

Prevention of groundwater contamination through reactive barrier material (RBM) for use in landfill liners and *in situ* barriers to immobilize chromium

R. C. VAISHYA¹, M. M. SETHY¹ & K. R. REDDY²

1 Department Civil Engineering, Motilal Nehru National Institute of Technology, Allahabad-211004, India

revaishya@yahoo.com

2 Department of Civil and Materials Engineering, University of Illinois at Chicago, Chicago, Illinois, USA

Abstract This paper presents the development of novel Reactive Barrier Material (RBM), to use as liner or barrier material for effective containment of toxic hexavalent chromium [Cr(VI)]. The results of batch kinetic experiments show that at equilibrium time, the percentage removal of Cr(VI) varies from 65 to 70% for various ratios of IOCS and Kaolin at initial pH of 8.61 ± 0.1 . The percentage removal of Cr(VI) decreased from 69 to 54% as sorbate concentrations in the solute increased from 10mg/L to 50 mg/L, keeping other experimental conditions similar. The results of isothermal studies conducted at different pH values show that adsorption data satisfied both the Langmuir and Freundlich isotherm models. The effect of pH on Cr removal by RBM was negligible; however, maximum sorption occurred at about pH 5.0 ± 0.1 - 6.0 ± 0.1 under similar experimental conditions. Wolborska and Pustelnik model was applied for breakthrough data of Cr(VI) with almost successful reproducibility of pore volume treated during column studies. The results suggest that RBM may be a viable alternative material to use in landfill liners to effectively contain Cr(VI) in leachate and in in-situ barriers to treat groundwater contaminated by Cr(VI).

Key words reactive barrier material; chromium; adsorption; groundwater; oxide coated sand; isotherms; model

INTRODUCTION

Chromium is a common groundwater contaminant in industrial regions throughout the world. Chromium contamination has been caused mainly by past industrial activities such as electroplating, wood preservation, leather tanning, and metal finishing. Chromium exists in two valence states, trivalent, Cr(III), and hexavalent, Cr(VI). Cr(VI) is more toxic and mobile as compared with Cr(III). It exists primarily in two anion forms, HCrO_4^- and CrO_4^{2-} (Fendorf and Zasoski, 1992; Chintamreddy and Reddy, 1998). Pump-and-treat groundwater remediation methods have proved to be expensive and in many cases ineffective at achieving the proposed level of clean up (Mackay and Cherry, 1989). A new technology being developed for the remediation of contaminated groundwater involves placing reactive barrier material below the ground surface in the path of flowing groundwater. These engineered barriers contain reactive solids, which act by various *in situ* transformations. For many dissolved solutes these transformations include reduction or oxidation reactions and subsequent precipitation of sparingly soluble solids.

Generally, landfill leachate contains both organic compounds and heavy metals (such as chromium). Currently, clay materials are selected as liner materials primarily based on their low hydraulic conductivity to prevent advective transport of leachate constituents. However, research studies (Astrop et al., 2000; Lo, 2003; Edil et al., 1991; Blowes et al., 1997; Bright et al., 2000; Abu-El-Sha'r et al, 2003) have shown that contaminants migrate through the liner due to diffusion. If there is a significant diffusive flux, potential for underlying groundwater contamination exists.

The present study assesses the ability of reactive barrier material to remove dissolved Cr(VI) from synthetic solution under dynamic flow conditions over a sustained period of time. The attenuating reactive barrier material (RBM) studied contains treatment mixtures of iron oxide coated sand (IOCS), and kaolin. Geochemical calculations and batch tests were conducted to pre-screen potential candidates for further study using column tests.

EXPERIMENTAL METHODOLOGY

Materials

All glassware were soaked in 2N HNO₃ for at least 24 h and then rinsed several times in distilled water before use. Analytical reagent grade chemicals (Merck, India) and distilled water were used for preparation of all solutions. Stock Cr(VI) solution was prepared as per Standard Methods (Chesceri et al., 1989). Quartz sand was procured from the bank of river Yamuna at Allahabad (India) and sieved for geometrical mean (GM) size of 505 µm. The coating was applied as per Edwards and Benjamin (1989). Three different types of reactive barrier material (RBM), i.e. 75% IOCS and 25% Kaolin (RBM I); 80% IOCS and 20% Kaolin (RBM II); and 90% IOCS and 10% Kaolin (RBM III) were prepared for further studies.

Batch experiments

Batch sorption studies were conducted to investigate kinetic uptake of Cr(VI) by RBM at room temperature on an end-to-end rotary shaker at 64 ± 2 rpm. The reaction mixture consisted of total volume of 100 mL in 300 mL borosilicate glass bottles containing different concentrations of Cr and selected weight of media dose for kinetic studies. The bottles were removed from shaker after desired contact time and supernatant was separated from adsorbent by 'Whatman-42' filter paper (ashless). The pH of each solution was measured before and after sorption experiments using of pH meter (model: Li 120, Elico, India,). Solution concentrations were determined for Cr(VI) using spectrophotometer (Model Genesys-20, Thermo Spectronic, USA) and Atomic Absorption Spectrophotometer (AAS) (Model Aanalysts-200, Perkin-Elmer, USA) for Total Cr.

Column experiments

Column experiments were conducted in a number of fixed reactors (glass columns of internal diameter 18 mm). The design parameters were evaluated by running FBRs at three different bed depths (h) i.e., 9, 14, and 20 cm. An average flow rate of 0.17 ml/min ($0.04 \text{ m}^3/\text{m}^2/\text{h}$) was maintained with an influent Cr(VI) concentration (C_0) of 100 mg/L through all the columns. The pH was maintained by addition of small amount of 0.1 N HCl or 0.1 N NaOH.

RESULTS AND DISCUSSION

Batch experiments

Results of batch sorption studies indicate the rate of removal of Cr from solution varies substantially for the different mixtures assessed (Figure 1). The percentage removal of Cr(VI) varied from 65 to 70% for RBM I, and it was greater than that of other media tested at initial pH of 8.61 ± 0.1 .

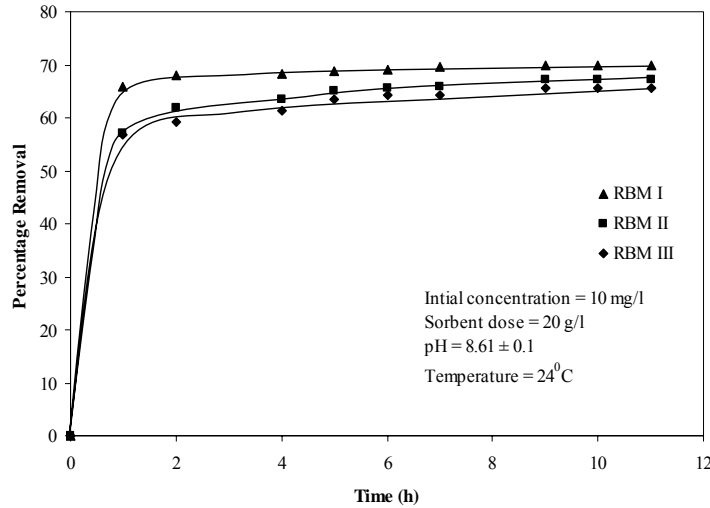


Figure 1 Percentage removal of Cr(VI) on reactive barrier material with different compositions

Figure 2 show the percentage removal of Cr(VI) was decreased from 69 to 54% as sorbate concentration in the solute was increased from 10 mg/L to 50 mg/L keeping other conditions similar. The higher percentage of kaolin in RBM I may have increased the surface area of solids, leading to higher Cr removal as compared with other media (RBM II and III). For the small surface area RBM III, the pore space is sufficient enough for salt penetration and subsequent better coating, even though this media had lower surface area as compared to RBM I.

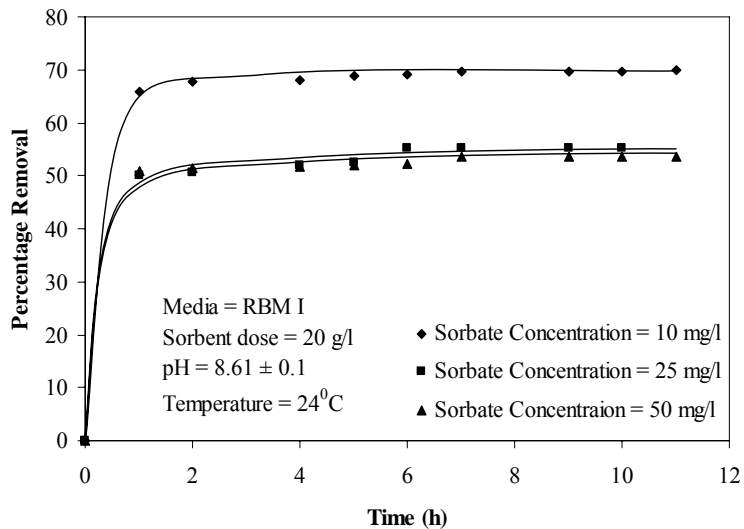


Figure 2 Percentage removal of Cr(VI) on RBM I for different concentration

The isothermal studies were conducted on RBM I for Langmuir isotherm (Figure 3) and Freundlich isotherm models (Figure 4). The slight departures of experimental data points from line of best fit indicates less than perfect fit into Langmuir and Freundlich isotherm models.

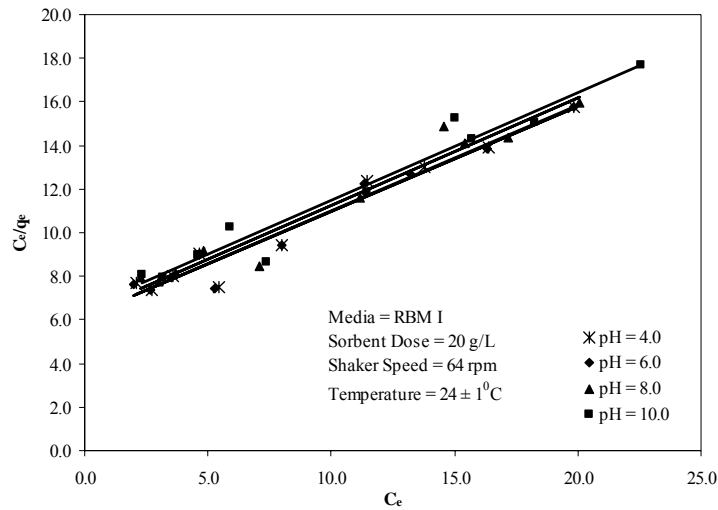


Figure 3 Linearised Langmuir isotherms for Cr(VI) adsorption for different pH

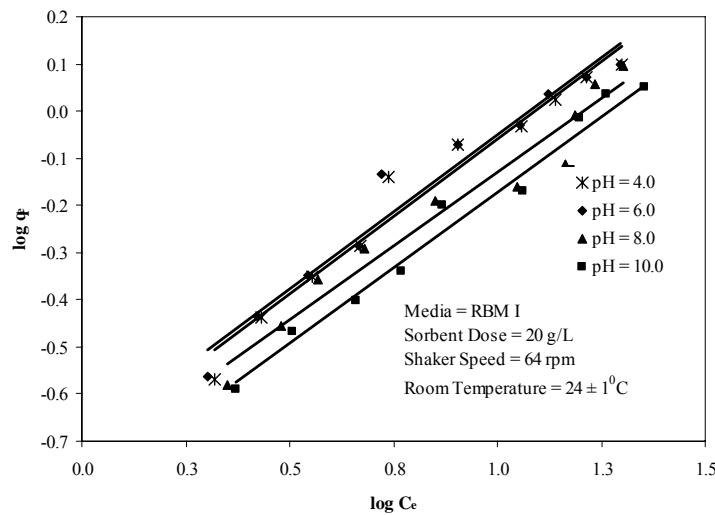
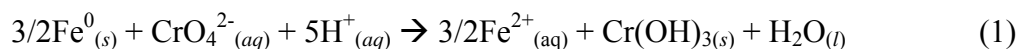


Figure 4 Linearised Freundlich isotherms for Cr(VI) adsorption for different pH

The ultimate sorption capacity for Cr(VI) was 2.067 mg/g as per Langmuir isotherm and 0.191 mg/g as per Freundlich isotherm models. However, for total chromium it was 1.367 mg/g as per Langmuir isotherm and 0.191 mg/g as per Freundlich isotherm models. The adsorption capacity of reactive barrier material slightly increases with decreasing pH. The co-precipitation of Cr(VI) by Fe(III) hydroxide may be one mechanism of removal. According to one hypothesis reduction of Cr(VI) to Cr(III) by reaction with zero valent iron [Fe(0)], on the reactive barrier material (RBM) and subsequent precipitation of Cr(III) oxyhydroxides occurs through the reaction (Kaplan and Gilmore, 2002):



The removal mechanism may also be explained based on surface complexation theory. The reactive barrier material (RBM) when placed in solution, a hydrous oxide layer forms on the surface of the media. As a result, the media is assumed to have oxide on the hydroxylated surface sites in the solution such as $>SOH_2^+$ and $>SOH$ representing positive and neutral charged sites. Since Fe is present in reactive barrier material surface, therefore surface sites may be $>FeOH_2^+$ and $>FeOH^{+2}$. The surface complexation of chromate ($HCrO_4^-$) is:



Here $S - OH$ is a hydroxide surface site. Equation 2 represents un-in-denate surface complexation in the near surface plane and incorporates the impacts of pH on adsorption equilibria. Figure 5 depict the effect of pH of Cr(VI) and total Cr by RBM I. The mechanism for removal of Cr(VI) can be explained as equation 2. The decrease in Cr(VI) removal in the pH range 6 – 10, may be result of negative charge on the RBM media ($>pH_{zpc}$). The dominant species of chromium in the pH range is $Cr(OH)^{2+}$ and $Cr(OH)_3$, disfavor adsorption on media surface.

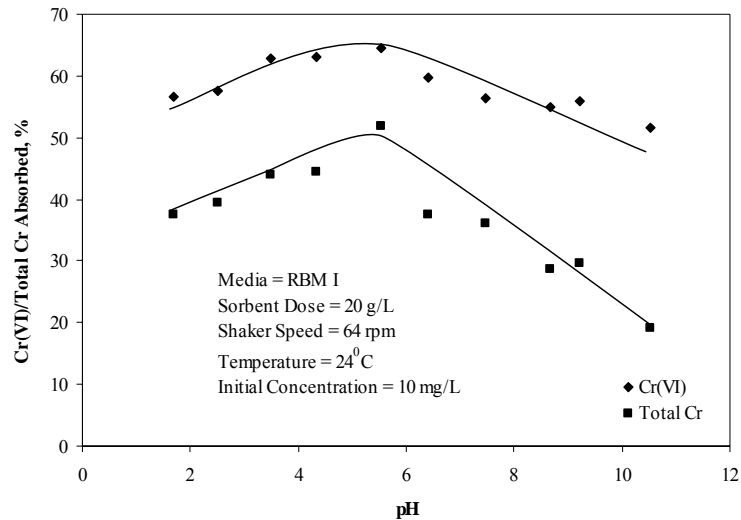


Figure 5 Adsorption of Cr(VI)/Total Cr on RBM I as a function of pH

Column experiments

Figure 6 shows breakthrough curves for three FBRs, which was packed with iron oxide coated sand and kaolin. The shapes of the breakthrough curves suggest Cr retardation results from anion adsorption, probably to the iron oxide coated sand and kaolin.

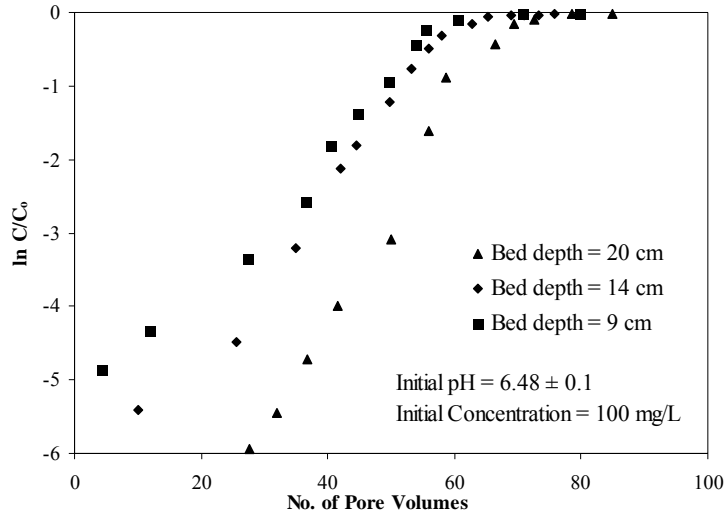


Figure 6 Breakthrough curves for Cr(VI) adsorption by RBM I at different bed depth

Column bed design by Wolborska and Pustelnik model

Wolborska and Pustelnik (1996) model was used for modelling of Cr(VI) adsorption from aqueous solution on the RBM columns. The experimental breakthrough curves (Figure 6) seems to be rectilinear and can be described by the following equation.

$$\ln \frac{C}{C_0} = Av + B \tag{3}$$

Where, A and B are constants. C is solution phase concentration of Cr(VI) at time t (mg/L). C₀ is initial Cr(VI) concentration (mg/L). Further the relationships and coefficients were determined using this model.

The constant A and B were determined using least square methods taking points that falls on straight line for particular breakthrough curve for a given effluent concentration. These constants and the correlation coefficients are given in Table 1. The observed and predicted values of breakthrough time in Table 1 are based on mean value of constant B. The form of correlation obtained is in agreement with equation derived by Wolborska and Pustelnik (1996) for the initial segment of breakthrough curve. Figure 7 presents the relation between constant B and the bed Height.

Kinetic coefficient of the process

The constant B determines, the relative concentration of the first batch of the solution leaving bed (t → 0). The distribution of this concentration along the column corresponds to the initial stage of the process. The constant B is determined by the following formula.

$$B = \ln \left(\frac{C}{C_0} \right)_{t \rightarrow 0} = - \frac{\beta_a h}{u} \tag{4}$$

Kinetic coefficients β_a , were calculated using the constant B, for each breakthrough curve and are presented in Table 1. Proportionality of constant B to bed height was confirmed by a series of experiment carried out at constant flow. From the data correlation in the system (B, h) a mean value of kinetic coefficient $\beta_a = 0.892 \times 10^{-3} \text{ s}^{-1}$ was calculated. According to the prior theoretical analysis, this is an effective coefficient, which reflects the effect of both mass transfers in the liquid phase and axial diffusion.

Table 1 Comparison of Calculated and Predicted Values of Breakthrough Number of Pore Volumes (Wolborska and Pustelnik Model)

Bed Depth (cm)	Constants in Equation (3)		Cc	Kinetic Coefficient $\beta_a \times 10^{-3} \text{ (s}^{-1}\text{)}$	No. of Pore Volume at Break Point	
	A	B			Observed	Predicted
9.0	0.158	-8.891	0.985	1.087	26.50	27.26
14.0	0.146	-8.910	0.985	0.700	35.00	42.95
20.0	0.125	-8.945	0.979	0.492	50.00	58.97

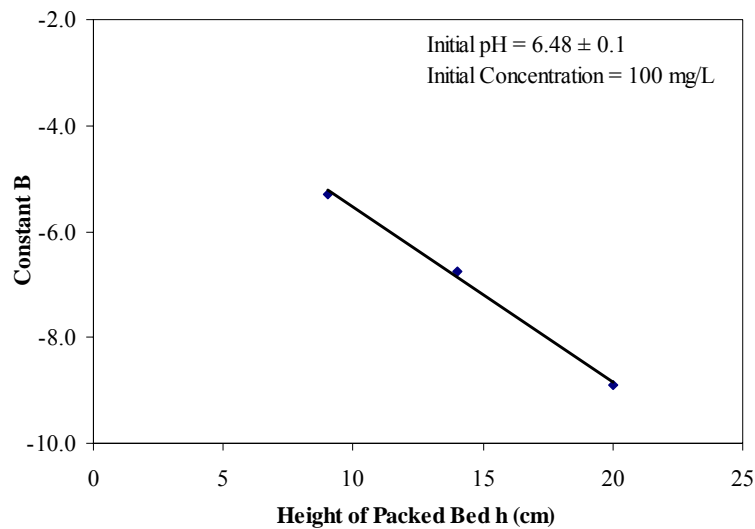


Figure 7 Relation between constant B and the bed Height

CONCLUSIONS

A good chromium sorption potential exists in tested reactive barrier material. RBM containing treatment mixtures of 75% iron oxide coated sand (IOCS) and 25% kaolin (RBM I) has shown maximum chromium uptake potential. Thus proposed reactive material will convert heavy metals into immobile form, thereby preventing potential groundwater contamination. It will be almost like in-situ treatment of leachate. Precipitation occurred on kaolin during experimentation indicates a lower rate of build-up on the IOCS. Thus, kaolin addition improves attenuation capacity by extending barrier lifetime; reducing hydraulic conductivity ensures reasonable

residence times for reaction. Modelling of column studies data results almost successful reproducibility of pore volume treated by observed and predicted values by Wolborska and Pustelnik model. The RBM may be a viable alternative material to use in landfill liners

REFERENCES

- Abu-El-Sha'r, W. Y., Batarsh, E.S., and Ammary, B.Y. (2003). Experimental assessment of the adequacy of clayey soils in Irbid to retard lead from aqueous solutions and leaded gasoline. *Environ. Geol.*, 43(5), 526 – 531.
- Astrup, T., Stipp, S.L.S., and Christensen, T.H. (2000). Immobilization of chromate from coal fly ash leachate using an attenuating barrier containing zero-valent iron. *Environ. Sci. & Technol.*, 34(19), 4163 – 4168.
- Blowes, D.W., Ptacek, C.J., and Jambor, J.L. (1997). In-situ remediation of Cr(VI)-contaminated groundwater using permeable reactive walls: laboratory studies. *Environ. Sci. & Technol.*, 31(12), 3348 – 3357.
- Bright, M.I., Thornton, S.F., Lerner, D.N., and Tellam, J.H. (2000). Attenuation of landfill leachate by clay liner materials in laboratory columns, 1. Experimental procedures and behaviour of organic contaminants. *Waste Mangmt. & Res.*, 18(3), 198-214.
- Chesceri, L.S., Greenberg, A.E., Trussel, R.R., and Franson, M.A. (1989). Standard Methods for the examination of water and wastewaters, *American Public Health Association*. Washington DC.
- Chinthamreddy, S. and Reddy, K.R. (1998). Geochemistry of chromium during electrokinetic remediation. 4th Inter. Sympo. *Environ. Geotech. and Global Sustain. Develop.*, August 9 – 13, Illinois, USA.
- Edil, T.B., Berthouex, P.M., Park, J.K., Hargett, D.L., Sandstorm, L., and Zelmanowitz, S. (1991). Effects of volatile organic compounds on clay landfill liner performance. *Waste Mangmt. & Res.*, 9(3), 171 – 187.
- Edwards, M., and Benjamin, M. (1989). Adsorptive filtration using coated sand: a new approach for treatment of metal-bearing wastes. *J. Water Pollut. Cont. Fedn.*, 61(9), 1523 – 1533.
- Fendrof, S.E., and Zasoski, R. (1992). Chromium(III) oxidation by δ -MnO₂. 1. Characterization. *Environ. Sci. & Technol.*, 26(1), 79 – 85.
- Kaplan, D.I. and Gilmore, T.J. (2002). Removal rates of aqueous Cr (VI) by zero-valent iron measured under flow conditions, Department of Energy, USA report No. WSRC –MS-2002-00150
- Lo, I.M. C. (2003). Innovative waste containment barriers for subsurface pollution control. *Pract. Period. of Hazard., Toxic, and Radioact. Wast. Managt.*, 7(1), 37 - 45.
- Mackay, D.M. (1989). Groundwater contamination: pump-and-treat remediation. *Environ. Sci. & Technol.*, 23(6), 630 – 635.
- Wolborska, A. and Pustelnik, P. (1996). A simplified method for determination of the breakthrough time of an adsorbent layer. *Water Res.*, 30(4), 2