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Chitosan Capped Nanozerovalent Iron as A Cost-Effective Adsorbent for the Removal of CR(VI) from Aqueous Solution : Equilibrium And Kinetics

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Abstract : The present study has been attempt to evaluate the removal of hexavelent chromium from aqueous solution using chitosan capped nanozerovelent iron as an cost effective adsorbent under various experimental parameters. The chitosan capped nanozerovelent iron was synthesized by the aqueous phase borohydride reduction method and the synthesized particles were characterized through X-ray diffractogram and scanning electron microscopy. Results on hexavalent chromium reduction indicated that chitosan capped nanozerovelent iron rapidly reduce hexavalent chromium in aqueous solution. The removal efficiency of hexavalent chromium increased with increasing adsorbent dosage and temperature whereas inversely with initial chromium concentration and pH. Maximum reduction rate (98.5%) was obtained when the concentration of adsorbent dosage at 0.4 g/L, and also chitosan capped nanozerovelent iron exhibited excellent adsorbent at an acidic pH. The adsorption kinetic mechanism was investigated using pseudo first order rate reaction. Moreover, the adsorption data on reduction of hexavalent chromium by chitosan capped nanozerovelent iron were then fitted with Langmuir and Freundlich isotherm models. Results obtained from this study indicated that nanozerovalent iron in the presence of chitosan would be a suitable and low cost adsorbent for the treatment of hexavalent chromium in aqueous environment.

Keywords : Nanozerovalent iron, Hexavalent chromium, Chitosan, Chemical reduction, Adsorption kinetics.

1. Introduction

Environmental contamination by heavy metals is a wide spread problem, with sources of pollution arising from industrial activities.Chromium (Cr) is the most frequent metal contaminants in the wastewaters. It is one of the top 20 contaminants on the superfund priority list of hazardous substances for the past 15 years[1]. It exists mainly in two oxidation states namelyhexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)]. Cr(VI) is extremely mobile in the environment and is toxic to humans, animals, plants, and microorganisms whereasCr(III)is less toxic, immobile and readily precipitates as $Cr(OH)_3$[2]. Because of its significant mobility, the maximum concentration limit for the discharge of Cr(VI) into inland surface water is 0.1 mg/L and in

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potable water is 0.05 mg/L[3].There are several techniques are available for Cr(VI) removal such as ion exchange, filtration, electrochemical precipitation, activated carbon adsorption, bioremediation, etc., However, these conventional methods are expensive and complicated.Thus a cost effective, easy to use and environmental friendly technique has been sought for the remediation of Cr(VI) contaminated sites.Nowadays, use of zerovalent iron (Fe^o) nanoparticles is becoming an increasingly popular method for treatment of hazardous and toxic wastes and for remediation of contaminated soil and ground water[4]. This is because, Fe^o nanoparticles provide a high surfacetovolume ratiowhich promotes mass transfer to and from the solid surface resulting in high potential for contaminant removal and degradation[5].Normally Fe^o nanoparticles are prepared by borohydride reduction of ferrous [Fe(II)] or ferric [Fe(III)] ions in aqueous solution. But it was observed that Fe^o nanoparticles prepared by this method tend to rapidly agglomerate to form larger aggregates due to Vander Waals and magnetic forces, rendering them undeliverable to the targeted contaminant locations[6]. In order to prevent aggregation, particle stabilization has been commonly adopted by attaching a stabilizer such as a soluble polymer or surfactant onto the nanoparticles[7].Chitosan is a well known biopolymer which is typically obtained by deacetylation of chitin under alkaline conditions. Chitosan displays interesting properties such as biocompatibility, biodegradability and its degradation products are non-toxic, non-immunogenic and non-carcinogenic. Hence the goal of present work is to test the ability of nanozerovalent ironin the presence of chitosan as capping agent to remove Cr(VI) from aqueous solution and evaluate the influence of adsorbent dosage, Cr(VI) concentration, variation in pH and temperature on the kinetics of Cr(VI) reduction.

2. Materials and Methods

2.1 Materials

Ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), Potassiumborohydride (KBH_4), Chitosan, 1, 5-Diphenylcarbazide ($C_{13}H_{14}N_4O$), Nitric acid (HNO_3) and Ethanol (C_2H_5OH) were purchased from Himedia (P) Ltd, Mumbai were used as starting materials without further purification. Potassium dichromate ($K_2Cr_2O_7$) was used as a model contaminant. Milli-Q water was used throughout the experiment.

2.2 Methods

2.2.1 Preparation and characterization of chitosan capped nanozerovalent iron (CH-Fe^o)

In the present study nanoscalezerovalent iron was fabricated using chitosan as a capping agent[8],.The resultant black colornanoparticles were separated from the solution by centrifugation at 4000 rpm for 5 min and then washed with N_2 saturated deionized water and at least three times with 99% absolute ethanol. Finally, the synthesized particles were dried in a hot air oven at 60^oC and the resultant particles were used for further analysis.X-ray diffraction patterns of synthesized nanoparticles were analyzed with an X'pert PROPAN analytical instrument and the average size of the particles was estimated using the Debye-Scherer's equation. Morphology of the as prepared chitosan capped nanozerovalent ironwasobserved by Scanning Electron Microscope (SU 1510).

2.3 Cr(VI) reduction studies

2.3.1 Adsorption experiments

The efficacy of chitosan capped nanozerovalent iron on the removal of Cr(VI) was evaluated under the influence of various parameters[9].The parameters used in the present investigation such asadsorbent dose (0.1 g/L to 0.4 g/L), initial Cr(VI) concentration (10 mg/L to 25 mg/L), pH (3 to 10) and temperature (15^oC to 45^oC). The percentage removal efficacy of Cr(VI) by CH-Fe^o was calculated spectrophotometrically using the formula,

$$\text{Percentage Removal of Cr(VI)} = \frac{\text{Co}-\text{Ce}}{\text{Co}} X100$$

Where, C_o and C_e represent initial and final concentration of Cr(VI).

The overall removal rate ofCr(VI) by CH-Fe^ocan be described using pseudo first order kinetic equation[10].

$$\ln[\text{Cr(VI)}]/[\text{Cr(VI)}_o] = -k_{obs}t$$

where, $[Cr(VI)_o]$ and $[Cr(VI)]$ are the initial and instantaneous Cr(VI) reactions in mg/g respectively. t is the reaction time (min) and k_{obs} is the observed pseudo-first order rate constant (min^{-1}). The k_{obs} values were calculated from the slope of the line for $\ln[Cr(VI)]/[Cr(VI)_o]$ versus reaction time.

2.3.2 Adsorption kineticsand isotherms

Adsorption kinetics describe the rate of uptake of chromium ions onto the CH-Fe^o.The amount of Cr(VI) adsorbed by CH-Fe^{o}was calculated from the difference between Cr(VI) reduction at an initial and equilibrium state, q_e was calculated by

$$q_e = (C_o - C_e) \text{ X } V/M$$

Where q_e (mg/g) is the amount of adsorbed Cr(VI) onto adsorbent, C_o (mg/L) the initial Cr(VI) concentration, C_e (mg/L) the Cr(VI) concentration after a certain period of time t, V (L) the volume of solution and M (g) the mass of the adsorbent used.

To examine the relationship between adsorbate concentrations in the aqueous phases at equilibrium, adsorption isotherm models are widely employed. The Langmuir and Freundlich models are most widely used to test equilibrium data of adsorption. The linerarized forms of the two isotherms are given as follows

$$\frac{C_e}{qe} = \frac{1}{q_m K_q} + \frac{1}{q_m} C_e$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where$q_e$and $C_e$are the equilibrium concentration of Cr(VI) in the adsorbed (mg/g) and aqueous phases (mg/L) respectively. q_m and $K_q$are the Langmuir constants related to adsorption capacity and energy of adsorption respectively, while $K_f$and $n$are Freundlich constants.

3. Results and Discussion

3.1 Preparation and characterization of chitosan capped nanozerovalent iron

CH-Fe^o nanoparticles were fabricated by aqueous phase borohydride reduction of Fe(II) ions in the presence of chitosan as capping agent. The X-ray diffraction pattern shows that the synthesized nanoparticles were in amorphous stage and in tetragonal system. In the respectivenanoparticles, the intensive diffraction peaks were observed at a 2θ value of 44.77° from the lattice plane (110) of body centered cubic (bcc) Fe unequivocally indicates that the particles are made of pure iron (Fig. 1).Characteristic peak appearing at 2θ value of 44.76° indicates the crystalline nature of Fe^{o}nanoparticles[11].The size of the particles was found to be 16.29 nm.Morphology of the nanoparticles revealed that the particles are almost spherical in nature (Fig.2).

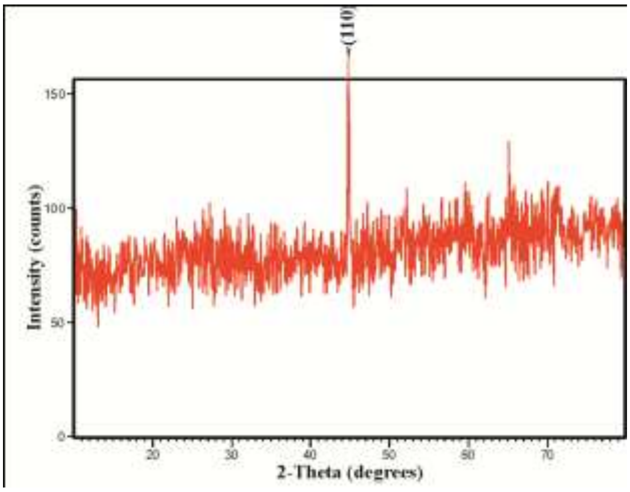

Fig.1. X-ray diffractogram of chitosan capped nanozerovalent iron

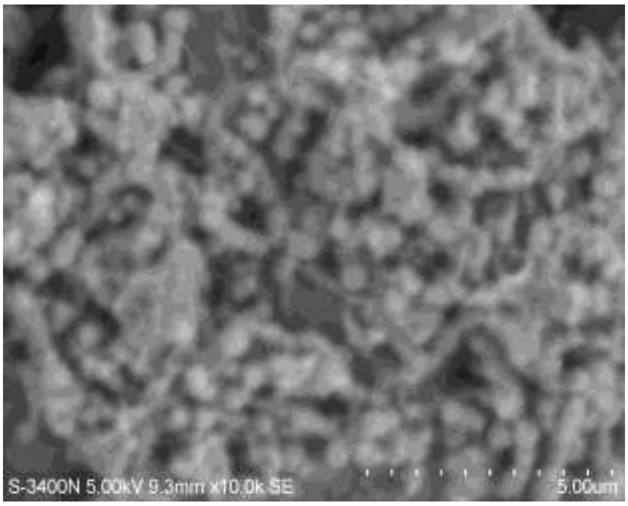

Fig.2.Scanning electron micrograph of chitosan capped nanozerovalent iron

The micrograph showed that the synthesized particles did not appear as discrete particles but form much larger dendritic flocs. The aggregation is attributed due to the vandarwaals forces and magnetic interactions among the particles. This finding is very much closer to the earlierreport[12].

3.2 Cr(VI) reduction studies

3.2.1 Effect of adsorbent dosage

The effect of adsorbent dosage on the percentage removal of Cr(VI) is shown in Fig. 3a. It showed that rapid increase in the reduction of Cr(VI) from 37.0% to 98.5% with the increase in the concentration of CH-Fe^{o}from 0.1g/L to 0.4g/L. It is believed that the Cr(VI) reductive reaction occurs on the nanoparticle surfaces. Reaction kinetics of Cr(VI) with CH-Fe^{o} showed pseudo-first order reaction and their rate constants are give in Table 1. Increasing the percentage of adsorption with adsorbent dose may be due to the increase in adsorbent surface area and availability of more adsorption sites[13].

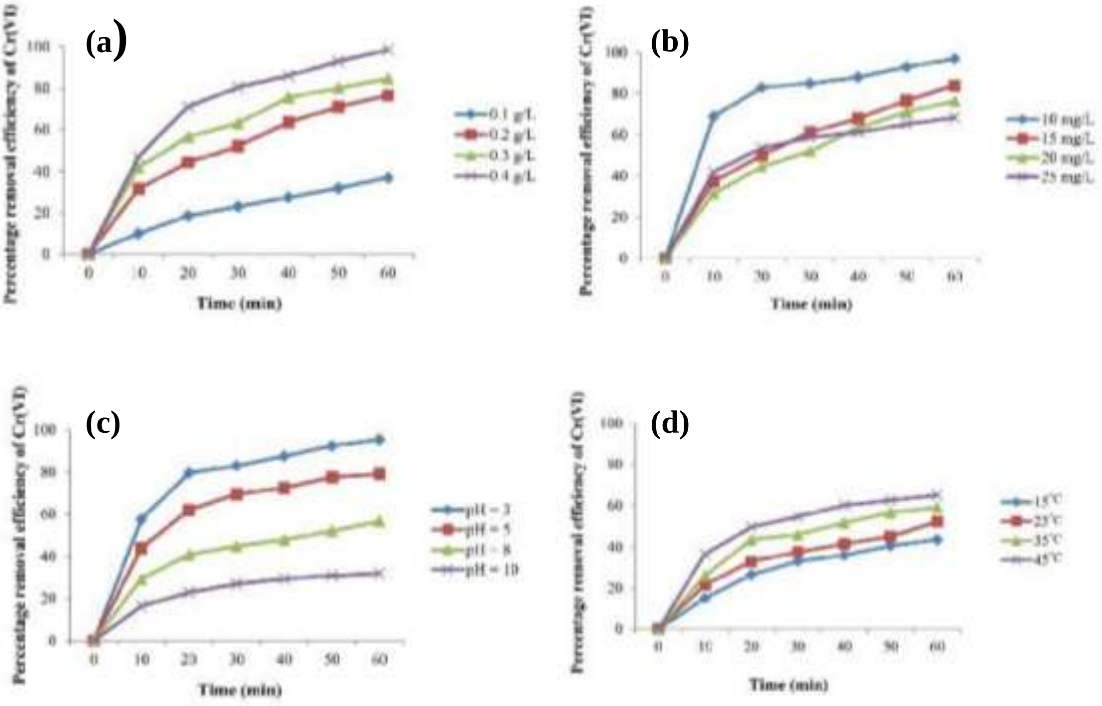

Fig. 3. Effect of initial adsorbent concentration (a), Cr(VI) concentration (b), pH (c), and temperature (d) on Cr(VI) removal efficiency by chitosan capped nanozerovalent iron

Table 1: Effect of various parameters on Cr(VI) reduction rate constants and their half lives for chitosan capped nanozerovalent iron

Parameters	**k_{obs}(min^{-1})**	**$t_{1/2\ obs}$ (min)**	**r^2**
Initial conc. of Fe^o (g/L)			
0.1	11.8± 1.2 x 10^{-3}	59.21± 6.26	0.989
0.2	42.8± 4.6 x 10^{-3}	16.37± 1.75	0.993
0.3	55.2± 4.0 x 10^{-3}	12.63± 0.87	0.997
0.4	68.7± 7.3 x 10^{-3}	10.19± 0.95	0.997
Initial conc. of Cr(VI) (mg/L)			
10	108.2± 9.5 x 10^{-3}	6.47± 0.65	0.999
15	50.3 ± 4.3 x 10^{-3}	13.87± 1.10	0.998
20	42.8 ± 4.6 x 10^{-3}	16.37± 1.75	0.993
25	47.5± 5.4 x 10^{-3}	14.79± 1.74	0.991
Initial pH			
3	80.6± 6.3 x 10^{-3}	8.65± 0.77	0.997
5	57.2± 3.2 x 10^{-3}	12.17± 0.72	0.998
8	33.2± 2.4 x 10^{-3}	21.01± 1.59	0.997
10	18.0 ± 2.4 x 10^{-3}	39.09± 4.46	0.991
Initial temp. (°C)			
15	16.0 ± 1.2 x 10^{-3}	43.55± 3.31	0.994
25	24.3± 7.5 x 10^{-3}	28.51± 0.89	0.998
35	26.8± 2.8 x 10^{-3}	26.10± 2.66	0.994
45	46.0 ± 1.8 x 10^{-3}	15.09± 0.61	0.996

3.2.2 Effect of Cr(VI) concentration

Cr(VI) adsorption was significantly affected by the initial concentration of Cr(VI) in the aqueous solutions. The results showed that increase in initial concentration of Cr(VI) led to decrease in the Cr(VI) percentage adsorption from 97.0% to 68.4% (Fig. 3b) due to saturation of the sorption sites on adsorbents.The rate constant values are decreased with increasing initial Cr(VI) concentration (Table 1).The decrease in the percentage removal and their rate constants can be explained that at low concentration of Cr(VI), the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions interact with the adsorbent and are removed quickly fromthe solution[14].

3.2.3 Effect of pH

pHof the metal solution is an important parameter affecting the adsorptionof Cr(VI) on the adsorbent surface. The relation between the initial pH of the solution and the percentage Cr(VI) removal is illustrated in Fig. 3c. It depicted that the percentage removal of Cr(VI) decreased from 95.5% to 32.0% withincreasing the initial pH of the solution from 3 to 10. Moreover, the observed results clearly indicated that the degradation kinetics of Cr(VI) increased with a decrease in pH (Table 1).This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent that ultimately led to the reduction in sorption capacity[15].

3.2.4 Effect of temperature

Fig. 3drepresents the effect of temperature on the removal efficiency of Cr(VI) ions. Itshowed that the removal efficiency of Cr(VI) increased by increasing the temperature, where the maximum adsorption (65.0%) is achieved at 45°C. In this order, calculated rate constant was increased with increasing temperature (Table 1). The possible reason for this might be the higher temperatures activate the metal ions for enhancing adsorption at the coordinating sites of the adsorbent, and the metal cations became faster[16].

3.3 Adsorption isotherms

In this study, both Langmuir and Freundlich isotherm models have been successfully applied to investigate the adsorption efficiency of Cr(VI) on CH-Fe^o surface. The linear plot of both isotherm models is presented in Figs. 4a & 4b. The results indicated that both isotherm models were adequate for describing the Cr(VI) removal because there was no considerable difference between them. From R^2 values, it may be concluded that both Langmuir and Freundlich adsorption isotherms simultaneously operate on the surface of the CH-Fe^o adsorbents (Table 5). The data represents that both isotherm models presented good fit for all studied parameters.

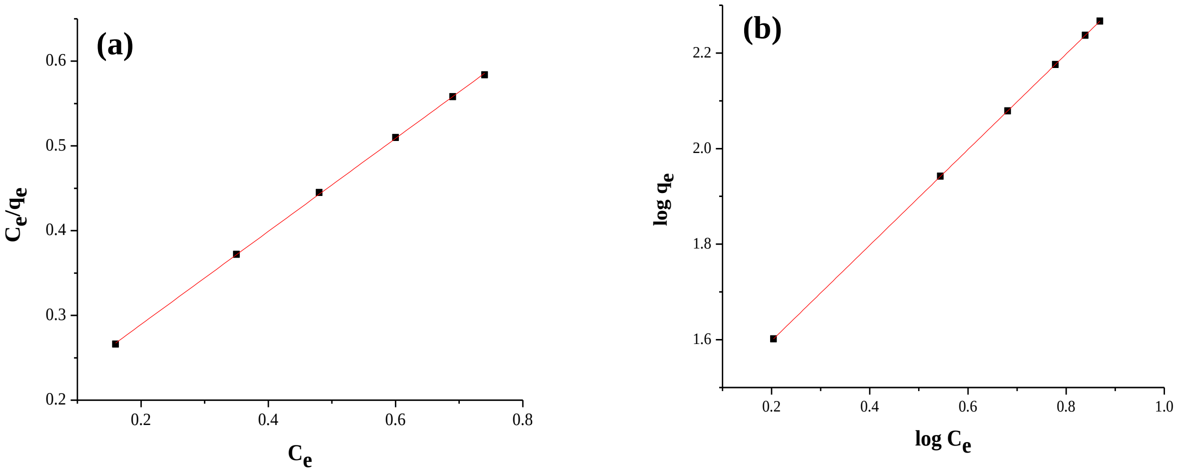

Fig. 4. Langmuir (a) and Freundlich (b) isotherms for Cr(VI) adsorption by chitosan capped nanozerovalent iron

Table 2: Adsorption isotherm constants for Cr(VI) reduction by chitosan capped nanozerovalent iron

Langmuir constants			**Freundlich constants**		
Q_m	**K_a**	**R^2**	**K_f**	***n***	**R^2**
0.549	0.179	0.999	1.0	1.398	1.0

4. Conclusion

This study reveals the feasibility of using Fe^o nanoparticlesin the presence of chitosan as an effective adsorbent to reduce Cr(VI) using potassium dichromate as the model contaminant. The adsorption performance is greatly affected by different parameters like adsorbent dosage, Cr(VI) concentration, pH and temperature. The adsorbent selected for the present study proved to be good adsorbent which was evident with the adsorption data obeying both Langmuir and Freundlich isotherms. The results clearly indicated that zerovalent iron nanoparticles in the presence of chitosan as a capping agent would be a very suitable adsorbent and provide cost-effective solutions to soil and groundwater remediation.

References

1. Chrysochoou, M. Johnston, C.P. and Dahal, G. A comparative evaluation of hexavalent chromium treatment in contaminated soil by calcium polysulfide and green-tea nanoscale zero-valent iron, J. Hazard.Mater.,2012, 201-202, 33-42.
2. Singh, R. Misra, V. and Singh, R. Synthesis, characterization and role of zero-valent iron nanoparticle in removal of hexavalent chromium from chromium-spiked soil, J.Nanoparticle Res., 2011, 13, 4063-4073.

3. Madhavi, V.Bhaskar Reddy, A.V.Gangadhara Reddy, K. and Madhavi, G. A simple method for the determination of efficiency of stabilized Fe^o nanoparticles for detoxification of chromium (VI) in water,J. Chem. Pharm. Res., 2012, 4, 1539-1545.
4. Li, X.Q. and Zhang, W.X. Iron nanoparticles: the core-shell structure and unique properties for Ni(II) sequestration, Langmuir, 2006, 22, 4638-4642.
5. Martin, J.E. Herzing, A.A. Yan, W. Li, X.Q.Koel, B.E.Kieley, C.J. and Zhang, W.X. Determination of the oxide layer thickness in coreshellzerovalent iron nanoparticles, Langmuir, 2008, 24, 4329-4334.
6. He, F. and Zhao, D. Preparation and characterization of new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water, Environ SciTechnol.,2005, 39, 3314-3320.
7. Cushing, B.L. Kolesnichenko, V.L. and O'Connor, C.J. Recent advances in the liquid-phase synthesis of inorganic nanoparticles,Chem. Rev., 2004,104, 3893-3946.
8. Geng, B. Jin, Z. Li, T. and Qi, X. Kinetics of hexavalent chromium removal from water by chitosan Fe^o nanoparticles, Chemosphere, 2009, 75, 825-830.
9. Selvarani, M. and Prema, P.Removal of toxic metal hexavalent chromium [Cr(VI)] from aqueous solution using starch-stabilized nanoscalezerovalent iron as adsorbent: equilibrium and kinetics, Int. J. Environ. Sci., 2012, 2, 1962-1975.
10. Franco, D.V. Da Silva, L.M. and Jardim, W.F.Reduction of hexavalent chromium in soil and ground water using zerovalent iron under batch and semi-batch conditions,Water Air Soil Pollut.,2009, 197, 49-60.
11. Geng, B. Jin, Z. Li, T. and Qi, X. (2009). Preparation of chitosan-stabilized Fe^o nanoparticles for removal of hexavalent chromium in water,Sci. Total Environ.,2009, 407, 4994-5000.
12. Yuvakumar, R.Elango, V.Rajendran, V. and Kannan, N. Preparation and characterization of zerovalent iron nanoparticles, Dig. J.Nanomater.Biostruct.,2011, 6, 1771-1776.
13. Garg, U.K. Kaur, M.P. Garg, V.K. and Sud, D. Removal of hexavalent chromium from aqueous solution by agricultural waste biomass,J.Hazard.Mater.,2007, 140, 60-68.
14. Wanees, S.A. Ahmed, A.M.M. Adam, M.S. and Mohamed, M.A. Adsorption studies on the removal of hexavalent chromium-contaminated wastewater using activated carbon and bentonite,Asian J. Chem., 2012, 2, 95-105.
15. Baral, S.S. Das, S.N. and Rath, P. Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust,Biochem. Eng. J., 2006, 3,216-222.
16. Inglezakis, V.J.Loizidou, M.D. and Grigoropoulou, H.P. (2004). Ion exchange studies on natural and modified zeolites and the concept of exchange site accessibility,J. Colloid. Interface Sci., 2004, 275, 570-576.

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