Available online at www.elixirpublishers.com (Elixir International Journal)

Pollution

Elixir Pollution 32 (2011) 2034-2040

ISSN: 2229-712X

Sorption of chromate and fluoride onto duolite a 171 anion exchange resin – a comparative study

Muniyappan Rajiv Gandhi[a], Govindasamy Kalaivani[a] and S. Meenakshi[a,*]

[a]Department of Chemistry, Gandhigram Rural University, Gandhigram- 624 302, Tamil Nadu, India.

ARTICLE INFO

Article history:
Received: 4 February 2011;
Received in revised form:
18 November 2010;
Accepted: 2 March 2011;

Keywords
Chromate,
Fluoride,
Sorption,
Duolite A 171,
Isotherms,
Kinetics.

ABSTRACT

Commercially available anion exchange resin, Duolite A 171 (DLE) has been used for the sorption of chromate and fluoride ions from aqueous solutions. DLE resin possesses an enhanced chromate sorption capacity of 202 mg/g in a minimum period of 60 min contact time and 0.6 mg/g for fluoride with 30 min contact time. Sorption capacity (SC) of DLE resin was compared under various equilibrating conditions like effect of pH and co-ions, temperature, contact time, for the removal of chromate and fluoride. The results showed that DLE resin is more selective for chromate rather than fluoride. The chromate and fluoride sorption was reasonably explained using Freundlich and Langmuir isotherm. Fourier transform infrared spectroscopy (FTIR) was used for the determination of functional groups responsible for chromate and fluoride sorption. Various thermodynamic parameters such as ΔG^o, ΔH^o, and ΔS^o have been calculated to understand the nature of sorption. The sorption kinetic mechanism was studied with reaction based and diffusion based models. The sorption process was found to be controlled by pseudo-second-order and intraparticle diffusion models.

© 2011 Elixir All rights reserved.

Introduction

Ion exchange is a traditional technique and has been successfully employed in various chemical research studies encompassing fundamental and practical fields. Ion exchange resins have been used in water softening, removal of toxic metals, waste water treatment, hydrometallurgy, sensors, chromatography, catalysis and bimolecular separations [1]. Chromium contamination in water is due to the effluents discharged from various industries such as electroplating, leather tanning, mining, steel making and pigments, which has significant impact on human health and other living organisms in the environment [2, 3]. The effluents from these industries contain both Cr(III) and chromate Cr(VI). Among them Cr(VI) is highly toxic. Cr(VI) compounds are carcinogenic that cause lung cancer, as well as kidney, liver and skin damage in human beings. The maximum permissible limit of chromium content in drinking water is 0.05 mg/L [4]. Cr(III) is not a significant ground water contaminant whereas Cr(VI) is approximately 100 times more toxic than Cr(III) [5]. It can diffuse as CrO_4^{2-} or $HCrO_4^-$ through cell membranes [6-9]. Cr(VI) in acidic solution demonstrates a very high positive redox potential (+1.33V) which denotes that it is strongly oxidizing [10]. Similarly the presence of fluoride ion in potable water has unique effects on human health. Fluoride is easily attracted by positively charged calcium in teeth and bones due to its strong electro-negativity, which results in dental, skeltal and non-skeltal forms of fluorosis and permissible limit of fluoride in drinking water is 1.5 mg/L[11].

A number of removal techniques have been suggested for the removal of chromate and fluoride. Depending upon their mode of action they are classified into three major types, viz., those based on chemical addition [12, 13], adsorption process [14, 15] and ion exchange mechanism [16-19]. Membrane such as reverse osmosis [20], nano filtration [21], electro dialysis [22] and Donnan dialysis [23] were recently investigated to reduce fluoride concentration in water. Ion exchange resins have been also widely used in recovery and preconcentration of metal ions. The polymeric resin containing specific functional groups are capable of complexing or ion exchanging the metal ions in aqueous solution [24]. The resin can be regenerated and reused for continuous process. Further, the main advantages of the polymeric resin are its high porosity in bead forms or cross-linking which can help in improving the kinetics by increasing the accessibility of the polymer –supported ligands to the metal ions.

A number of studies have been performed using ion exchange resins which have received considerable attention in recent years due to their suitability at field conditions and reusability. They are also adaptable to continuous process involving columns and chromatographic separations. Their insolubility renders to environmentally compatible state since the cycle of loading /regeneration/reloading allows them to be used for many years. Ion exchange is identified as an efficient ion scavenger due to the presence of its reactive functional groups [24]. Resin chelates, exchanges or adsorbs metal ions selectively irrespective of other ions present in the water system. Polymeric resins of various types viz., anionic and cationic/chelating resins have been employed for the chromate and fluoride removal.

In the present work Deolite A 171 (DLE) which is an anion exchange resin has been used for chromate and fluoride removal for the first time. The sorption capacity is very high and this resin can be used for the technology development. DLE A 171 is very cheap than compare to other types of polymeric resin and can be regenerated using the NaCl. At present this resin used for colour removal form industrial waste water in many industries.

Tele: +91-451-2452371; fax: +91-451-2454466.
E-mail addresses: drs_meena@rediffmail.com (S.Meenakshi)

© 2011 Elixir All rights reserved

The main objective of this work is to identify the selectivity of ion exchange resin for chromate and fluoride removal from aqueous solution and establish the probable mechanism of chromate and fluoride sorption. The various influencing parameters viz., contact time, solution pH and the presence of other ions on SC were optimized. The equilibrium sorption data was fitted with various isotherms and kinetic models to find the best fit model for the sorption system.

Materials and methods

Materials

Duolite A 171 (DLE) was supplied by Auchtel Products Ltd., Mumbai (India). DLE is a styrene/divinylbenzene copolymeric matrix containing quaternary amino functional group with chloride ion as exchangeable group. Sodium fluoride, potassium dichromate purchased from Merck, Mumbai, and all other chemicals and reagents were of analytical grade and used without further purification. The main properties of chromate and fluoride are given in Table 1. As per the guidelines of the manufacturers, the commercially available resin is specially prepared for colour removal purpose and specifications given by the manufacturer are given in Table 2. All the solutions used for the laboratory studies were prepared using double distilled water. The chromate, fluoride solutions of various concentrations were made by dissolving required quantity of respective potassium dichromate and sodium fluoride in double distilled water.

Sorption studies

The batch adsorption experiments were carried out by mixing 0.1 g of resin with 50 ml of an aqueous solution of 100 mg/L of Chromate (pH 4) and 50 ml of (pH 7) F^- with 10 mg/L each separately. The mixtures were shaken in a thermostatic shaker at a speed of 200 rpm at room temperature and the filtrates were analyzed for chromate and fluoride. The influence of various parameters viz., contact time, pH and presence of other ions normally present in water on the SC of the sorbent was investigated. The SC of the resins was determined separately for chromate and fluoride by varying the contact time in the range of 10-60 min at 303 K by mixing 0.1 g of resin with 50 ml of an aqueous solution of Chromate (pH 4) having 100 mg $HCrO_4^-$/L and having 10 mg F^-/L (pH 7) respectively. SC of the resin was determined at five different pH levels viz.3, 5, 7, 9 and 11. The pH of the working solution was controlled by adding HCl / NaOH solution. For the temperature studies, the effect of different initial concentrations viz., 40, 50 and 60 mg/L for chromate and fluoride viz., 8, 10 and 12 mg/L at 303, 313 and 323 K on sorption rate was studied by keeping the mass of sorbent as 0.1 g and volume of solution as 50 ml. The solution was then filtered and the residual chromate and fluoride concentration were measured.

Methods of analysis

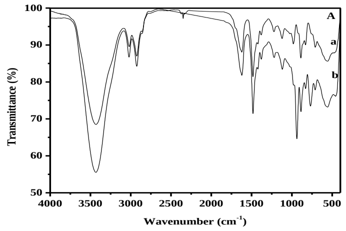
The concentration of chromate was measured using UV-Visible spectrophotometer (Pharo 300 Merck) at 540 nm, according to the 1,5-diphenyl-carbazide method [25]. Fluoride determination was done using expandable ion analyzer EA 940 and the fluoride ion selective electrode BN 9609 (Orion USA made). The pH measurements were carried out with the expandable ion analyzer EA 940 with pH electrode [25]. pH_{zpc} (pH of zero point charge) was determined by pH drift method [26]. FTIR spectra of the solid samples were recorded with JASCO- 460 plus model (Japan) FTIR spectrophotometer to detect the functional groups. Computations were made using Microcal Origin (Version 6.0) software. The effectiveness of fit was discussed using regression correlation coefficient (r), chi-square analysis and standard deviation (sd).

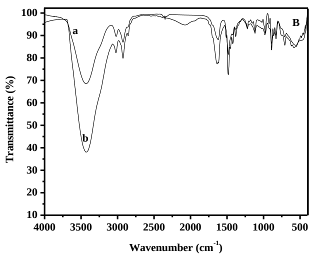
Results and discussion

Characterisation of DLE

As per the specifications of the manufacturer DLE is an anion exchanger in Cl^-form (cf. Table 2). Fig.1A a and b and 1B a and b depict the FTIR spectra of the DLE resin before and after chromate and fluoride sorption respectively. In the FTIR spectra of the resin before sorption of either $HCrO_4^-$ or F^- a band at 3442 cm^{-1}, represents a strong and broad band of the O-H stretching vibrations. The band at 3018, 2922, 2858 cm^{-1} appeared and these bands are related to the symmetric or asymmetric, stretching vibrations of the ring C-H bonds and -CH_2 groups of the matrix (cross-linked polystyrene) of the resin (3018 cm^{-1} υ_{as}(C-H); 2922 cm^{-1} υ_{as} (-CH_2); 2858 cm^{-1} υ_{as} (-CH_2). The vibrations of the O-H group is of the water molecule present in the resin at 1615 cm^{-1} (δ(O-H). The asymmetric, stretching vibrations of carbon-carbon bonds in the ring (υ_{as}(C-C)) as well as the asymmetric, scissoring vibrations of methylene groups (δ_{as} (-CH_2) appeared at 1487, 1421, 1383 cm^{-1} respectively. The deformation vibrations of 1,4-disubstituted benzene ring is due to the styrene-divinylbenzene matrix of resin which observed at 976 and 826 cm^{-1} [27-30]. The quaternary ammonium group in resin is confirmed by the bands at 1488 to 1463 cm^{-1}, symmetric deformation and asymmetric angular bending of methyl groups of quaternary nitrogen -$N^+(CH_3)_3$) and N-CH_3 bending at 1494 cm^{-1} [31-33]. Even after the sorption of chromate and fluoride, the bands and their positions on spectra are very similar to those before sorption, but the intensity of a few bands changed after the sorption process. Before the sorption process, the peaks at 872 and 713 cm^{-1} were found for resin whereas after sorption these peaks disappeared in chromate sorbed resin. The formation of new peak 936, 766 cm^{-1} and 540 cm^{-1} is due to Cr-O bonds in the chromate treated resin [34, 35]. A slight broadening of band at 1488 cm^{-1} in the fluoride-sorbed and chromate sorbed resin may be taken as an indication of electrostatic adsorption between the quaternary ammonium group of the resin and chromate and fluoride respectively [31].

Fig. 1A. FTIR spectra of (a) DLE resin and (b) chromate-sorbed DLE resin.

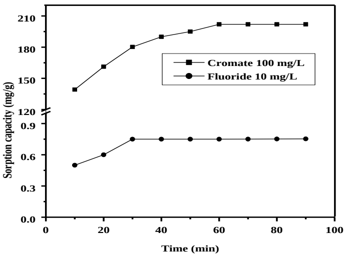




Effect of contact time

As it is evident from Fig. 2, SC of DLE reached saturation after 60 minutes for chromate whereas fluoride attains saturation after 30 minutes. Hence, in all the experiments the contact time was fixed as 60 minutes for chromate and 30 minutes for fluoride. The SC of DLE was found to be 202 and 0.6 mg/g for chromate and fluoride respectively. The higher SC for chromate may be due to the higher valency and density which gets ion exchanged rapidly than the fluoride.

Fig.2. Effect of contact time on SC of the resin at 303 K.



Effect of pH

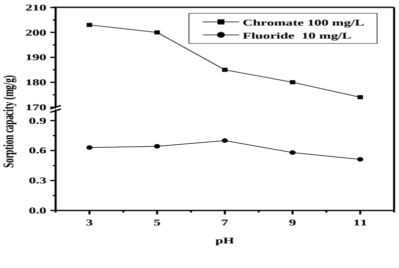
The removal of chromate and fluoride ions from the aqueous solution was highly dependent on the solution pH in many cases as it altered the surface charge on the sorbent resin [18]. Cr(VI) can exist in several forms such as $Cr_2O_7^{2-}$, $HCrO_4^-$, $HCrO_7^-$ and CrO_4^{2-} and the relative abundance of particular complex depends on the concentration of the chromium ion and pH of the solution. In acidic solutions Cr(VI) exist as $HCrO_4^-$. The effect of pH on the sorption of chromate ions onto the DLE resin is depicted in Fig. 3. At pH 2- 4 the uptake was high, while a slight decrease was observed in the range of 6-11. At alkaline pH SC is only 70%. In acidic conditions, complete sorption was observed, and at this region the chromate removal originates from electrostatic adsorption rather than ion exchange due to more positive charge on the DLE resin.

Throughout the study, pH of the chromium solution was maintained at pH 4. After the sorption experiments solution pH becomes neutral.

The effect of pH on the sorption of fluoride ions onto DLE resin is depicted in Fig.3. Contrary to chromate ions, fluoride sorption capacity was not significantly altered from acidic to neutral pH of the environment. While decreasing from pH 7, the removal of fluoride ion was found to be slight altered. At alkaline pH SC is only 60%. Hence, throughout the study, the pH of the medium was maintained at neutral pH.

The pH_{zpc} value of DLE was found to be 7.22. Lower SC in alkaline medium can be explained by the fact that above 7.22 pH_{zpc} value the sorbent surface acquires negative charge in alkaline pH and hence there is repulsion between the negatively charged surface and sorbate and below 7.22 pH_{zpc} value the sorbent surfaces attains positive charge and the $HCrO_4^-$ and F^- adsorbed.

Fig. 3. Influence of pH on the on SC of the resin at 303 K.



Effect of co-ions in the medium

The dependence of SC of the resin in the presence of other co-ions which are commonly present in water namely Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, Ca^{2+} and Mg^{2+} was investigated with varying initial concentrations of these ions 200 mg/L by keeping 100 10mg/L as initial chromate and fluoride respectively.

As shown in Fig. 4A, these ions do not have any significant effect on SC of the DLE resin which may be attributed to the fact that DLE selectively removes chromate.

However, in case of the fluoride (Fig. 4B), the results indicate 20, 35 45 and 60%, significant reduction of SC presence Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-} and NO_3^- respectively. Therefore, it is presumed that the DLE resin removes other ions also present in the medium to some extent and as a consequence there is a decrease in the SC. Since the sorption process of DLE is controlled by ion exchange mechanism it is quite obvious that the higher concentrated co-ions get exchanged first than the dilute fluoride solutions but sorption of chromium is not affected by the co-ions which is due to large charge density and higher valency when compared to other co-ions. It is interesting to note that the SC of the sorbents were found to be influenced both anions and cations. This could be due to the fact that the sorption may be controlled by both adsorption / ion exchange mechanism.

Fig. 4A.Effect of co-ions on the SC of DLE resin for chromate at 303 K.

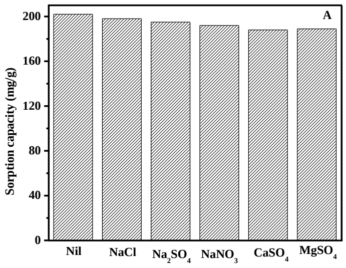
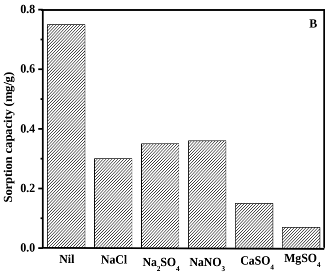


Fig. 4B.Effect of co-ions on the SC of DLE resin for fluoride at 303 K.



Adsorption Isotherm

Adsorption isotherm is the basic requirement for designing for sorption system. Several mathematical models have been developed quantitatively to express the relationship between the extent of sorption and the residual solute concentration. The most widely used models are the Freundlich and Langmuir adsorption isotherm models [36, 37].

Freundlich isotherm

The linear form of Freundlich [36] isotherm is represented by the equation,

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

(1)

where q_e is the amount of chromium adsorbed per unit weight of the sorbent (mg/g), C_e is the equilibrium concentration of chromium in solution (mg/L), k_F is a measure of adsorption capacity and 1/n is the adsorption intensity. A linear plot of log q_e vs. log C_e indicates the applicability of Freundlich isotherm. The values of 1/n and k_F of AlCs composite are listed in Table 3. The values of 1/n lying between 0 and 1 and the n value in the range of 1 to 10 confirm the favorable conditions for adsorption. The k_F values increased with the rise in temperature, which indicates that the chromium and fluoride sorption by DLE resin is an endothermic process.

Langmuir isotherm

Langmuir [37] isotherm model can be represented by the equation

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{C_e}{Q^o} \tag{2}$$

where Q^o is the amount of adsorbate at complete monolayer coverage (mg/g), which gives the maximum sorption capacity of the sorbent and b (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption. The linear plot of C_e/q_e vs. C_e indicates the applicability of Langmuir isotherm. The values of Q^o and b are listed in Table 3. The values of Q^o and b increase with the rise in temperature indicating the endothermic nature of chromium and fluoride sorption.

In order to find the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L [38]

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where b is the Langmuir isotherm constant and C_o is the initial concentration of chromium (mg/L). The R_L values lying between 0 and 1 indicate favorable adsorption for all the temperatures studied (cf. Table 3).

Chi-square analysis

To identify a suitable isotherm model for the sorption of chromium on DLE resin, this analysis has been carried out. The equivalent mathematical statement is

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{4}$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g) and q_e is experimental data of the equilibrium capacity (mg/g). If data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ, χ^2 will be a bigger number.

The results of chi-square analysis are presented in Table 3. As Freundlich isotherm possesses lower χ^2 values and hence this isotherm can be considered as the best fitting model for the sorption of chromate and fluoride on resin than Langmuir model.

Thermodynamic treatment of the sorption process

Thermodynamic parameters associated with the adsorption, viz., standard free energy change (ΔG^o), standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o) were calculated as follows

The free energy of sorption process, considering the sorption equilibrium coefficient K_o, is given by the equation

$$\Delta G^o = -RT \ln K_o \tag{5}$$

where ΔG^o is the standard free energy of sorption (kJ/mol), T is the temperature in Kelvin and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). The sorption distribution coefficient K_o, was determined from the slope of the plot ln (q_e/C_e) against C_e at different temperatures and extrapolating to zero C_e according to the method suggested by Khan and Singh [39]

The sorption distribution coefficient may be expressed in terms of ΔH^o and ΔS^o as a function of temperature:

$$\ln K_o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{6}$$

where ΔH^o is the standard enthalpy change (kJ/mol) and ΔS^o is the standard entropy change (kJ/mol K). The values of ΔH^o and ΔS^o can be obtained from the slope and intercept of a plot of ln K_o against 1/T.

The values of thermodynamic parameters are shown in Table 4. The negative values of $\Delta G°$ confirm the spontaneous nature of chromate and fluoride sorption. The value of $\Delta H°$ is positive indicating that the sorption process is endothermic in nature. The positive value of $\Delta S°$ indicates the possibility of randomness at the solid/liquid interface during chromate and fluoride sorption.

Sorption kinetic models

The two main types of sorption kinetic models namely reaction-based and diffusion-based models were adopted to fit the experimental data

Reaction-based models

The most commonly used pseudo-first-order and pseudo-second-order models were employed to explain the solid/liquid adsorption.

A simple pseudo-first-order kinetic model [40] is given as.

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303} t \tag{7}$$

where q_t is the amount of ion on the surface of the composite at time t (mg/g) and k_{ad} is the equilibrium rate constant of pseudo-first-order sorption (min^{-1}). The linear plots of log (q_e-q_t) against t give a straight line that indicates the applicability of pseudo-first-order model. The slope of the straight line plot of log (q_e-q_t) against t sorption at different temperatures viz., 303, 313 and 323 K give the value of the pseudo-first-order rate constant (k_{ad}) and r are listed in Table 4.

In addition, the pseudo-second-order model is also widely used. There are four types of linear pseudo-second-order kinetic models [41], the most popular linear form is

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}, \tag{8}$$

where $q_t = \frac{q_e^2\ kt}{1 + q_e kt}$, amount of chromium on the surface of the composite at any time, t (mg/g), k is the pseudo-second-order rate constant (g/mg min), q_e is the amount chromium ion sorbed at equilibrium (mg/g) and the initial sorption rate, h = kq_e^2 (mg/g min). The value of q_e (1/slope), k ($slope^2$/intercept) and h (1/intercept) of the pseudo-second-order equation can be found experimentally by plotting t/q_t against t. In addition, the fitness of the data and the values of q_e, k, h and r of the pseudo-second-order model were obtained from the plots of t/q_t vs. t for chromium sorption at different temperatures viz., 303, 313 and 323 K of DLE resin are presented in Table 5-6. The values of q_e increase with the increase in temperature indicating chromate and fluoride sorption increases with the rise in temperature. The higher correlation coefficient (r) values obtained for pseudo-second-order model than pseudo-first-order indicating the applicability of the pseudo-second-order model for the chromate and fluoride sorption onto the resin.

Diffusion-based models

A simple equation for the particle diffusion controlled process [42] is given as follows,

$$\ln\left(1-\frac{C_t}{C_e}\right)=-k_p t \tag{9}$$

where k_p is the particle rate constant (min^{-1}). The value of particle rate constant is obtained by the slope of ln (1- C_t /C_e) against t.

The intraparticle diffusion model used here refers to the theory proposed by Weber and Morris [43] and its equation is

$$q_t = k_i \, t^{1/2} \tag{10}$$

where k_i is the intraparticle rate constant (mg/g $min^{0.5}$). The slope of the plot of q_t against $t^{½}$ will give the value of intraparticle rate constant.

The respective straight line plots of ln ($1-C_t/C_e$) vs. t and q_t vs. $t^{0.5}$ indicate the applicability of particle and intraparticle diffusion models. The k_p, k_i and r values at different temperatures viz., 303, 313 and 323 K for both particle and intraparticle diffusion models are illustrated in Table 5-6. The higher r values obtained for intraparticle diffusion model suggest that the chromate and fluoride diffusion on resin follows intraparticle diffusion model.

The assessment of the employed kinetic models for fitting the sorption data was made by standard deviation (sd) and the model which possesses lower values of sd show better fit to sorption data. The sd values of resin for all the kinetic models are summarized in Table 5-6. Smaller sd values observed for the pseudo-second-order and intraparticle diffusion models indicate that these two models are significant in defining the chromate and fluoride sorption process and suggest that the sorption of chromate and fluoride ion were onto the pore of resin.

3.8. Sorption mechanism

From the above studies, it is clear that the mechanism of chromate and fluoride removal by resin is mainly governed by ion-exchange. At acidic environment the percentage of electrostatic sorption is higher for both the ions. As the pH increases the percentage of removal of both the ions found to decrease, which may be due to the completion of OH^- ions also for the exchange. DLE resin removes hydrogen chromate ion and fluoride by means of ion exchange in neural pH.

The FTIR spectra of chromate loaded sorbent has a new band at 540 cm^{-1} that confirms the formation of Cr-O in the chromate sorbed resin [34, 35]. The preference of exchange of anions may be in the following order, $HCrO_4^- > F^- > Cl^- > NO_3^- > SO_4^{2-}$. As chromate has higher charge density than fluoride, chromate has been sorbed more when compared with fluoride. Lower ionic radius of chromium(VI) (0.044 nm) than fluoride (0.136 nm) also makes it to get exchanged easily (cf. Table 1).

$$\text{Resin} - N(CH_3)_3^+Cl^- + HCrO_4^- \Longrightarrow \text{Resin} - N(CH_3)_3^+ HCrO_4^- + Cl^-$$

Duolite A 171 Exhausted resin

$$\text{Resin} - N(CH_3)_3^+Cl^- + F^- \Longrightarrow \text{Resin} - N(CH_3)_3^+ F^- + Cl^-$$

Duolite A 171 Exhausted resin

Conclusions

The chromate and fluoride sorption characteristics of DLE resin were studied under various equilibrium and thermodynamic conditions. DLE resin displayed good selectivity towards chromate than the fluoride due to density and lower ionic radiation of chromates. The SC of DLE resin was influenced by pH of the medium and in the presence of co-ions. After sorption, irrespective of initial pH ranges, the final pH of the treated water was found to be neutral. The nature of the reaction was spontaneous and endothermic. The sorption of chromate and fluoride on DLE resin followed Freundlich isotherm. The pseudo-second -order kinetic model is found to be the best correlation of the data for chromate and fluoride removal on DLE resin. The kinetics of the reaction follows intraparticle diffusion models. The mechanism of chromate sorption by DLE resin was mainly governed by ion exchange and adsorption. DLE resins can be effectively used for chromate removal than the fluoride removal.

Acknowledgements

The authors are grateful to Defence Research and Development Organization (ERIP/ER/0703670/M/01/1066) and Department of Science and Technology (DST/TDT/WTI/2k8/82) New Delhi, India for their providing of financial support to carry out this research work.

References

1. Alexandratos SD. Ion-Exchange resins: A retrospective from industrial and engineering chemistry research. Ind. Eng. Chem. Res. 2009; 48: 388-398.
2. Afkhami A and Conway BE. Investigation of removal of Cr(IV), Mo(VI), W(VI),V(VI), and V(V) oxy- ions form industrial waste -waters by adsorption and electrodeposition at high-area carbon cloth. J. Colliod. Interf. Sci. 2002; 251: 248-255.
3. Cimino G, Passerini A, and Toscazo. Removal of toxic cations and Cr(VI) from aqueous solutions by hazelnut shell. Water Res. 2000; 34: 2955-2962.
4. WHO Guidelines for drinking-water quality, 2nd edn, vol. 2. World Health Organization, Geneva, 1996.
5. Kabay N, Arda M, Saha B and Streat M. Removal of chromate by solvent impregnated resins (SIRs) stabilized by coating and chemical crosslinking.I. Batch mode sorption studies, React. Funct. Polym. 2003; 54: 103-115.
6. Anderson RA. Chromium as an essential nutrient for humans. Toxicol. Pharm. 1997; 26: S35-S41.
7. Costa M. Potential hazards of hexavalent chromate in our drinking wate. Toxicol Appl. Pharm. 2003; 118: 1-5.
8. Baral A and Engelken RD. Chromoim- based regulations and greeing in metal finishing industries in USA, Environ. Sci. Policy. 2002; 5: 121-133.
9. Mertz W. Chromium and its relation to carbohydrate metabolism. Med. Clin. North. Am. 1976; 60: 739-744.
10. Gode F and Pehlivan E. Removal of Cr(VI) from aqueous

solution by two Lewatit- anion exchange resins. J. Hazard. Mater. 2005; 119: 175-182.

11. WHO, Report, Fluoride and Fluorides: Environmental Health Criteria, World Health Organisation, Geneva, 1984.

12. Alonso AI, Galan B, Gonzalez M and Oritiz I. Experimental and theoretical analysis of a non-dispersive solvent extraction pilot plant for removal of Cr(VI) from galavanic process wastewaters. Ind. Eng. Chem. Res. 1999; 38: 1666-1675.

13. Karthikeyan G, Shanmuga Sundarraj A, Meenakshi S and Elango KP. Adsorption dynamics and the effect of temperature of fluoride at alumina-solution interface. J. Indian. Chem. Soc. 2004; 81: 461-466.

14. Mor S, Ravindra K and Bishnoi NR. Adsorption of chromium from solution by activated alumina, and activated charcoal. Bioresour. Technol. 2007; 98: 954-957.

15. Viswanathan N, Sairam Sundaram C, Meenakshi S. Development of multifunctional chitosan beads for fluoride removal. J. Hazard. Mater. 2009; 167: 325-331.

16. Cavaco SA, Fernandes S, Quina MM and Ferreira LM. Removal of chromium from electroplating industry effluents by ion exchange resins. J. Hazard. Mater. 2007; 144: 634-638.

17. Meenakshi S and Viswanathan N. Identification of selective ion-exchange resin for fluoride sorption. J. Colloid. Interf. Sci. 2007; 308: 438-450.

18. Viswanathan N and Meenakshi S. Effect of metal ion loaded in a resin towards fluoride retention. J. Fluorine. Chem.2008; 129: 645-653.

19. Viswanathan N and Meenakshi S. Enhanced fluoride sorption using. La(III) incorporated carboxylated chitosan beads. J. Colloid. Interf. Sci. 2008; 322: 375-383.

20. Joshi SV, Mehta SH, Rao AP and Rao RV. Estimation of sodium fluoride using HPLC in reverse osmosis experiments. Water Treat. 1992; 7: 207-211.

21. Simons R. Trace element removal from ash dam waters by nano filteration and diffusion dialysis. Desalination 1993; 89:325-341.

22. Adhikary SK, Tipnis UK, Harkare WP, Govindan KP. Defluoridation during desalination of brackish water by electrodialysis. Desalination 1989; 71: 301-312.

23. Dieye A. Defluoridation des beaux par dialyze biunique croisee, thesis, University Paris XII, 1995.

24. Beauvais RA and Alexandratos SD. Polymer- supported reagents for the selective complexation of metal ions: an overview. React. Funct. Polym. 1998; 36: 113-123.

25. APHA. Standard Methods for the Examination of Water and Waste Water, American Public Health Association, Washington, DC, 2005.

26. Lopez-Ramon MV, Stoeckli F, Moreno-Castilla C and Carrasco-Marin F. On the characterization of acidic and basic surface sites on carbons by various techniques. Carbon 1999; 37: 1215-1221.

27. Kołodynska D, Ryczkowski J and Hubicki Z. FT-IR/PAS studies of chelates adsorption on anion exchangers. Eur. Phys. J. Special Topics 2008; 154: 339-343.

28. Socrates G. Infrared and Raman Characteristic Group Frequencies: Tables and Charts, Third ed., John Wiley & Sons, Ltd, Chichester, New York, 2001.

29. Wronski G, Pasieczna-Patkowska S and Hubicki Z. Mechanism of sorption sulphoderivative organic chelating agents on strong base anion exchanger Amberlite IRA-402 by FT-IR/PAS and DRS methods. Eur. Phys. J. Special Topics 2008; 154: 377-380.

30. Wolowicz A and Hubicki Z. Sorption of palladium (II) complexs onto the styrene- divinylbenzene anion exchange resins. Chem. Eng. J. 2009; 152: 72-79.

31. Gurgel LVA, De Melo JCP, De Lena JC and Gil LF. Adsorption of chromium (VI) ion from aqueous solution by succinylated mercerized cellulose functionalized with quaternary ammonium groups. Bioresour. Technol. 2009; 100: 3214-3220.

32. Spinelli VA, Laranjeira MCM and Favere VT. Preparation and characterization of quaternary chitosan salt: adsorption equilibrium of chromium(VI) ion. React. Funct. Polym. 2004; 61: 347-352.

33. Lee B, Bao LL, Im HJ, Dai S, Hagaman EW and Lin JS. Synthesis and characterization of organic-inorganic hybrid mesoporous anion-exchange resins for perrhenate (ReO4-) anion adsorption. Langmuir 2003; 19: 4246-4252.

34. Music S, Maljkovic M, Popovic S and Trojko R. Formation of chromia from amorphous chromium hydroxide. Croat Chem Acta. 1999; 72: 789-802.

35. Kyzas GZ, Kostoglou M and Lazaridis NK. Copper and chromium (VI) removal by chitosan derivatives-Equilibrium and kinetic studies. Chem. Eng. J. 2009; 152: 440-448.

36. Freundlich HMF. Uber die adsorption in lösungen. Z. Phys. Chem. 1906; 57A: 385-470.

37. Langmuir I. The constitution and fundamental properties of solids and liquids. J Am. Chem. Soc. 1916; 38: 2221-2295.

38. Weber TW and Chakravorti RK. Pore and solid diffusion models for fixed bed adsorbers. Am. Inst. Chem. Eng. J. 1974; 20: 228-238.

39. Khan AA and Singh RP. Adsorption thermodynamics of carbofuran on Sn (IV) arsenosilicate in H^+, Na^+ and Ca^{2+} forms. Colloids Surf**.** 1987; 24: 33-42.

40. Lagergren S. Zur theorie der sogenannten adsorption gelöster stoffe. K. Sven Vetenskapsakad. Handl. 1898; 24: 1-39.

41. Ho YS. Second order kinetic model for the sorption of cadmium on to tree fern: A comparison of linear and non linear methods. Water Res. 2006; 40: 119-125.

42. Viswanathan N and Meenakshi S. Enhanced fluoride sorption using La(III) incorporated carboxylated chitosan beads. J. Colloid Interf. Sci. 2008; 322: 375-383.

43. Weber WJ and Morris J.C. Equilibria and capacities for adsorption on carbon. J. Sanitary Eng. Div. 1964; 90: 79-107.

Table 1- Physico-chemical properties of chromate and fluoride

Property	**Cr(VI)**	**F^-**
Atomic number	24	9
Salt form	$K_2Cr_2O_7$	NaF
Purity (%)	99	99
Atomic weight (g/mol)	51.996	18.998
Pauling Electronegativity	1.6	4
Density (g.cm^{-3} at 20°C)	7.19	1.8×10^{-3}
Vanderwaals radius (nm)	0.127	0.135
Ionic radius (nm)	0.044	0.136
Energy of first ionization (kJ. mol^{-1})	651.1	1680.6
Standard potential (V)	+1.33 (Cr^{6+} / Cr^{3+})	- 2.87

Table 2 - Physical and chemical properties of resin

Constituents	DLE Resin
Matrix	Styrene - divinylbenzene copolymer.
Functional groups	-N - (CH3)3
Physical form	Opaque beads
Ionic form	Cl^-
Total ion capacity	Min 1.0 eq / l (Cl^-form)
Mesh/Bead size	450 µm
Moisture holding capacity	54 - 60 % (Cl^-form)
Particle size	0.3 to 1.2 mm
Opearating pH range	0 to 14
Chemical stability	Insoluble in water, dilute solutions of acids or bases and common solvents.
Maximum operating temperature K	373

Table 3 - Freundlich and Langmuir isotherms constant of DLE.

	Temp. (K)	**Freundlich isotherm**					**Langmuir isotherm**				
		1/n	n	K_F $(mg/g)\ (L/mg)^{1/n}$	r	χ^2	Q^o (mg/g)	b (L/g)	R_L	r	χ^2
	303	0.467	2.141	88.45	0.999	9.0E-04	332.45	0.246	0.063	0.998	0.1395
Chromate	313	0.447	2.237	94.23	0.999	9.3E-04	344.52	0.260	0.071	0.998	0.0025
Fluoride	323	0.427	2.341	49.88	0.999	8.1E-04	356.23	0.275	0.057	0.998	0.1465
	303	0.579	1.72	3.10	0.987	0.003	10.09	0.43	0.189	0.959	0.004
	313	0.551	1.81	3.32	0.997	0.0006	9.46	0.53	0.086	0.987	0.001
	323	0.536	1.87	3.70	0.999	6.85E-05	9.33	0.66	0.070	0.997	0.005

Table 4 - Thermodynamic parameters of DLE

Thermodynamic parameters		**Chromate**	**Fluoride**
ΔG^o (kJ mol^{-1})	303 K	-5.63	-3.42
	313 K	-5.61	-3.17
	323 K	-5.56	-2.80
ΔH^o (kJ mol^{-1})		6.64	1.04
ΔS^o (kJ $mol^{-1}K^{-1}$)		0.003	0.21

Table 5 -Kinetic parameters of reaction based and diffusion based models for chromate sorption.

Kinetic models	**Parameters**	**303 K**			**313 K**			**323 K**		
		90 mg/L	**100 mg/L**	**110 mg/L**	**90 mg/L**	**100 mg/L**	**110 mg/L**	**90 mg/L**	**100 mg/L**	**110 mg/L**
Pseudo-first-order	k_{ad} (min^{-1})	0.090	0.099	0.101	0.158	0.154	0.122	0.128	0.131	0.170
	r	0.883	0.824	0.881	0.795	0.896	0.864	0.859	0.892	0.841
	sd	0.433	0.622	0.496	0.103	0.698	0.647	0.693	0.603	0.993
Pseudo-second-order	q_e (mg/g)	202.2	206	210.8	204.2	210.8	212.8	205.5	209.5	214.2
	k (g/mg min)	0.0018	0.0014	0.0015	0.0019	0.002	0.0017	0.0021	0.0027	0.0021
	h (mg/g min)	15.84	15.527	19.267	17.241	22.72	23.31	19.267	29.411	28.169
	r	0.998	0.994	0.997	0.998	0.998	0.997	0.999	0.999	0.998
	sd	0.0126	0.0211	0.0138	0.0120	0.009	0.0123	0.0100	0.0059	0.0114
Particle diffusion	k_p (min^{-1})	0.089	0.099	0.101	0.159	0.155	0.122	0.128	0.131	0.170
	r	0.883	0.824	0.881	0.795	0.896	0.864	0.859	0.892	0.841
	sd	0.998	1.433	1.142	2.541	1.609	1.489	1.596	1.390	2.228
Intraparticle diffusion	k_i (mg/g $min^{0.5}$)	4.754	5.03	5.45	4.47	4.43	4.61	4.21	4.15	3.87
	r	0.994	0.967	0.979	0.990	0.992	0.978	0.991	0.958	0.967
	sd	0.972	2.483	2.143	1.167	1.019	1.855	1.028	2.353	1.921

Table 6 - Kinetic parameters of reaction based and diffusion based models for fluoride sorption.

Kinetic models	**Parameters**	**303 K**			**313 K**			**323 K**		
		10 mg/L	**15 mg/L**	**20 mg/L**	**10 mg/L**	**15 mg/L**	**20 mg/L**	**10 mg/L**	**15 mg/L**	**20 mg/L**
Pseudo-first-order	k_{ad} (min^{-1})	0.130	0.140	0.170	0.140	0.150	0.19	0.15	0.16	0.21
	r	0.967	0.972	0.988	0.987	0.980	0.975	0.995	0.986	0.983
	sd	0.055	0.022	0.017	0.011	0.004	0.007	0.009	0.008	0.009
Pseudo-second-order	q_e (mg/g)	5.946	7.611	9.717	4.773	6.741	9.867	5.086	8.6349	11.016
	k (g/mg min)	0.011	0.014	0.0147	0.054	0.053	0.0165	0.0495	0.0127	0.0124
	h (mg/g min)	0.398	0.840	1.389	1.235	2.422	1.607	1.2814	0.948	1.5085
	r	0.998	0.999	0.998	0.998	0.999	0.999	0.997	0.999	0.998
	sd	0.157	0.024	0.136	0.170	0.037	0.076	0.193	0.078	0.115
Particle diffusion	k_p (min^{-1})	0.117	0.114	0.104	0.092	0.116	0.092	0.143	0.171	0.106
	r	0.868	0.996	0.901	0.910	0.965	0.971	0.942	0.962	0.982
	sd	0.697	0.108	0.207	0.468	0.327	0.234	0.342	0.347	0.208
Intraparticle diffusion	k_i (mg/g $min^{0.5}$)	0.923	0.090	0.222	0.942	0.100	0.254	0.951	0.255	0.426
	r	0.938	0.984	0.981	0.962	0.994	0.990	0.997	0.995	0.989
	sd	0.088	0.021	0.059	0.177	0.013	0.048	0.026	0.036	0.085