Use of orange peel as an adsorbent for the removal of Cr(VI) from its aqueous solution

R M Naik*, Sheel Ratan & Indu Singh

Department of Chemistry, University of Lucknow 226 007
Uttar Pradesh, India

E-mail: radheynaik@gmail.com

The adsorption of Cr(VI) on activated carbon of orange peel (waste material) has been studied. Orange peel after carbonization and acid activation respectively, is found to be highly suitable for the removal of Cr(VI) from its aqueous solution. The effects of adsorbents surface, pH change, concentration of Cr(VI), adsorbent dosages and contact time on Cr(VI) removal have been studied. FTIR, BET and SEM analysis are used to characterize the adsorbent. The UV-Visible spectrophotometric technique is used for the estimation of concentration of Cr(VI) after adsorption. The equilibrium data are applied on Langmuir and Freundlich isotherm models and the values of their corresponding constants are evaluated from the slopes and intercepts of their respective plots. The kinetic data are analyzed using the pseudo-first order, pseudo-second order equations. The results show that the activated carbon of orange peel (ACOP) can be utilized as a low-cost adsorbent for the removal of Cr(VI) ions from its aqueous solution. It's easy availability and abundance makes it a strong choice in the investigation of economic way of metal removal.

The pollution of water resources due to the release of heavy metal ions into our environment is of great concern. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders. Metal contaminants in water are an important class of pollutants due to their toxic effects on human, animals and environment[1-3]. In recent past, several wastewater treatment methods: such as ion exchange and precipitation[4], ultra filtration[5,6], membrane processes and reverse osmosis[7], electro-dialysis[8], solvent extraction[9], adsorption on activated carbon, chemical oxidation/reduction[10,11] etc., have been employed for removal of heavy metal ions from aqueous solutions. Many of these methods are often complicated and time consuming and may be ineffective or expensive and create sludge disposal problem[12-14]. Adsorption on activated carbons is one of the important methods for the removal of heavy metals[15]. Due to the high cost of commercial activated carbons, there is a need to produce cheaper and readily available materials which can be used economically on large scale as low cost adsorbent, the researchers have developed many cheaper alternatives, non-conventional and low cost agricultural by-products as adsorbents, such as fruit peels and fibers[16-19], groundnut shell[20], banana and orange peels[21], Coir-pith[22], tea leaves[23] etc., for the removal of heavy metals from waste water. The use of low cost adsorbents for the water treatment system is a good alternative[24]. In present study a non-conventional adsorbent orange peel was developed, which was used for the removal of Cr(VI) from aqueous solution. The parameters investigated in this study included pH, contact time, initial concentration of Cr(VI), adsorbent dosage and temperature. The kinetics of Cr(VI) adsorption on activated orange peel was also evaluated. The aim of this study was to develop the activated carbons with good adsorption capacity from orange peel, using physiochemical method. The resulting carbons were evaluated for adsorption efficiency and adsorption capacity toward the metal ions Cr(VI).

Experimental Section

Preparation of adsorbent

The orange peel used in this study was obtained from local juice market, Lucknow, Uttar Pradesh, India. The orange peel was extensively washed with distilled water 2-3 times to remove soil and dirt particles from surface and dried for 2-3 days and after that in a hot air convection oven at 60°C for 48 h. washed and dry orange peel carbonized in muffle furnace at 200°C for 2 h in inert atmosphere of CO_2. After carbonization, the carbonized orange peel was milled into a powder using grinder and washed with double distilled water for 2-3 times and dried in air oven at 110°C. Washed and dried carbonized orange peel (100g) was soaked in 1.0 L of 40% H_2SO_4 in a mechanical shaker at 300 rpm for 24. The acid activated carbonized orange peel (ACOP) filtered and rinsed with double distilled water, until the pH was neutral than dried for 4- 6 hr at 110°C in air oven and

sieved to obtain constant size particles (100 µm). The dry and sieved ACOP sealed in an air tight container and stored in desiccators for further use.

Preparation of stock solution

The stock solution of Chromium-metal ions (1000 mg/L) has been prepared by dissolving calculated quantity of $K_2Cr_2O_7$ in de-ionized water. Other sample solutions were prepared by diluting the stock solution. All other chemicals used in this study were AR Grade.

Batch adsorption studies

The adsorption experiments were conducted by mixing various amounts of ACOP (0.5-10.0 g/L) in 50 mL of Cr(VI) aqueous solution(100 mg/L concentration) in 100 ml conical flasks. The effect of pH was studied in the range of 1.5-6.0. The effect of initial metal-ion concentration on the metal removal was studied in the range of 25-300 mg/L at optimal conditions of pH (2.5), contact time (120 min), temperature (30°C) and adsorbent dosage (5 mg). The results of these equilibrium studies were verified with Langmuir and Freundlich isotherms. Metal-ions concentration was analyze by using double beam UV-Visible spectrophotometer (Systronic 2203). The amount of metal-ions adsorbed (q_e) from aqueous solution and percentage removal of metal-ions were determined by using the following equations.

$$q_e = \frac{(C_o - C_e)V}{m} \qquad \qquad ...(1)$$

$$\% \text{ Removal} = \frac{(C_o - C_e)V}{C_o} * 100 \qquad ...(2)$$

where, C_o and C_e are the initial and equilibrium concentration respectively of metal-ion solution, V is the volume of Cr(IV) solution in L, m is the amount of adsorbent in g.

Characteristics techniques

The surface area and pore size of the ACOP was measured by using BET technique (BEL Japan). SEM (scanning electron microscope) used to determine surface morphology of ACOP. The FT-IR spectra of ACOP before and after adsorption of Cr(VI) were obtained to demonstrate the functional groups on surface.

Results and discussion

Characteristics of the adsorbent

The surface area and pore size of the ACOP was determined by adsorption phenomenon. The BET

surface area of ACOP was found to be 4.3312 m^2/gm and mean pore diameter is 21.793 nm by using. The irregular and porous structures on surface of adsorbent examined by SEM are shown in Fig. 1, which plays an important role in adsorption[25]. Fourier transform infrared spectra (FTIR) was used to investigate the changes in vibrational frequency in the functional groups of the adsorbents due to Cr(VI) adsorption. The adsorbent was scanned in the spectral range of 4000-400 cm^{-1}. Figure 2 shows the FTIR spectra of ACOP before and after adsorption was studied. The spectra indicated a number of changes in
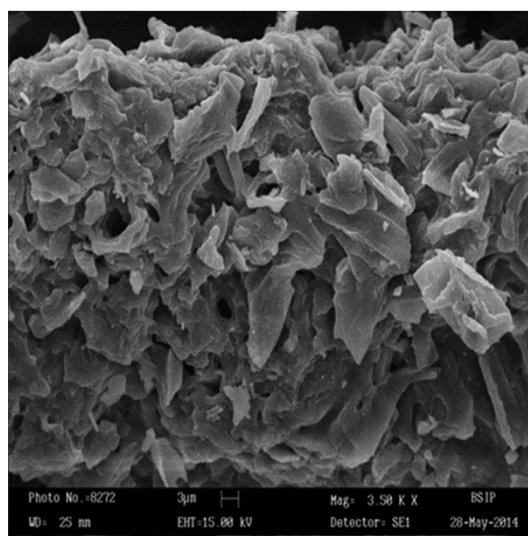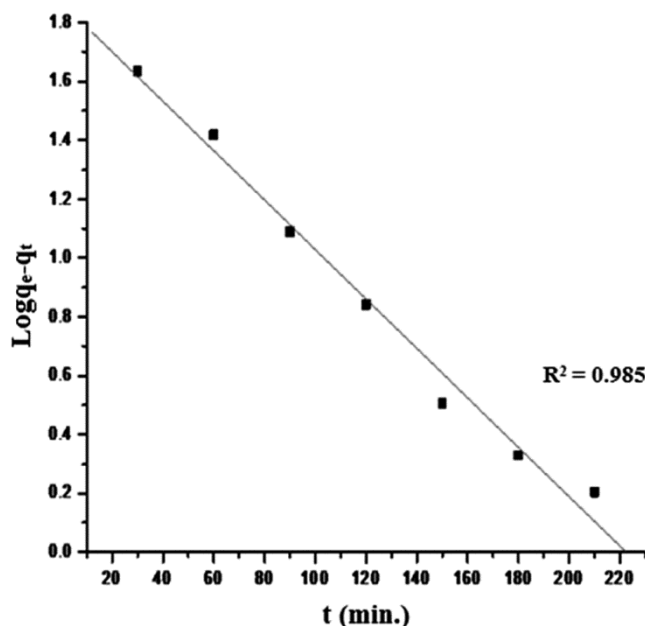

Fig. 1 — SEM image of ACOP.

Fig. 2 — Pseudo-first order plots for adsorption of Cr (VI) on ACOP.

peaks, which show the complex nature of the adsorbent. The functional group is one of the key factors to understand the mechanism of metal binding process on natural adsorbents. Table 1 represented the shift in the wave number of dominant peak associated with the fresh and Cr(VI) loaded ACOP in the FT-IR plots. The shifts in the wave length showed that there was metal binding process taking place at the surface of the ACOP[26,27]. There was a clear shift from wave number of 3404.25 cm^{-1} (orange peel) to 3431.26 cm^{-1} (metal-ion loaded orange peel), which indicate surface –OH group is one of the functional group responsible for adsorption Cr(VI) on ACOP. Aliphatic C-H stretching (2922.91 cm^{-1} to 2927.99 cm^{-1}) and aromatic C=C stretching (1588.17 cm^{-1} to 1596.28 cm^{-1}) may be responsible for Cr(VI) adsorption onto ACOP. The shift in the absorption peaks generally observed indicates the existence of metal binding process taking place on the surface of ACOP.

Effect of *p*H

The *p*H of the aqueous metal solution is an important operating variable in the adsorption process because the values of *p*H affect the surface properties of the adsorbent. The effect of *p*H on the adsorption of chromium by orange peel was studied by varying the initial *p*H in the range of 1.5-6.0 under constant process parameters at equilibrium conditions. The results show maximum adsorption between 1.5-3.5 *p*H. Lower value of *p*H favor the adsorption with increase in *p*H from 3.5 to 6.0, the removal percentage decreased.

Effect of adsorbent dosage

The surface area made available for the contact with the adsorbate is decided by the amount of adsorbent used, so adsorbent dosage is an important parameter. Therefore, the effect of ACOP dosage on Cr(VI) removal was studied in the range of 0.25-10.0 g/L while keeping other parameters at optimal. The percentage metal removal was 21.2539 % (at 1.0 g/L of adsorbent dosage) and increased to 96.4874 % (at 10.0 g/L of adsorbent dosage). The increase in removal percentages with increasing ACOP dosage is related

to the increase in surface area and by extension the increased number of ion exchangeable sites available for interaction with chromium ions. The decrease in metal adsorbed (gm/g) with increase in dosage is due to the increase in surface vacant site. Thus, the optimal adsorbent dosage was identified as 5.0 g/L for this experiment.

Effect of contact time

The effect of contact time between adsorbent and initial metal ion concentration on the batch adsorption of metal solution containing 100 mg/L of Cr(VI) at 30°C and *p*H 2.5 is shown in. It was observed that the general uptake rate was fast during first 2 hr. After which adsorption was achieved a steady state. The initial rapid uptake rate within the first 2 hr may be due to the more availability of the surface vacant sites.

Effect of Initial metal-ion concentration

The effect of initial metal-ion concentration on the metal removal was studied in the range of 0-300 mg/L at optimal conditions of *p*H, contact time and adsorbent dosage. It was observed that the percentage removal of metal-ion decrease with increase in initial metal-ion concentration of Cr(VI).

Kinetic studies

In this study, Pseudo first order and pseudo second order kinetic models were used to analyze the nature of the adsorption kinetics for Cr(VI) on ACOP. Specifically, the results obtained for adsorption of Cr(VI) onto ACOP as function time were fitted to pseudo-first order and pseudo second order. The Lagergren[28] first-order reaction rate model (pseudo-first order adsorption kinetics) is represented as

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1 t}{2.303}\right) \qquad ...(3)$$

where q_e (mg/g) is the maximum adsorption capacity at equilibrium and q_t (mg/g) is the amount of metal-ion adsorbed at time, t, and k_1 (min^{-1}), k_2 (g/mg min) are the equilibrium rate constants for pseudo-first order (Fig. 2) and pseudo-second order (Fig. 3) kinetics respectively.

Ho's[29] second-order reaction rate model (pseudo-second order adsorption kinetics) is represented as

$$\frac{t}{q_t} = \frac{1}{k_2 q_1^2} + \frac{1}{q_e} t \qquad ...(4)$$

Results of the kinetic data indicated that the pseudo-second order model best describes the

Table 1 — Wave number (cm^{-1}) for the dominant peak from FT-IR for Cr(VI) adsorption.

Functional Groups	ACOP	Cr(VI) loaded ACOP
Surface O-H stretching	3404.25 cm^{-1}	3431.26 cm^{-1}
Aliphatic C-H stretching	2922.91 cm^{-1}	2927.99 cm^{-1}
Aromatic C=C stretching	1588.17 cm^{-1}	1596.28 cm^{-1}

adsorption of Cr(VI) on ACOP. The R^2 value for the pseudo-second order was higher than that of pseudo first order kinetic model.

Adsorption isotherms

Adsorption isotherms describe the behaviour of adsorption process and interaction of the adsorbate with the adsorbent. In the present work, two adsorption isotherms, Langmuir and Freundlich, were used for fitting the obtained experimental adsorption data.

Langmuir isotherm

The Langmuir isotherm (Fig. 4) explains monolayer adsorption, the linearized form of Langmuir isotherm[30] can be represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \qquad ...(5)$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of metal ion adsorbed per unit mass of adsorbent at equilibrium (mg/g), q_{max} is the theoretical maximum adsorption capacity (mg/g), K_L is the Langmuir isotherm constant (L/mg). The values of R^2, K_L and q_{max} are listed in Table 2, was determined from the slopes and intercepts of the linear plots of C_e/q_e against C_e.

Freundlich isotherm

Freundlich isotherm (Fig. 5) explains heterogeneous surfaces and multilayer adsorption, the linearized form of Freundlich isotherm[31] can be represented by the following equation.

$$Logq_e = LogK_F + \frac{1}{n} LogC_e \qquad ...(6)$$

where: q_e is the amount of metal ion adsorbed per unit mass of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), K_F is the Freundlich adsorption constant related to the adsorption capacity of the adsorbent K_F (mg/g) $(mg/L)^{1/n}$ and n are dimensionless constants of the adsorbents, which can be used to explain the adsorption intensity between the solute concentration and adsorbent respectively. The values of R^2, K_F and n are listed in Table 2, was determine from the slopes and intercepts of the linear plots of Log q_e against Log C_e.

Thermodynamic studies

The effects of temperatures on the adsorption of Cr(VI) onto ACOP surface have been presented in
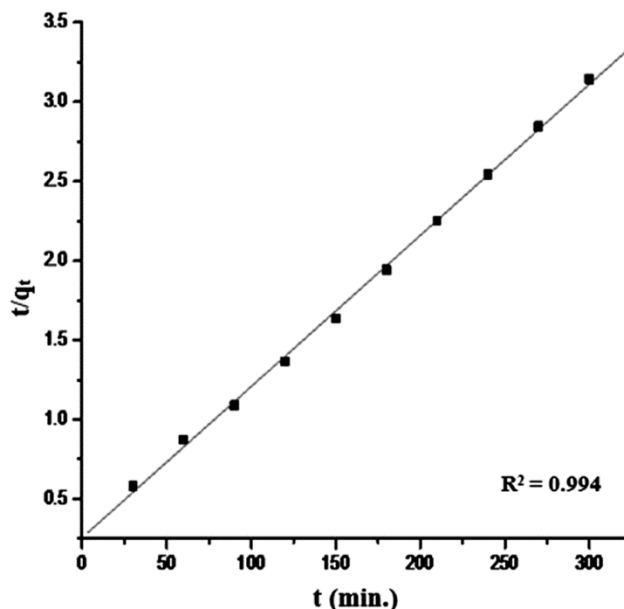
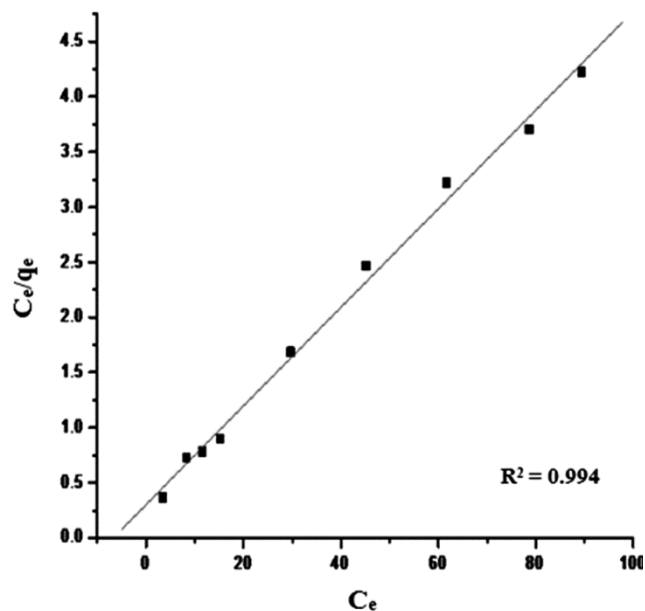Fig. 3 — Pseudo-second order plots for adsorption of Cr (VI) on ACOP.

Fig.4 — Langmuir studies of equilibrium

Table 2 — Langmuir and Freundlich Isotherm constants for the adsorption of Cr(VI) ion onto ACOP

Langmuir isotherm			Freundlich isotherm		
q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g)	R^2
22.72727	0.1462	0.994	4.2918	73.0979	0.916

Fig. 6. The graph shows slight increase in adsorption on increase in temperature. This may be due to a greater kinetic energy acquired by the metal-ions with increase in temperature. The correlation of standard
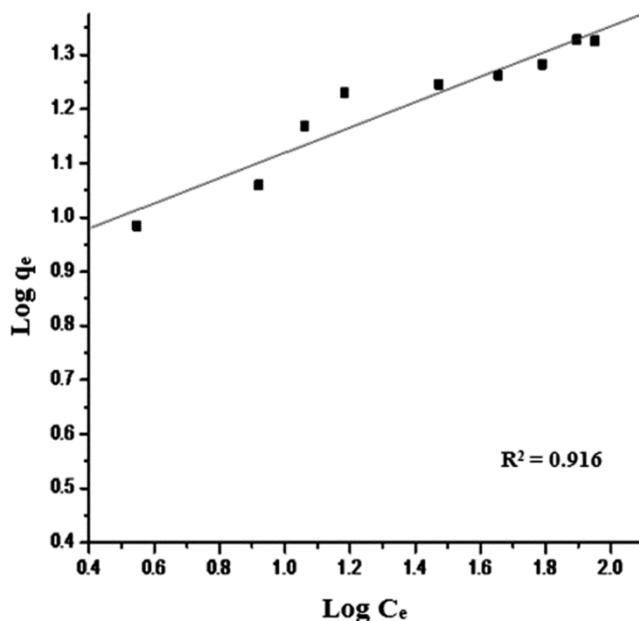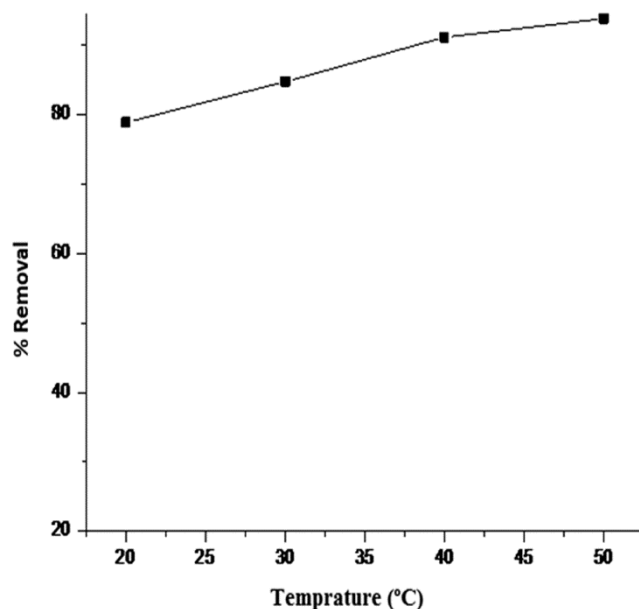
Fig. 5 — Freundlich studies of Equilibrium

Fig. 6 — The effect of temperature on percentage removal of Cr(VI) from solution onto ACOP. Initial metal ion concentration 100 mg/L, *p*H 2.5, adsorbent dose 5.0 g, and contact time 120 min.

Gibbs free energy ($\Delta G°$) and thermodynamic equilibrium constant Kc can be expressed by following equation.

$$\Delta G° = -RT \text{ Ln Kc} \qquad ...(7)$$

Adsorption enthalpy ($\Delta H°$), and adsorption entropy ($\Delta S°$), is related to the standard Gibbs free energy ($\Delta G°$) presented by Van't Hoff equation[32].

Table 3 — Thermodynamic parameters for the adsorption of Cr(IV) from solution onto ACOP.

T (K)	Kc	$\Delta G°$(kj/mol)	$\Delta H°$	$\Delta S°$	R^2
293	3.7348	−3.2098	37.937	140.09	0.990
303	5.5568	−4.3204			
313	10.3016	−6.0693			
323	15.1799	−7.3042			

$$\text{Ln Kc} = -\left(\frac{\Delta G°}{RT}\right) = -\left(\frac{\Delta H°}{RT}\right) + \left(\frac{\Delta S°}{R}\right) \qquad ...(8)$$

Kc is defined by following equation

$$\text{Kc} = \frac{C_a}{C_e} \qquad ...(9)$$

where: C_a is the amount of metal-ions adsorbed at equilibrium and C_e is the equilibrium concentration.

The values of $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of the plot (ln Kc versus 1/T) and the calculated thermodynamic parameter values are presented in Table 3.

Conclusion

The study successfully demonstrated the application of carbonized and acid activated orange peel powder as an adsorbent for the removal of Cr (VI) ions. An increase in *p*H was favourable up to 3.5 where an increase in adsorbent dosage resulted in increased removal efficiencies and decreased uptake capacities. The Langmuir isotherm was demonstrated to provide the best fit for the equilibrium adsorption data confirming a monolayer adsorption pattern. The pseudo-second order model fitted well (with $R^2 > 0.99$) for the kinetic data. From this study, we conclude that activated orange peel powder can be used for the removal of Cr(VI) from aqueous solution.

Acknowledgements

References

1   Ko DCK, Porter J F & Mckay G, *Chem Eng Sci*, 55 (2000) 5819.
2   Thirumavalavan M, Lai Y L, Lin L C & Lee J F, *J Chem Eng Data*, 55 (2010) 1186.
3   Yaoa Z Y, Qib J H & Wanga L H, *J Haz Mater*, 174 (2010) 137.
4   Feng D, Aldrich C & Tan H, *Min Eng*, 13 (6) (2000) 623.
5   Canizares P, de Lucas A, Pérez A & Camarillo R, *J Membr Sci*, 253 (2005) 149.

6   Trivunac K & Stevanovic S, *Chemosphere*, 64 (2006) 486.
7   Ozaki H, Sharma K & Saktaywin W, *Desalination*, 144 (2002) 287.
8   Marder L, Sulzbach G O, Bernardes A M & Ferreira J Z, *J Electrochem Soc*, 14 (2003) 610.
9   Yun C H, Prasad R, Guha A K & Sirkar K K, *Ind Eng Chem Res*, 32 (1993) 1186.
10 Zhang F S & Itoh H, *Chemosphere*, 65 (1) (2006) 125.
11 Yoona J, Shimb E, Baec S & Jooa H, J Haz Mater, 16 (2–3) (2009) 1069.
12 Meena A & Rajagopal C, *Indian J Chem Technol*, 310 (2000) 72.
13 Cossich E S, Da Silva E A, Tavares C R G, Filho L C & Ravagnani T M K, *Adsorption* 10 (2004) 129.
14 Sud D, Mahajan G & Kaur M P, *Bioresour Technol*, 99 (2008) 6017.
15 Amarasinghe B M W P K & Williams R A, *Chem Eng J*, 132 (1–3) (2007) 299.
16 Davis T A, Volesky B & Mucci A, *Water Res*, 37 (18) (2003) 4311.
17 Saeed A, Iqbal M & Akhtar M W, *Sep Purif Technol*, 45 (2005) 25.
18 Iqbal M & Saeed A, *Environ Environmental Technol*, 23 (2002) 1091.
19 Lai Y L, Annadurai G, Huang F C & Lee J F, *Bioresour Technol*, 99 (14) (2008) 6480.
20 Ajmal M, Rao R A K, Ahmad J & Ahmad R, *J Environ Sci Eng*, 48 (3) (2006) 221.
21 Annadurai G, Juang R S & Lee D J, *J Haz Mater*, 92 (3) (2002) 263.
22 Amarasinghe B M W P K, *J Trop Forestry Environ*, 01 (1) (2011) 36.
23 Ahluwalia S S & Goyal D, *Eng Life Sci*, 5 (2005) 158.
24 Lim Ai P & Aris A Z, *Rev Environ Sci Biotechnol*, 13 (2014) 163.
25 Vafakhah S, Bahrololoom M E, Bazarganlari R & Saeedikhani M, *J Environ Chem Eng*, 2 (2014) 356.
26 Srivastava V C, Mall I D & Mishra I M, *J Haz Mater*, B134 (2005) 257.
27 Pavasnt P, Apiratikul R, Sungkhum V, Suthiparinyanont P, Wattanachira S & Marhaba TF, *Bioresour Technol*, 97(18) (2006) 2321.
28 Lagergren S, *Ksven Vetenskapsakad Handl*, 24 (4) (1898) 1.
29 Ho Y S & Mckay G, *Can J Chem Eng*, 76 (1998) 822.
30 Langmuir I, *J Amer Chem Soc*, 40 (1918) 1361.
31 Freundlich H M F, *J Phys Chem*, 57 (1906) 385.
32 Liang S, Guo X, Feng N & Tian Q, *J Hazard Mater*, 174 (2010) 756.