process. In addition, the low R_L values reveal that the interaction between dye molecules and the PJBC might be relatively strong (Sharma and Forster, 1993). In this work the obtained Langmuir isotherm dimensionless constant separation factor R_L lies between ($0 < R_L < 1$). So the adsorption process is favorable for the adsorption of chromium onto PJBC.

3.4. Kinetic studies

The equilibrium kinetic profiles were characterized to determine the rate limiting steps involved in the process of sorption of Cr onto PJBC. Lagergren's Pseudo first order (Eq. (6)) and Pseudo second order (Eq. (7)) kinetic models were applied (Lagergren, 1898; Allen et al., 2005; Ho and McKay, 1999;

Table 1 Isotherms and their forms.

Isotherms	Non-linear	Linear	Plot	Reference
Freundlich	$q_e = K_F D_e^{1/nF}$	$\log(q_e) = \log(K_F) + \frac{1}{nF} \log(C_e)$	$\log(q_e)$ vs. $\log(C_e)$	Freundlich (1906)
Langmuir-1	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{q_e}$ vs. C_e	Langmuir (1916)
Langmuir-2		$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right) \frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ 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	

Table 2 Isotherm parameters obtained by using linear method.

Isotherms	Parameters	Temperature (K)				
		303	313	323	333	343
Langmuir 1	q_m (mg g ⁻¹)	9.5374	9.4904	10.5452	10.2428	11.2095
	K_a (L mg ⁻¹)	0.0110	0.0111	0.0090	0.0095	0.0080
	r^2	0.9983	0.9933	0.9827	0.9944	0.9810
Langmuir 2	q_m (mg g ⁻¹)	6.6738	6.6085	6.8306	6.7454	6.9478
	K_a (L mg ⁻¹)	0.0483	0.0488	0.0484	0.0491	0.0488
	r^2	0.9151	0.9193	0.9204	0.9354	0.9366
Langmuir 3	q_m (mg g ⁻¹)	0.2263	0.2450	0.2400	0.2351	0.2307
	K_a (L mg ⁻¹)	0.0687	0.0655	0.0652	0.0650	0.0645
	r^2	0.9763	0.9802	0.9801	0.9788	0.9781
Langmuir 4	q_m (mg g ⁻¹)	0.2307	0.1695	0.1654	0.1634	0.2119
	K_a (L mg ⁻¹)	0.0521	0.0642	0.0701	0.0759	0.0746
	r^2	0.9655	0.946	0.9361	0.9320	0.9406
Freundlich	$1/n$	0.2464	0.2482	0.2571	0.2990	0.3659
	K_F (mg g ⁻¹)(L g ⁻¹)	1.1725	1.1849	1.2035	1.2462	1.3058
	r^2	0.9274	0.9356	0.9311	0.9315	0.9353

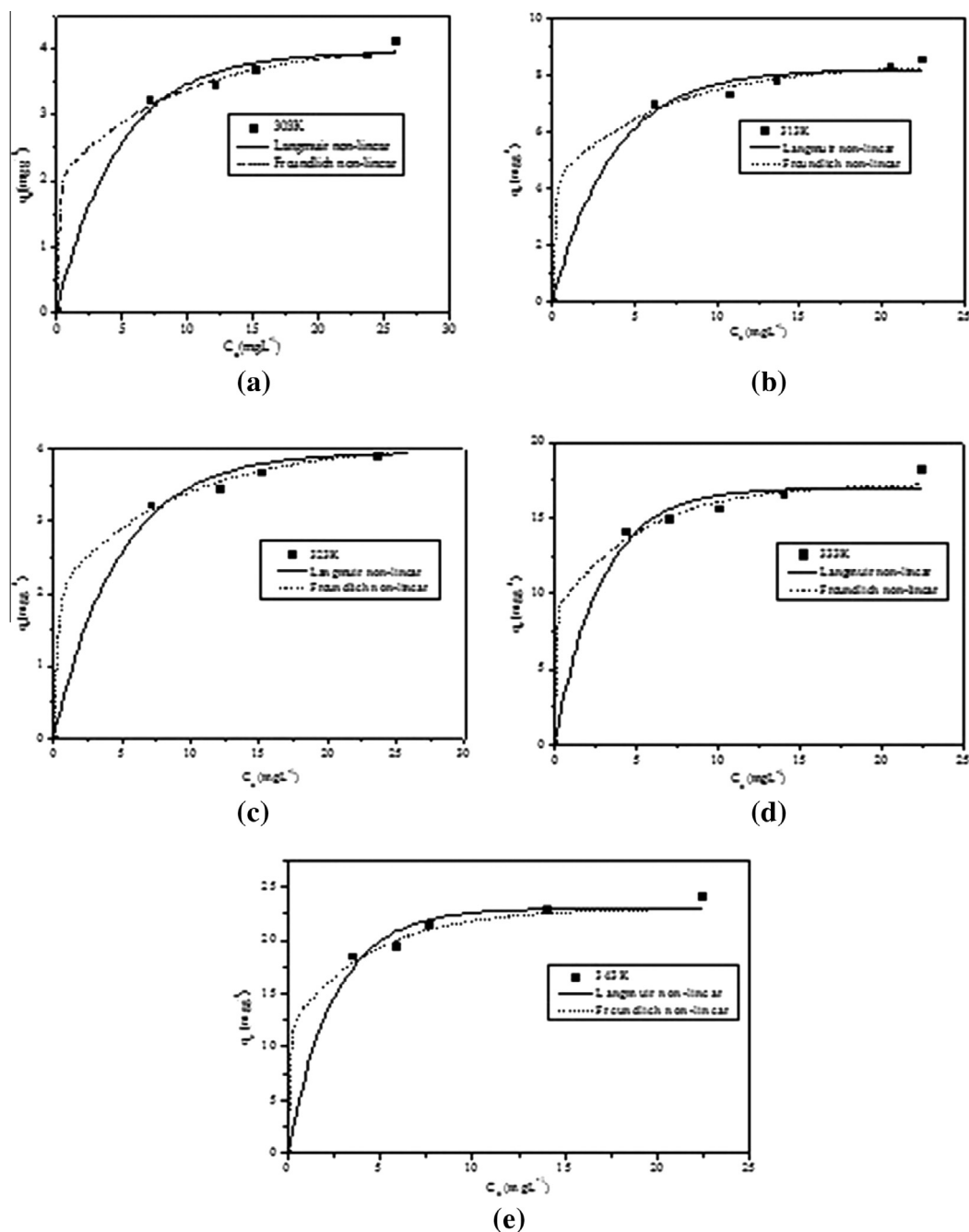


Figure 5 (a) Adsorption isotherm of Cr onto PJBC at 303 K, (b) Adsorption isotherm of Cr onto PJBC at 313 K, (c) Adsorption isotherm of Cr onto PJBC at 323 K, (d) Adsorption isotherm of Cr onto PJBC at 333 K and (e) Adsorption isotherm of Cr onto PJBC at 343 K.

Table 3 Isotherm parameters obtained by using non-linear method.

Isotherms	Parameters	Temperature (K)				
		303	313	323	333	343
Non-linear Langmuir	q_m (mg g^{-1})	0.2024	0.2725	0.2105	0.3510	0.3990
	K_a (L mg^{-1})	0.3753	0.4474	0.6835	0.1678	0.1087
	r^2	0.9996	0.9959	0.9939	0.9956	0.9888
Non-linear Freundlich	$1/n$	0.9396	0.1300	0.7016	0.1900	0.4266
	K_F ($\text{mg g}^{-1})(\text{L g}^{-1})$	0.3753	0.4702	0.4766	0.3002	0.3389
	r^2	0.9719	0.9762	0.9801	0.9622	0.9700

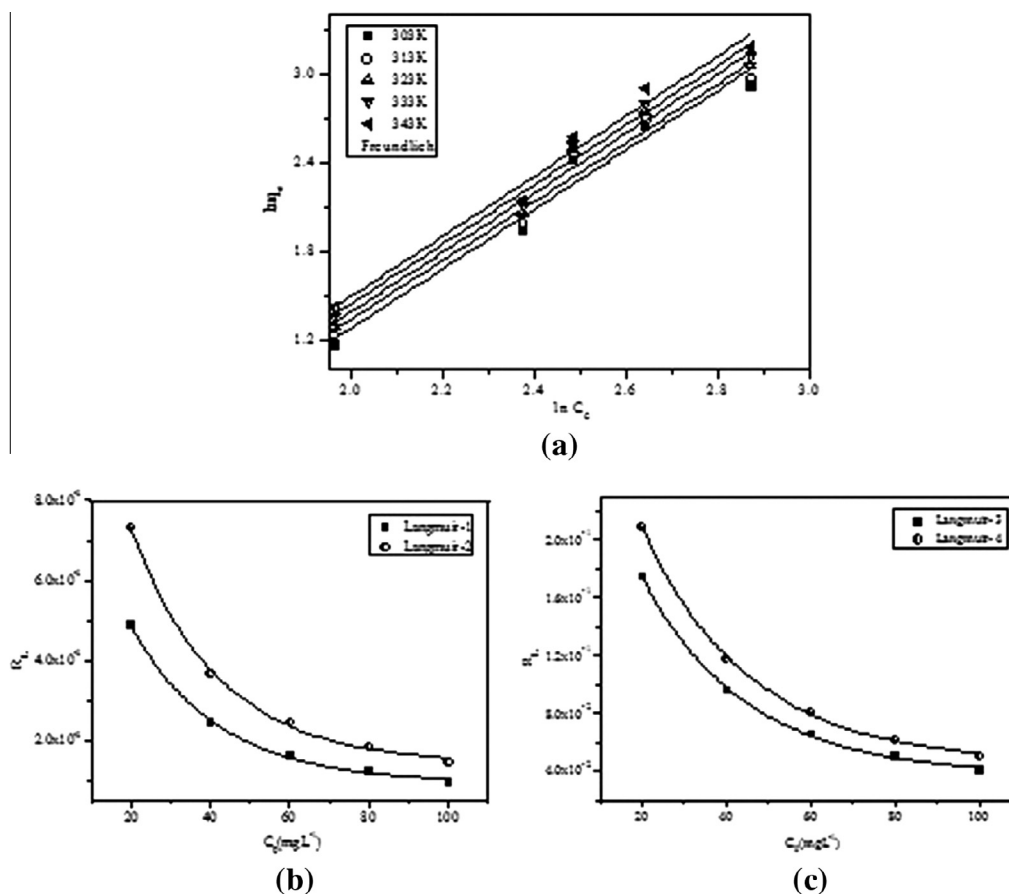


Figure 4 (a) Freundlich isotherm for the adsorption of Cr onto PJBC, (b) Separation factor R_L vs. initial concentration C_0 for Cr onto PJBC and (c) Separation factor R_L vs. initial concentration C_0 for Cr onto PJBC.

Table 4 Pseudo-first order and second order rate equations and their forms.

Type	Non-linear	Linear	Plot	Reference
Pseudo first order	$q = q_e(1 - e^{-K_1 t})$	$\log(q_e - q) = \log q_e - \frac{K_1 t}{2.303}$	$\log(q_e - q)$ vs. t	Lagergren (1898)
Pseudo second order	$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$	$\frac{t}{q} = \frac{1}{K_2 q_e} + \frac{1}{q_e} t$	$\frac{t}{q}$ vs. t	

Hamadi et al., 2001). The linearized form of the pseudo-first order equation is

$$\log(q_e - q) = \log(q_e) - \frac{K_1 t}{2.303} \quad (6)$$

Where, K_1 is the pseudo first order adsorption rate constant, q_e is the amount of dye adsorbed onto PJBC at equilibrium (mg g^{-1}), q_t amount of Cr adsorbed onto PJBC at any time t (mg g^{-1}). The linearized form of the pseudo-second order form is

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where, K_2 is the pseudo second order adsorption rate constant, q_e is the amount of dye adsorbed onto PJBC at equilibrium (mg g^{-1}), q_e^2 is the pseudo second order adsorption rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). Various forms of pseudo-first order and pseudo-second order kinetic equations are presented in the Table 4.

From the experiments (Fig. 6a and b), the calculated value of pseudo-first order rate constant (K_1), pseudo-second order

rate constant (K_2), equilibrium uptake capacity (q_e) and regression coefficient (r^2) are presented in Table 5. From the Table the coefficient values of pseudo-first order rate constant and the obtained q_e values are very low when compared with pseudo-second order kinetic values.

On the other hand the obtained values of pseudo-second order kinetics have shown the correlation coefficient value 0.9861 while pseudo-first order shows 0.8011. Hence, the results intimate that the sorption process follows second order rate equation throughout the process. Moreover, the rate of the process does not depend on the concentration factor (Pseudo-first order) but depends on both concentration as well as time (Pseudo-second order).

3.5. Thermodynamic studies

The effect of heat of adsorption of the adsorbate onto the adsorbent material was determined using the thermodynamic parameters like free energy change (ΔG^0), enthalpy change

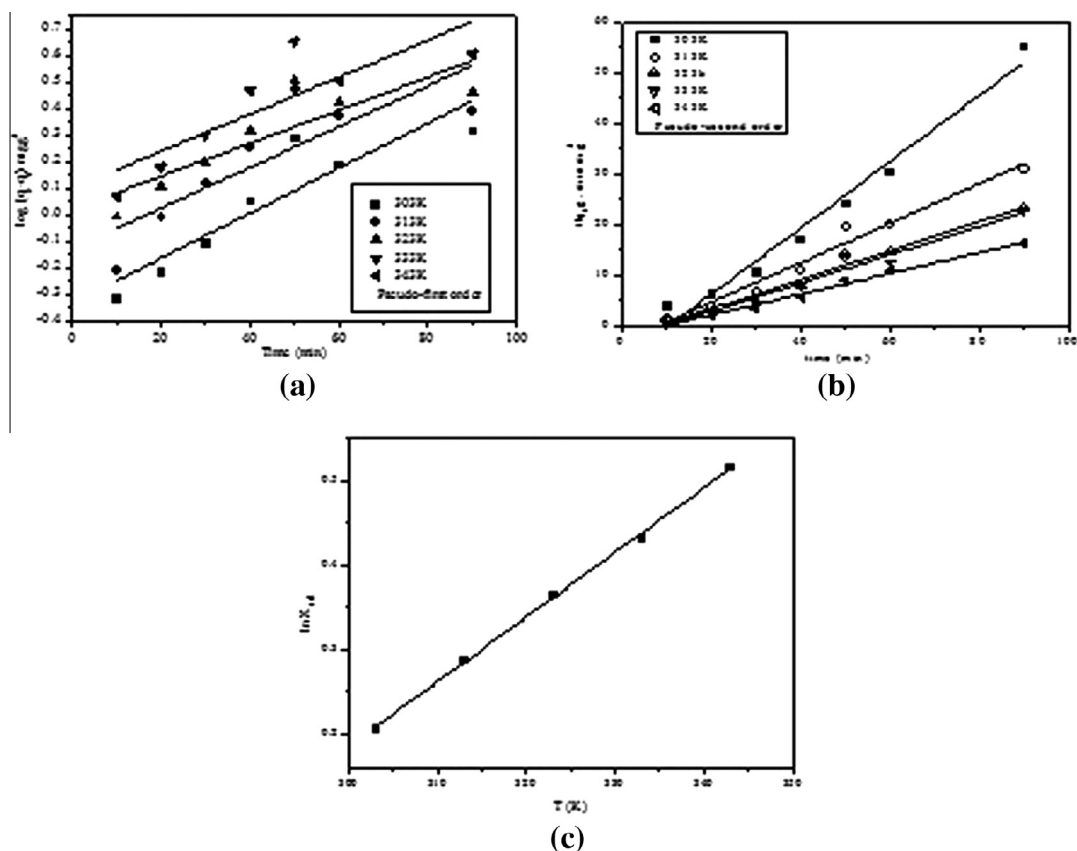


Figure 6 (a) Pseudo-first order kinetic model for the adsorption of Cr onto PJBC, (b) Pseudo-second order kinetic model for the adsorption of Cr onto PJBC and (c) Van't Hoff plot for the adsorption of Cr onto PJBC.

Table 5 Pseudo-first order and second order rate constants for the sorption of Cr onto PJBC.

C_0	Pseudo-first order kinetics			Pseudo second order kinetics			
	K_1	q_e	r^2	q_e .exp	K_2	q_e .cal	r^2
20	0.0194	0.4785	0.8011	6.82	0.0625	1.5308	0.9720
40	0.0176	0.8893	0.6398	14.32	0.0480	2.5579	0.9690
60	0.0143	1.6929	0.6862	10.12	0.0353	3.4917	0.9762
80	0.0160	1.0048	0.6714	14.91	0.0294	3.6033	0.9604
100	0.0160	1.0048	0.6714	17.70	0.0220	4.8845	0.9833
120	0.0168	1.2044	0.7154	19.58	0.0215	5.3584	0.9861
140	0.0156	1.3045	0.6954	21.35	0.0210	5.6584	0.9758

(ΔH^0), and entropy change (ΔS^0), were calculated from the Van Hoff's equation using the following equations (Albadarina et al., 2012; Krishna et al., 2000).

$$K_d = \frac{q_e}{C_e} \quad (8)$$

$$\Delta G = -RT \ln K_d \quad (9)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (10)$$

where, K_d is the distribution coefficient, T – temperature and R – gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$). From Figure, the thermodynamic parameters ΔS^0 and ΔH^0 are calculated using the linear regression analysis of Van't Hoff plot using the parameters $\ln K_d$ vs. $1/T$.

The negative value of the enthalpy change of ΔH^0 value shows that the exothermic nature of the reaction involved during the adsorption process. The entropy (ΔS^0) shows negative value, this indicates that there was a decreased randomness between the solid-solution interface (Wang et al., 2006) during the adsorption process (Table 6). The Gibbs free energy change (ΔG^0) shows a negative value which reveals that the adsorption process is spontaneous in nature for the adsorption of chromium onto PJBC.

3.6. Desorption studies

The presence of chromium(VI) in the environment may create a serious environmental issue because the chromium(VI) ions are highly hazardous to living organisms. So it is essential to

Table 6 Thermodynamic parameters for the sorption of Cr onto PJBC.

T (K)	ΔG^0 (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (kJ mol ⁻¹ K ⁻¹)
303	-0.04	-3.12	-25.58
313	-0.08		
323	-0.12		
333	-0.19		
343	-0.25		

remove the chromium(VI) from the adsorbent after adsorption using the desorption method. The percentage of Cr(VI) desorbed for distilled water using NaOH and HCl shows various desorption percentages as follows 15.65%, 25.43% and 36.56%, 55.07% and 33.24% and 19.38%, respectively. The remaining chromium ions bound to the adsorbent sites may lead to the minimum recovery percentage as compared to the initial desorption on PJBC. The undesorbed chromium(VI) ions present in the aqueous solution after desorption process mainly due to the strong electrostatic interaction (Bulut and Baysal, 2006) may be involved in the adsorption of chromium(VI) onto PJBC.

4. Conclusion

From the experimental results obtained from the present study, the non-linear regression analysis shows better result rather than the linear regression method for both Langmuir and Freundlich equations. Langmuir-I form was the most favorable method for the adsorption of chromium as compared with the other Langmuir equations. Langmuir isotherm dimensionless constant separation factor R_L lies between 0 and 1. So the adsorption process was favorable for the adsorption of chromium onto PJBC. The kinetic result shows that the adsorption process follows pseudo-second order kinetics, which implies that the adsorption process depends on both time and concentration. The thermodynamic parameter change in enthalpy (ΔH^0) shows negative value intimating that the adsorption process was exothermic in nature. The change in entropy (ΔS^0) shows a negative value indicating a decreased randomness between the solid-solution interface. The Gibbs free energy change (ΔG^0) shows a negative value revealing that the adsorption process is spontaneous in nature. The FTIR spectrum shows a well characterized variation before and after adsorption with reduction in peak height and intensity. The SEM images showed a well defined morphological variation in the activated carbon and Cr loaded carbon images. The XRD pattern also evidently shows that the chemical forces adsorption of Cr onto the PJBC. The desorption study shows that the chromium ions were strongly adsorbed onto the PJBC due to the involvement of a strong electrostatic force.

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