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# Removal of chromium(VI) from water and wastewater by using riverbed sand: Kinetic and equilibrium studies

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## Abstract

Cr(VI) is a priority pollutant and has been documented to be harmful to fauna, flora and human beings and chromium containing water and wastewater are hazardous. Removal of Cr(VI) by adsorption on a non-toxic natural substance, riverbed sand has been investigated. A maximum removal of 74.3% was noted at $0.50 \times 10^{-4}$ M concentration of Cr(VI) in solution. Kinetic and equilibrium studies of Cr(VI) removal have been carried out. Chemical analysis of the adsorbent revealed $SiO_2$ to be its major component. Kinetic data of adsorption was fitted by Lagergreen's model and $k_{ad}$, the rate constant of adsorption, was found be maximum $2.69 \times 10^{-2}$ min$^{-1}$ at 25 °C with minimum at 35 °C. Values of coefficients of intra-particle diffusion and mass transfer have been determined at different values of temperature. Langmuir's model has been used for equilibrium studies and the constants have been calculated. The studies conducted show the process of Cr(VI) removal to be exothermic in nature.
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## 1. Introduction

Metals and metallic compounds are vital for industrial growth of any society. Like other metallic species chromium also occurs on earths surface but it is found in small proportions [1]. Chromium has applications in a variety of industries. It is frequently used in leather tanning, pigment manufacture, textile and dyeing, and makes an important component for a number of alloys [2]. Discharge of untreated effluents from these applications into water resources is a major source of pollution of chromium to these resources. Rivers are the major source of water for mankind and it is a fact that in most cities the industrial effluents are discharged into the rivers. It is obvious that in a river system, the metallic species would be distributed in aqueous, suspended and in the riverbed sediments. Chromium occurs in +3 and +6 oxidation states. In +3 oxidation state chromium is essential for human beings but the water containing Cr(VI)

makes it hazardous. Exposure to hexavalent chromium causes dermatitis, allergic skin reactions and gastrointestinal ulcers. It has been reported to be a teratogen and also a carcinogen. It has high acute toxicity and mutagenicity also.

Main techniques for removal of chromium from aqueous solutions and industrial effluents are chemical reduction, precipitation, ion-exchange, and adsorption. Scrap rubber has been successfully used as an adsorbent for removal of metallic species from wastewater [3]. Removal of metallic species by adsorption on activated carbon has been a popular choice of scientific workers world over [4–8]. Many workers have reported excellent results for the removal of pollutant species by modified activated carbons [9–12]. Application of activated carbon for large-scale treatment of industrial effluents is quite expensive and is unaffordable for developing nations. Emphasizing on this aspect many workers have used unconventional materials as adsorbents for removal of metallic species and other pollutants from aqueous solutions and industrial effluents [13–16].

In the present work, bed sediment of river subernarekha has been used for removal for Cr(VI) from aqueous solutions. Main purpose of this study is two-fold. First, to understand the adsorption characteristics of the bed sediments, and second, to suggest

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## Nomenclature

| | |
|---|---|
| $b$ | Langmuir constant related to energy of adsorption $(l\,mg^{-1})$ |
| $C_e$ | adsorbate concentration at equilibrium $(mg\,l^{-1})$ |
| $C_o$ | initial concentration of adsorbate $(mg\,l^{-1})$ |
| $C_t$ | adsorbate concentration at any time $(mg\,l^{-1})$ |
| $d_p$ | diameter of adsorbent particle $(\mu m)$ |
| $D$ | coefficient of pore diffusion $(cm^2\,s^{-1})$ |
| $k$ | Langmuir's constant $(Q_o b)$ $(l\,g^{-1})$ |
| $k_{ad}$ | rate constant of adsorption $(min^{-1})$ |
| $k_p$ | rate constant of pore diffusion $(mg\,g^{-1}\,min^{-0.5})$ |
| $m$ | mass of adsorbent per unit volume of particle free slurry $(g\,l^{-1})$ |
| $q$ | amount of chromium adsorbed at equilibrium $(mg\,g^{-1})$ |
| $q_e$ | amount of chromium adsorbed at any time $(mg\,g^{-1})$ |
| $Q^o$ | Langmuir constant related to capacity of adsorption $(mg\,g^{-1})$ |
| $r_o$ | radius of adsorbent particles $(cm)$ |
| $S_s$ | outer surface of the adsorbent per unit volume of particle free slurry $(cm^{-1})$ |
| $t$ | time $(min)$ |
| $t_{1/2}$ | time for half adsorption of chromium $(min^{-0.5})$ |

*Greek letters*

| | |
|---|---|
| $\beta_l$ | coefficient of mass transfer $(cm\,s^{-1})$ |
| $\rho_p$ | density of the adsorbent particles $(g\,cm^{-3})$ |
| $\varepsilon_p$ | porosity of the adsorbent |

an economically viable and non-toxic treatment for the water and wastewater rich in Cr(VI). The present work deals with the kinetic and equilibrium studies of the process of removal of Cr(VI) on riverbed sediments.

## 2. Experimental

### 2.1. Sediment sampling and storage

The sediment samples were collected from shallow waters near the bank from upstream. Samples were taken from upper 5 cm of the sediments where flow rates were low and sedimentation was assumed to occur [17–19]. After sampling, the sediments were stored in polyethylene bags, which were properly cleaned with 1 M KMnO$_4$ and 1 M HNO$_3$. Sediment samples were thoroughly washed and passed through sieves to remove all earthen impurities. Particle sizes of adsorbent samples were maintained using different sieves. Sieved samples were dried in an oven at 105 °C overnight and were allowed to remain in desiccators for cooling. Thereafter, the sediment samples were stored in airtight containers.

The surface area of the adsorbent was determined by a 'three point' N$_2$ gas adsorption method using a Quantasorb Surface Area Analyzer, Model-QS/7 (Quantachrome Corp., USA) and

average particle size was measured by particle Size Analyser, model HIAC-320 (ROYCO Instrument Div., USA). The porosity and density of the adsorbent were measured by using a mercury porosimeter and specific gravity bottles, respectively. The physical and surface properties of the adsorbent were determined by the methods reported elsewhere [20]. Chemical analysis of the adsorbent sediments was carried out using Indian Standard Methods [21]. All chemicals used in the experiments were AR/GR grade and were obtained from BDH, Bombay (India) and de-ionized water was used throughout the experiments.

Batch adsorption experiments were conducted by taking 50 ml solution of Cr(VI) of desired concentrations in 250 ml pre-cleaned polyethylene bottles. Afterwards solution pH was maintained by 1 M NaOH/HCl and was monitored by a control dynamics pH meter (Model CD 901, Century Instruments Ltd., Chandigarh, India), 1.0 g of adsorbent was then added to this solution. Ionic strength of the solutions was maintained by 0.01 M NaClO$_4$ solution. The agitation was carried out in a temperature-controlled thermostat. For equilibrium studies, the experiments were carried out at different values of temperature. The progress of adsorption was measured by determining the concentrations of Cr(VI) by using Atomic Absorption Spectrophotometer (GBC, Australia) at a wavelength of 357.9 nm [22]. It was ensured that there are no reductants in the samples.

## 3. Results

### 3.1. Physicochemical characterization of the adsorbent

In order to understand the adsorption of Cr(VI) onto riverbed sand, physicochemical characterization of the adsorbent was carried out. The analysis of the adsorbent shows (Table 1) silica to be its major (86.24%) constituent. Calcium oxide (11.23%) is the next major constituent of the adsorbent. The oxides of Mg, Fe, and Al are in traces. The surface area of the adsorbent was measured and found to be 10.24 m$^2$ g$^{-1}$, which is quite significant. Other physical parameters of the adsorbent were analyzed and are recorded in Table 1.

### 3.2. Effect of contact time and initial concentration on removal of chromium

Effect of contact time and initial concentration on removal of Cr(VI) by adsorption on riverbed sand was studied.

Table 1
Physicochemical analysis of the adsorbent

| Components | wt. % |
|---|---|
| SiO$_2$ | 86.24 |
| CaO | 11.23 |
| MgO | 0.37 |
| Fe$_2$O$_3$ | 0.24 |
| Al$_2$O$_3$ | 0.47 |
| Porosity | 0.38 |
| Density (g cm$^{-3}$) | 4.89 |
| Mean particle diameter ($\mu$m) | 100 |
| Surface area (m$^2$ g$^{-1}$) | 10.24 |

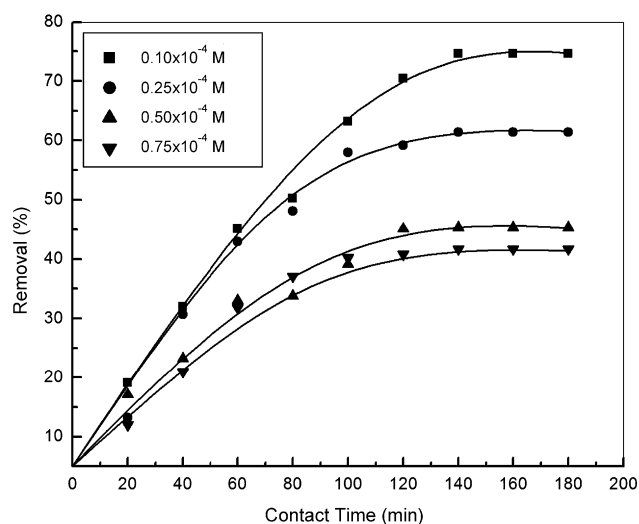Fig. 1. Effect of contact time and initial concentration on removal of Cr(VI) by adsorption on riverbed sand.

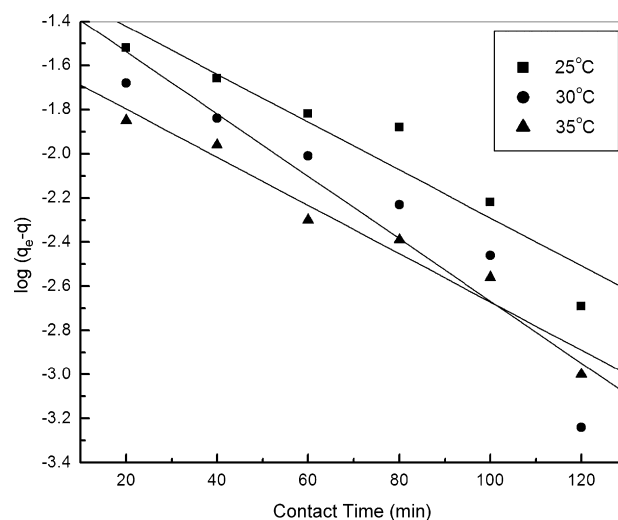

Fig. 2. Lagergren's plot for determination of rate constants for the removal of Cr(VI) at different temperatures by adsorption on riverbed sand.

The concentrations selected for studies were $0.10 \times 10^{-4}$, $0.25 \times 10^{-4}$, $0.50 \times 10^{-4}$, and $0.75 \times 10^{-4}$ M, respectively. These correspond to 1.05, 2.61, 5.23, and 7.84 mg l$^{-1}$, respectively. The results obtained have been plotted as 'removal (%) versus contact time' (Fig. 1). The graph shows that for all the concentrations, removal increases in initial stages, goes on increasing and acquires maximum value in 110 min. After 110 min, there is no increment in removal. This stage is known as equilibrium stage. As shown in Fig. 1, the removal of Cr(VI) increased from 41.7 to 74.3% by decreasing the initial concentration of chromium from $0.75 \times 10^{-4}$ to $0.10 \times 10^{-4}$ M at 2.5 pH, 0.01 M NaClO$_4$ ionic strength, temperature $25 \pm 0.5$ °C, 100 rpm and at a particle size of 100 μm. The amount adsorbed (mg g$^{-1}$) increases with increase in initial concentration of the adsorbate. An increase in initial concentration of Cr(VI) resulted in increase in amount adsorbed of chromium and this can be attributed to an increase in deriving force of the concentration gradient with increase in concentration of Cr(VI) in solution. Apparently, the initial concentration of chromium plays an important role and affects the adsorption capacity of Cr(VI) on the adsorbent. It is also clear from Fig. 1 that in initial stages the removal/adsorption is faster in lower ranges of concentration. This finding has industrial importance as in most cases, lower concentrations of adsorbates and pollutants are encountered in real life systems.

### 3.3. Kinetic studies

In order to understand the kinetics of removal of Cr(VI) by adsorption many models were tried. Finally, the Lagergreen's

model [23,24]:

$$\log(q_e - q) = \log q_e - \left(\frac{k_{ad}}{2.303}\right) t \tag{1}$$

was found suitable for the present system. The straight-line plots of '$\log(q_e - q)$ versus $t$' (Fig. 2) indicate that the proposed model fits well the data of the system studied. The value of $k_{ad}$, the rate constant of adsorption, was found to be $2.09 \times 10^{-2}$ min$^{-1}$ at $0.10 \times 10^{-5}$ M Cr(VI) concentration, 2.5 pH, 0.01 M NaClO$_4$ ionic strength and 25 °C. The values of $k_{ad}$ were determined at other values of temperature and have been recorded in Table 2. Results show that the values of $k_{ad}$ decrease with temperature. The adsorption of Cr(VI) on bed sediments may also follow intra-particle diffusion as this has been found to be an important rate limiting step for many processes which are carried out in rapidly stirred batches. This possibility was explored by plotting a graph 'amount of Cr(VI) adsorbed versus square root of time, $\sqrt{t}$' (Fig. 3). These plots show a double straight-line nature: initial and final stages.

The initial stages indicate boundary layer diffusion [25] and straight-line portions in final stages indicate that the process of removal is dominated by intra-particle diffusion in this part of process [26]. Values of the rate constant of intra-particle diffusion, $k_p$, at different temperatures were calculated by using slopes of Fig. 3 and have been given in Table 2. It clearly shows that values of $k_p$ also decrease with increasing temperature. The

Table 2
Parameters for adsorption kinetics viz. the rate constant, $k_{ad}$, the coefficient of pore diffusion, $k_p$, the coefficient for pore diffusion $D$, the coefficient of mass transfer, $\beta_1$, and the rate parameter

| Temperature (°C) | $k_{ad}$ (min$^{-1}$) ($\times 10^{-2}$) | $k_p$ (min$^{-1/2}$) ($\times 10^{-2}$) | $D$ (cm$^2$ s$^{-1}$) ($\times 10^{-11}$) | $\beta_1$ (cm s$^{-1}$) ($\times 10^{-2}$) | Rate parameter (min$^{-1}$) ($\times 10^{-2}$) |
|---|---|---|---|---|---|
| 25 | 2.69 | 1.80 | 1.67 | 1.18 | 12.08 |
| 30 | 1.82 | 1.71 | 1.42 | 0.88 | 9.01 |
| 35 | 1.78 | 1.58 | 1.10 | 0.75 | 7.68 |

Fig. 3. Intra-particle diffusion plot for removal of Cr(VI) by adsorption on riverbed sand.
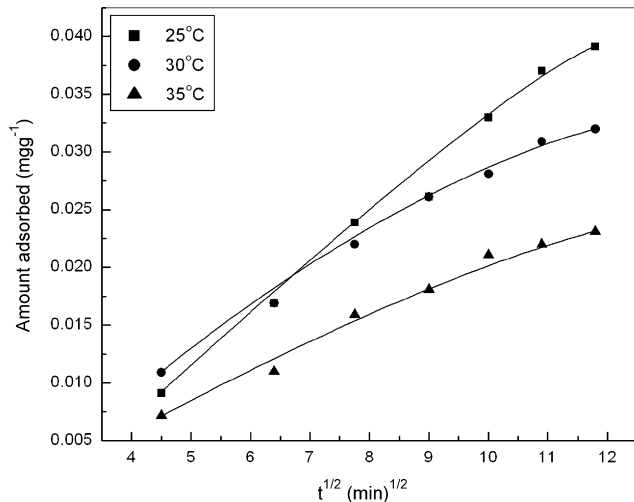


Fig. 4. Mass transfer plot for the removal of Cr(VI) by adsorption on riverbed sand.

following equation [27]:

$$D = \frac{0.03r_o^2}{t_{1/2}} \qquad (2)$$

was used for determination of the coefficient of intra-particle diffusion, $D$. $t_{1/2}$ is time for half adsorption of Cr(VI) on the adsorbent phase. The values of $D$ (Table 2) were found to be in order of $10^{-11}\,cm^2\,s^{-1}$, and the values of $D$ indicate that intra-particle diffusion is the process which decides the rate of uptake of Cr(VI) [27].

### 3.4. Mass transfer studies

For any process of removal by adsorption it is important to know the extent of transfer of pollutant species from bulk to the surface of the solid adsorbent particles and at the interface of solid adsorbent particles or at the interface of liquid and solid particles. For the present studies this probability was examined by using following mass transfer model [28]:

$$\ln\left[\frac{C_t/C_0 - 1}{1 + mk}\right] = \ln\left[\frac{mk}{1 + mk}\right] - \left[\frac{1 + mk}{mk}\right]\beta_l S_s t \qquad (3)$$

where '$k$' is a constant and is the product of Langmuir's parameters.

The values of '$m$' and '$S_s$' have been determined as follows:

$$m = \frac{W}{V} \qquad (4)$$

$$S_s = \frac{6m}{d_p \rho_p (1 - \mathbb{C}_p)} \qquad (5)$$

where $\mathbb{C}_p$ is porosity of the adsorbent. Values of $\beta_l$, the coefficient of mass transfer, were calculated at different values of temperature by the slopes and intercepts of the plots of '$\ln[C_t/C_o - 1/(1 + mk)]$' versus $t$' (Fig. 4) and the values are given in Table 2. The value of $\beta_l$, however, was found to be $1.18 \times 10^{-2}\,cm\,s^{-1}$ at $25\,°C$, 100 rpm, 0.01 M NaClO$_4$ ionic strength and 2.5 pH.
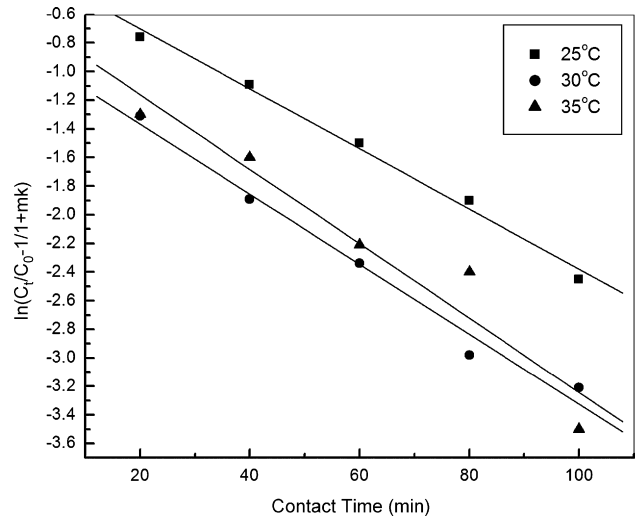
All the values of mass transfer coefficient are indicative of a sufficiently rapid transfer of adsorbate species from bulk to the surface/interface [29]. A value of $\beta_l$ in the order of $10^{-5}$ or greater shows that the rate of transfer of mass from bulk to the solid surface is rapid enough [25] and the system of 'Cr(VI)–riverbed sand' can be recommended for removal of Cr(VI) from wastewaters. This is interesting to note that the rate parameter, '$\beta_l S_s$' has the dimensions of $k_{ad}$, the rate constant for adsorption and its values have also been found to be in the same order and this further approves the validity of used mass transfer model [29]. Further, though at laboratory scale the adsorbent used has shown good results but the commercial extraction of riverbed sand can create problems to biota. Thus, keeping this fact in mind, this adsorbent should also be regenerated the way other adsorbents are regenerated.

### 3.5. Equilibrium studies

Equilibrium studies for any process of removal are of immense importance, specially to recommend the process for large-scale application. The equilibrium studies for the present process were carried out by using Langmuir's isotherm model [30]. Further, the isotherm studies are carried out to determine the adsorption capacity of the adsorbent:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \qquad (6)$$

The plots of '$C_e/q_e$ versus $C_e$' (Fig. 5) at different temperatures were found to be linear and indicate that the used model fits well the data of studies performed. Further, the Langmuir's model is based on assumption that adsorption takes place at specific homogenous sites at and within the adsorbent. The model has been used to explain many adsorption processes successfully [20–25].

The values of the Langmuir's parameters namely, '$Q_o$', the term related to the capacity of adsorption and '$b$', the term related to energy of adsorption were found to be 0.15 mg g$^{-1}$ and
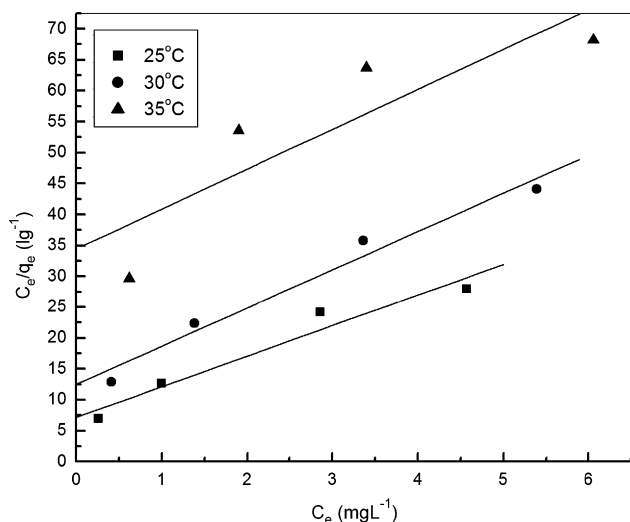
Fig. 5. Langmuir's plot for equilibrium modeling of removal of Cr(VI) by adsorption on riverbed sand.

Table 3
Langmuir's constants for the removal of Cr(VI) by adsorption on riverbed sand

| Temperature (°C) | $Q^0$ (mg g$^{-1}$) ($\times 10^{-1}$) | $b$ (l mg$^{-1}$) ($\times 10^{-1}$) | $K$ (=$Q^0 b$) (l g$^{-1}$) ($\times 10^{-2}$) |
|---|---|---|---|
| 25 | 1.50 | 6.34 | 9.50 |
| 30 | 0.82 | 5.82 | 4.70 |
| 35 | 0.75 | 4.79 | 3.60 |

0.634 l g$^{-1}$ at 25 °C, 100 rpm, 0.01 M NaClO$_4$ ionic strength and 2.5 pH. Values of these parameters at other temperatures have been calculated and have been given in Table 3. On perusal of the values of the Langmuir's parameters '$Q_o$' and '$b$', it is clear that the values are in decreasing pattern with temperature and hence confirm the exothermic nature of the present process [19].

Table 4 provides an interesting review of the adsorption capacities of some clay minerals viz. wollastonite [31], china clay [32], waste materials, namely exhausted coffee, nutshell, saw dust, wall nut shell, fly ash, dead biomass, etc. [33–37]. In all the cases the reported adsorption capacities were significant. Dead biomass showed an adsorption capacity of 162.23 mg g$^{-1}$.

Table 4
Adsorption capacities of some non-conventional and commercial adsorbents used for adsorption of Cr(VI)

| Adsorbents | Adsorption capacity (mg g$^{-1}$) |
|---|---|
| Wollastonite | 0.686 |
| China clay | 1.083 |
| Exhausted coffee | 1.42 |
| Nut shell | 1.47 |
| Saw dust | 16.05 |
| Wall nut shell | 1.33 |
| Chitosan | 27.3 |
| Dead biomass | 162.23 |
| Zeolite | 0.65 |
| Fly ash | 1.24 |
| Activated carbon (column) | 188.20 |
| Activated carbon (column) | 212.12 |

Zeolite displayed a capacity of 0.65 mg g$^{-1}$ and the adsorption capacity for chitosan [38] was reported to be 27.3 mg g$^{-1}$. Commercially available activated carbons were reported to have the maximum adsorption capacities of 188 and 212 mg g$^{-1}$ [39,40]. Riverbed sand, the adsorbent used in the present work has an adsorption capacity of 6.34 mg g$^{-1}$ and this value is quite significant. It is important to note that the adsorbent once used for the removal of Cr(VI) from aqueous solutions/wastewater should be regenerated for reuse. Recovery of the adsorbed species from the used adsorbent can also be done but the cost aspect has to be given due consideration. At last, the completely exhausted adsorbent has to be safely disposed by following well known methods of disposal of wastes of similar category.

## 4. Conclusions

On the basis of the results the following conclusions may be drawn:

i. Riverbed sand can be successfully used for Cr(VI) removal from aqueous solutions.
ii. The data generated on various studies can be used to design various treatment plants for the treatment of Cr(VI) rich wastewaters.
iii. Process adopted is simple and economically viable.
iv. Langmuir's constants show suitability of riverbed sand as adsorbent for Cr(VI) removal.
v. Mass transfer analysis shows the process of transfer of Cr(VI) onto the adsorbent surface to be rapid enough and confirms its suitability for the present system.

Further, river bed sand is a natural material and may provide a non-toxic process of Cr(VI) removal. It seems that riverbed sand can make a good choice for treatment of Cr(VI) rich wastewaters and industrial effluents.

## References

[1] V. Subramanian (Ed.), Environmental Hazards in South Asia, Capital Pub. Co., N.D., India, 2002.
[2] K. Kannan, Fundamentals of Environmental Pollution, S Chand and Co. Ltd., N.D., India, 1995.
[3] S. Lee, K. Lee, J. Park, Simultaneous removal of Cd and Cr(VI) using Fe-loaded zeolite, J. Environ. Eng. ASCE 132 (2006) 445–450.
[4] C.P. Huang, M.H. Wu, The removal of chromium by carbon adsorption, J. Water Pollut. Control Fed. 47 (1975) 2437–2446.
[5] J.Y. Hu, T. Aizawa, Y. Magara, Evaluation of adsorbability of pesticides in water on powdered activated carbon by using octanol-water partition coefficient, Water Sci. Technol. 35 (1997) 219–228.
[6] R.L. Ramos, J.R.R. Mendez, J.M. Barron, L.F. Rubio, R.M.G. Coronado, Adsorption of cadmium(II) from aqueous solution onto activated carbon, Water Sci. Technol. 35 (1997) 205–211.
[7] C.P. Huang, P.K. Wirth, Activated carbon for treatment of cadmium wastewater, J. Environ. Eng. ASCE 104 (1979) 1280–1299.
[8] R.S. Summers, S.M. Hooper, G. Solarik, D.M. Oven, S. Hongm, Bench scale evaluation of GAC for NOM control, J. AWWA 87 (1995) 69–80.
[9] P.T. Orr, G.J. Jones, G.R. Hamilton, Removal of saxitoxins from drinking water by granulated activated carbon, O$_3$ and H$_2$O$_2$-implications for compliance with the Australian drinking water guidelines, Water Res. 38 (2004) 4462–4474.

[10] E.G. Servano, T. Cordero, J.R. Mirasol, L. Cotoruelo, J.J. Rodriguez, removal of water pollutants with activated carbons prepared from $H_3PO_4$ activation of lignin from kraft black liquors, Water Res. 38 (2004) 3043–3050.

[11] C.M. Castilla, J.V. rivera, M.V. Lopez, F.C. Marin, Adsorption of some substituted phenols on activated carbons from a bituminous coal, Carbon 35 (1995) 845–851.

[12] G.J. Alaerts, V. Jitjaturunt, P. Kelderman, Use of coconut shell based activated carbon for Cr(VI) removal, Water Sci. Technol. 21 (1989) 1701–1704.

[13] R. Naseem, S.S. Tahir, Removal of Pb(II) from aqueous acidic solutions by using bentonite as an adsorbent, Water Res. 35 (2001) 3982–3986.

[14] S. Zheng, Z. Yang, D.H. Jo, Y.H. Park, Removal of chlorophenols by chitosan adsorption, Water Res. 38 (2004) 2315–2322.

[15] T.S. Anirudhan, M.K. Sreedhar, Adsorption thermodynamics of Co(II) on polysulphide treated saw dust, Indian J. Chem. Technol. 5 (1998) 41–47.

[16] G. Singh, B. Rohira, Adsorption kinetics of dihydroxipyrimidine on mild steel in 1N phosphoric acid, Indian J. Chem. Technol. 2 (1996) 263–268.

[17] C.K. Jain, D. Ram, Adsorption of lead and zinc on bed sediments on the river Kali, Water Res. 31 (1997) 154.

[19] H. Sakai, Y. Kojima, K. Saito, Distribution of metals and sieved sediments in the Toyohira river, Water Res. 20 (1986) 559–567.

[20] V. Subramanian, R.V. Grieken, D.L. Vant, Heavy metal distribution in the sediments of Ganges and Brahmaputra rivers, Environ. Geol. Water Sci. 9 (1987) 93–103.

[21] C. Raji, T.S. Anirudhan, Chromium(VI) adsorption by saw dust carbon: kinetics and equilibrium, Indian J. Chem. Technol. 4 (1997) 228–236.

[22] Indian Standard Methods of Chemical Analysis of Fire Clay and Silica Refractory Materials IS: 527, 1960.

[23] Standard Methods for the Analysis of Water and Wastewater, APHA, AWWA, WPCF, 16th ed., Washington, DC, 1985.

[24] Y.C. Sharma, Effect of temperature on interfacial adsorption Cr(VI) on wollastonite, J. Colloid Interface Sci. 233 (2001) 265–272.

[25] G.S. Gupta, G. Prasad, V.N. Singh, Removal of colour from wastewater by sorption for water reuse, J. Environ. Sci. Health A23 (1988) 205–218.

[26] J. Crank, The Mathematics of Diffusion, Clarendon press, London, 1965.

[27] G. McKay, M.S. Otterburn, A.G. Sweeny, The removal of colour from effluents using various adsorbents, III silica, Water Res. 14 (1980) 15–20.

[28] L.D. Michelson, P.G. Gideon, E.G. Pale, L.H. Vutal, USDI Office of Water Research and Tech Bulletin No. 74, 1975.

[29] G. McKay, M.S. Otterburn, A.G. Sweeny, Surface mass transfer process during colour removal from effluents using silica, Water Res. 15 (1981) 321–331.

[30] K.P. Yadava, K.K. Pandey, B.S. Tyagi, V.N. Singh, Fly ash for the treatment of Cd(II) rich effluents, J Environ. Technol. Lett. 8 (1987) 225–234.

[31] C.H. Weng, J.H. Wang, C.P. Huang, Adsorption of Cr(VI) onto $TiO_2$ from dilute aqueous solutions 35 (1997) 55–62.

[32] Y.C. Sharma, G.S. Gupta, G. Prasad, D.C. Rupainwar, Use of wollastonite in the removal of Ni(II) from aqueous solutions, Water Air Soil Pollut. 49 (1990) 69–79.

[33] Y.C. Sharma, G. Prasad, D.C. Rupainwar, K.K. Panday, Inexpensive adsorption technique for to remove Cr(VI) from aqueous solutions, Int. J. Environ. Anal. Chem. 39 (1990) 310–321.

[34] Y. Orhan, H. Buyukgungor, The removal of heavy metals by using agricultural wastewater, Water Sci. Technol. 28 (1993) 247–256.

[35] V.P. Dikshit, I.C. Agrawal, N.P. Shukla, Bituminous coal for adsorption of hexavalent chromium from aqueous wastes, Asian Environ. 12 (1990) 64–69.

[36] A.K. Bhattacharya, C. Venkobachar, Removal of Cd(II) by low cost adsorbents, J. Environ. Eng. Div. 110 (1984) 110–122.

[37] H.L. Kutat, D.L. Michelson, Removal and recovery of ionic mercury from wastewater using tannery hair, AICHE Symp. Ser. Water 136 (1973) 384–392.

[38] J.N. Jha, L. Iyengar, A.V.S.P. Rao, Removal of cadmium using chitosan, J. Environ. Eng. ASCE 144 (1988) 962–973.

[39] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solutions, J. Sanit. Eng. Div. ASCE 89 (1963) 31–39.

[40] J. Kim, J. Joltek, Chromium removal with activated carbon, Prog. Water Technol. 9 (1977) 943–952.