

Removal of chromium by riverbed sand from water and wastewater: Effect of important parameters

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Abstract

Application of riverbed sand, a non-toxic substance for the removal of Cr(VI) for aqueous solutions has been investigated. Removal of Cr(VI) was dependent on initial concentration and removal increased from 43.2% to 74.3% by decreasing initial concentration from 7.5×10^{-5} M to 1.0×10^{-5} M at 25 °C, 1.0×10^{-2} M NaClO₄ ionic strength and 100 rpm. Higher removal was obtained at particles of smaller sizes of the adsorbent. Removal decreased from 74.3% to 40.7% by increasing temperature from 25 °C to 35 °C exhibiting exothermic nature of the process of removal. Thermodynamic parameters, namely change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), were calculated and were found to be $-0.81 \text{ kcal mol}^{-1}$, $-17.21 \text{ kcal mol}^{-1}$ and $56.94 \text{ cal mol}^{-1}$, respectively at 25 °C. pH of the solution has pronounced effect on the removal and higher removal was obtained in acidic pH ranges, maximum (74.3%) being at 2.5 pH.

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1. Introduction

Metals and metallic compounds are essential for economic growth of any nation. Like many other metallic species chromium also has variety of applications. It is used in leather tanning, explosives, ceramics, paint pigments, photography and wood preservation [1,2]. Disposal of untreated effluents from the above applications is source of pollution of aquatic systems. Spent chrome liquors and waste from tanneries contain 2900–4500 mg l⁻¹ and 10–50 mg l⁻¹ of chromium, respectively [3]. Chromium exists in many forms but Cr(VI) is reported to be 100 times more toxic than Cr(III) [4] and is important from environment viewpoint. Exposure to Cr(VI) causes dermatitis, allergic skin reactions and ulceration of intestine. Cr(VI) is also reported to be carcinogen to animals [5].

Solvent extraction, ion exchange, osmosis and precipitation are amongst established techniques for treatment of chromium containing effluents and waters. Adsorption is an attractive and versatile method for the removal of metallic species. Activated

carbon adsorption is a popular choice for reclamation of metal rich wastewaters [6–8], but high cost of activated carbon restricts its application for developing countries. During recent past, there has been an increasing interest amongst scientific workers worldwide to use various naturally available low-cost materials as adsorbents for the removal of metallic pollutants [9–11]. Present work has been addressed to the use of riverbed sediments for removal of Cr(VI) from aqueous solutions and wastewaters. Effect of various parameters on the removal has been discussed.

2. Experimental

2.1. Materials

All the chemicals used in the experiments were of AR grade and were supplied by BDH, Bombay, India. The adsorbent selected for the studies was procured from bed sediments of the river Subernarekha. The adsorbent sample was washed several times with distilled water to remove physical earthen impurities. Then prior to experiments it was dried in a hot air oven at 110 °C. Stock suspensions of the adsorbent were prepared several weeks prior to the experiments to ensure complete hydration of the surface of the adsorbent.

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2.2. Methods

2.2.1. Collection of adsorbent

The active sediment samples were collected from shallow waters nearer the bank of the river and were taken from upper 5.0 cm layer of the deposits at the places of low flow rates as sedimentation was assumed to occur [12]. Then the samples were stored in properly cleaned, rinsed and washed (finally with 10% HNO₃) polythene bags and stored at 4 °C till further processing.

2.2.2. Physicochemical analysis of the adsorbent

Physicochemical analysis of the adsorbent was carried out by using standard methods [5]. The average particle size of the adsorbent sample was measured by Particle Size Analyzer, model HIAC-320 (ROYCO Institute Div., USA) and the surface charge by laser zee meter, model 500 (Penkem Inc., NY, USA). The surface area was determined by a “Three point” N₂ gas adsorption method using Quantasorb Surface Area Analyzer, Model-QS/7 (Quantochrome Corp., USA) and porosity by mercury porosimeter.

2.2.3. Adsorption experiments

Adsorption experiments were carried out in batches and were conducted by shaking 1.0 g of the adsorbent, riverbed sand with 50 ml aqueous solution of chromium of desired concentration, temperature, and pH in properly treated reagent bottles on a thermostat shaker. Shakings speed was maintained at 100 rpm throughout the experiments as it was convenient to maintain and produced better results. At the end of equilibrium time the adsorbent was removed from the solutions by centrifugation and the progress of adsorptive separation was assessed by determining the amount of chromium left in aliquot by Atomic Absorption Spectrophotometer, Model GBC 2100, Australia. All the experiments were repeated five times and then their average was taken as final value.

3. Results and discussions

3.1. Characterization of the adsorbent

Physicochemical analysis of the adsorbent was carried out and has been given in Table 1. Its surface area was found to be 1024 cm²/g and density 4.89 g/cm³. This table shows that silica (SiO₂) is the major component of the adsorbent. Calcium

Table 1
Physicochemical analysis of the adsorbent

Constituents	% by weight
SiO ₂	86.24
CaO	11.23
MgO	0.37
Fe ₂ O ₃	0.24
Al ₂ O ₃	0.47
Surface area (cm ² /g)	1024
Porosity	0.38
Density (g/cm ³)	4.89
Mean particle diameter (μm)	100

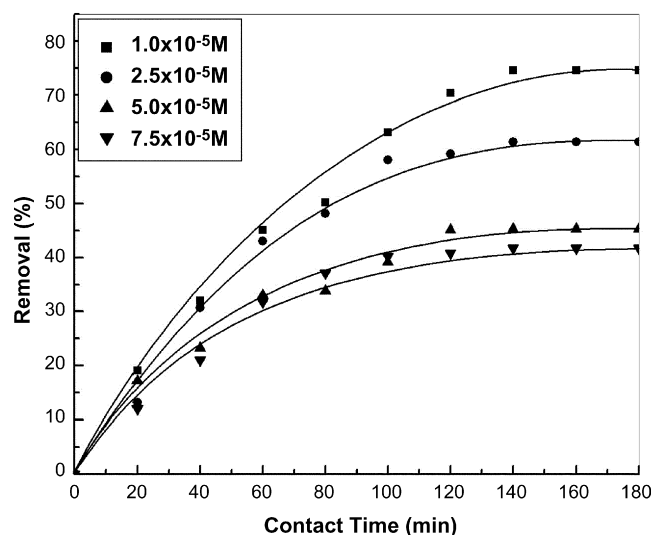


Fig. 1. Effect of contact time and initial concentration on removal of Cr(VI).

oxide was 11.23% and oxides of other metals were present in traces.

3.2. Effect of contact time and concentration

Contact time and concentration have pronounced effect on removal of pollutant species from aqueous solutions. The removal of Cr(VI) increased from 41.7% to 74.3% (Fig. 1) by decreasing concentration of Cr(VI) from 7.5×10^{-5} M to 1.0×10^{-5} M at 25 °C, 1.0×10^{-2} M NaClO₄ ionic strength and 100 rpm agitation speed. It is clear from this figure that in initial stages removal is rapid, is slow later on and becomes constant after attaining maxima at ‘equilibrium’. It is also clear from this figure that time of equilibrium is same for all initial concentrations.

3.3. Effect of particle size

Average particle size of adsorbent is directly related to its specific surface. Small particle size offers a larger surface area [13]. In the present finding, removal of Cr(VI) increased from 43.2% to 74.3% (Fig. 2) by decreasing the average particle size from 150 μm to 100 μm at 1.0×10^{-5} M initial concentration of Cr(VI) in solution at 25 °C, pH 2.5 and 1.0×10^{-2} M NaClO₄ ionic strength. It is, however, also clear that the increase in removal is not directly proportional to increase in surface area. A plausible explanation to this may be the fact that the lower free concentration for smaller adsorbent particles is significantly less than that for larger sand particles which consequently results in smaller extent of adsorption maxima for adsorbates [14].

3.4. Effect of temperature

Temperature is a significant parameter controlling adsorption of species in a system. This is also a fact that most adsorption processes are exothermic in nature and hence lower temperatures favor removal by adsorption [15]. In the present studies, removal

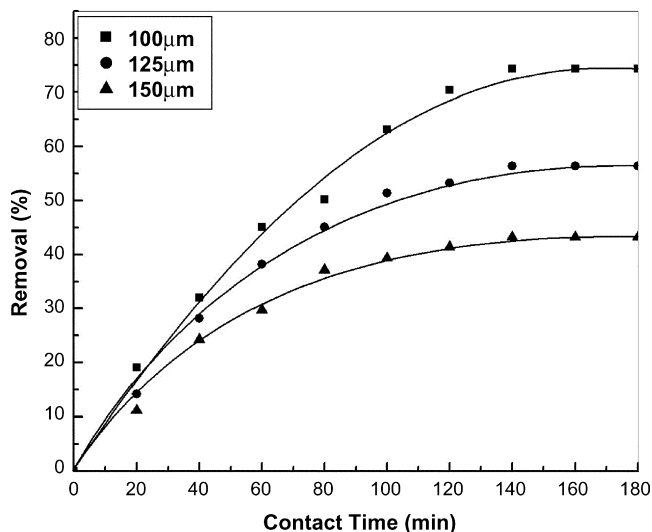


Fig. 2. Effect of particle size on removal of Cr(VI).

of Cr(VI) decreased from 74.3% to 40.7% (Fig. 3) on increase of temperature from 25 °C to 35 °C at 1.0×10^{-5} M initial concentration, 100 μm particle size, 1.0×10^{-2} M NaClO₄ ionic strength and pH 2.5. This also shows the process of removal of Cr(VI) by bed sediment is exothermic in nature. The decrease in removal at increasing values of temperature can be attributed to the fact that at enhanced temperature, relative escaping tendency of Cr(VI) species gets enhanced which consequently results in reduction of boundary layer thickness [16]. The role of increasing solubility of Cr(VI) at higher temperature also cannot be ruled out as a possible reason of decrease in removal at increasing value of temperature.

3.5. Thermodynamic studies

Effect of temperature was further studied in detail by calculating various thermodynamic parameters. Thermodynamic parameters studied were change in free energy (ΔG°), enthalpy

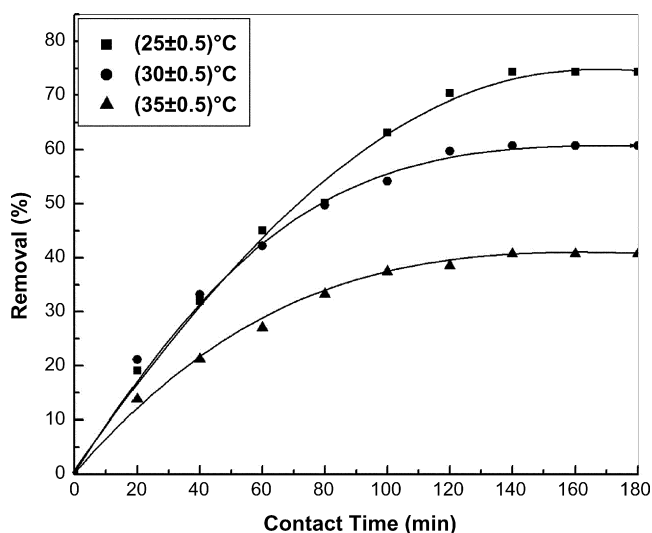


Fig. 3. Effect of temperature on removal of Cr(VI).

Table 2

Thermodynamic parameters for the removal of Cr(VI) by adsorption in riverbed sand

Temperature (°C)	$-\Delta G^\circ$ (kcal mol ⁻¹)	$-\Delta H^\circ$ (kcal mol ⁻¹)	$-\Delta S^\circ$ (cal mol ⁻¹)
25	0.81	17.21	56.94
30	0.48	9.23	28.87
35	0.28		

(ΔH°) and entropy (ΔS°) for the process of removal of chromium. The values of these parameters were calculated at different temperatures using following relations [17,18]:

$$\Delta G^\circ = -RT \ln K \tag{1}$$

$$\Delta H^\circ = R \frac{T_2 T_1}{T_2 - T_1} \ln \left(\frac{K_2}{K_1} \right) \tag{2}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{3}$$

The negative values of free energy (ΔG°) indicate the process of Cr(VI) removal to be spontaneous. The negative values of enthalpy change (ΔH°) (Table 2) further confirm the exothermic nature of the process of removal and negative values of entropy (ΔS°) confirm the possibility of favorable adsorption.

3.6. Effect of pH

pH of the sample plays an important role during removal of Cr(VI) by adsorption on bed sediments. Because of its importance, the parameter has been termed as master variable [19,20]. In the present studies also removal was drastically affected by variation in pH. Removal of Cr(VI) was high in acidic and low in alkaline range. Removal decreased from 74.3% to 28.2% by increasing pH of the solution from 2.5 to 8.0 (Fig. 4) at 1.0×10^{-5} M initial concentration, 25 °C, 100 μm particle size, 100 rpm and 1.0×10^{-2} M NaClO₄ ionic strength. The pH_{ZPC} of riverbed sand is 2.8 (Table 1) and it indicates that the sur-

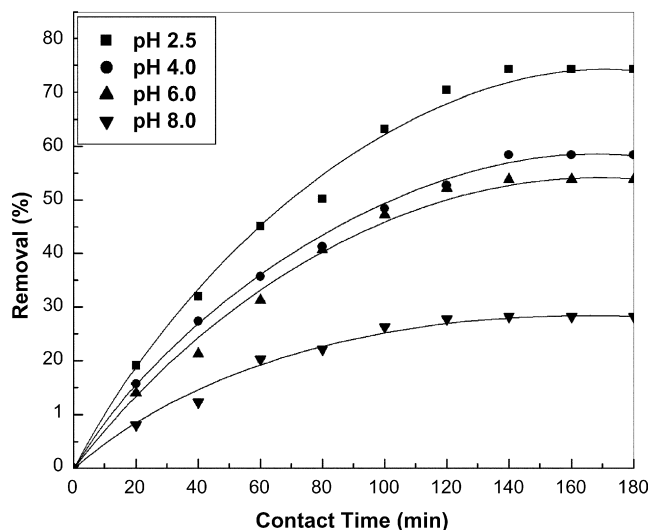
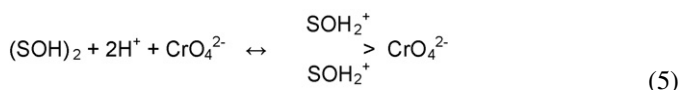
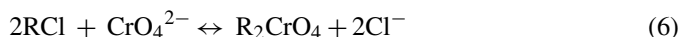


Fig. 4. Effect of pH on removal of Cr(VI).

face of the adsorbent will be positively charged around pH 2.5 and it will be quite favorable for adsorption of HCrO_4^- species [21]. The adsorption of Cr at neutral and negatively charged surfaces cannot be explained on the basis of electrostatic attractive forces alone. Specific chemical interactions and surface complexations also contribute in the process of removal. Speciation of chromium [20] also suggests that beyond pH 4.5, CrO_4^{2-} species are present in solution and removal may occur according to the following scheme [22]:



The above surface complexation model has also been reported by other scientific workers [23]. Alternatively, chemisorption has been reported to be operated during the process of removal [23]. Maximum removal of chromium around pH 2.5 may be associated with the presence of significantly high electrostatic attraction between adsorbate and adsorbent resulting in fixation of surface compounds [23]. In acidic range there is presence of Cl^- in the double layer and chromate–chloride ion-exchange has also been reported to explain removal of Cr(VI):



A detailed account of the effect of pH on the removal of chromium and other metallic species has been provided by various workers [24,25] and our results are according to their explanations.

Table 3 provides an interesting review of the adsorption capacities of some clay minerals viz. china clay [26], waste materials namely exhausted coffee, nutshell, saw dust, wall nut shell, fly ash, dead biomass, etc. [27–33]. In all the cases the reported adsorption capacities were significant. Dead biomass showed an adsorption capacity of 162.23 mg g^{-1} . Zeolite displayed a capacity of 0.65 mg g^{-1} and the adsorption capacity for chitosan was reported to be 27.30. Commercially available activated carbons were reported to have the maximum adsorption capacities of 212.12 mg g^{-1} [32,33]. Riverbed sand, the adsorbent used in part of the present work has an adsorption capacity of 0.15 mg g^{-1} [16] and this value is quite significant.

Table 3
Adsorption capacities of some non-conventional and commercial adsorbents used for adsorption of Cr(VI)

Adsorbent	Adsorption capacity (mg g^{-1})
Wollastonite	0.68
China clay	1.08
Exhausted coffee	1.42
Nut shell	1.47
Saw dust	16.05
Wall nut shell	1.33
Chitosan	27.30
Dead biomass	162.23
Zeolite	0.65
Fly ash	1.24
Activated carbon (column)	212.12
Riverbed sand ^a	0.15

^a This study.

4. Conclusions

On the basis of above studies the following conclusions may be drawn:

- (i) Riverbed sand, a non-toxic natural material has been successfully used for the removal of Cr from water and wastewater.
- (ii) Effect of various parameters on the removal of chromium has been studied.
- (iii) Higher removal was found in low concentration range with maximum (74.3%) at $1.0 \times 10^{-5} \text{ M}$ of Cr(VI) concentration in aqueous solutions.
- (iv) Removal decreased with increasing temperature with maximum removal (74.3%) at 25°C out of 25, 30 and 35°C , the temperatures undertaken in the studies. Removal was found to be higher at smaller particle size ($100 \mu\text{m}$) of the adsorbent.
- (v) pH was found to affect the removal significantly and higher removal of chromium was obtained in acidic pH ranges.
- (vi) Comparison of the adsorption capacity of riverbed sand, the adsorbent taken in the studies shows that it can serve as a potential material for removal of chromium from effluents.

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