

A new reactive barrier material for use in landfill liners and *in situ* barriers to immobilize chromium

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Abstract This paper presents the development of a novel reactive barrier material (RBM) 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 iron oxide coated sand (IOCS) and kaolin at an 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 10 to 50 mg/L, keeping other experimental conditions similar. The results of isothermal studies conducted at different pH values show that adsorption data satisfies 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 to 6.0 ± 0.1 under similar experimental conditions. The Wolborska & Pustelnik model was applied to the breakthrough data of Cr(VI) with good reproducibility of pore volumes treated during column studies. The results suggest that the RBM may be a new viable alternative material for use in landfill liners to effectively contain Cr(VI) in leachate and in *in situ* barriers for treating 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 valance 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 anionic forms, HCrO_4^- and CrO_4^{2-} (Fendorf & Zasoski, 1992; Chintamreddy & 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 & 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 that 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 (Edil *et al.*, 1991; Blowes *et al.*, 1997; Bright *et al.*, 2000; Astrup *et al.*, 2000; Abu-El-Sha'r *et al.*, 2003; Lo, 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 solutions 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 using *Standard Methods* (Chesceri *et al.*, 1989). Quartz sand was procured from the bank of the River Yamuna at Allahabad (India) and sieved for a geometrical mean (GM) size of 505 μm . The coating was applied as per Edwards & 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 the shaker after the desired contact time and supernatants were separated from adsorbent by Whatman-42 filter paper (ashless). The pH of each solution was measured before and after sorption experiments using a pH meter (model: Li 120, Elico, India.). Solution concentrations were determined for Cr(VI) by spectrophotometer (Model Genesys-20, Thermo Spectronic, USA) and by 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 ($0.04 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$) was maintained with an influent Cr(VI) concentration (C_0) of 100 mg/L through all the columns. The initial pH was maintained either by addition of small amounts 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 (Fig. 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 2 shows how the percentage removal of Cr(VI) decreased from 69 to 54% as sorbate concentration in the solute was increased from 10 mg/L to 50 mg/L whilst 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 for salt penetration and subsequent better coating, even though this media had a lower surface area as compared to RBM I.

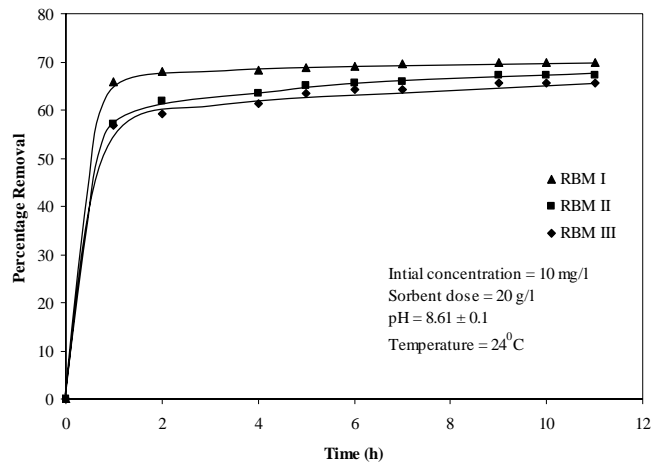


Fig. 1 Percentage removal of Cr(VI) on the three reactive barrier materials.

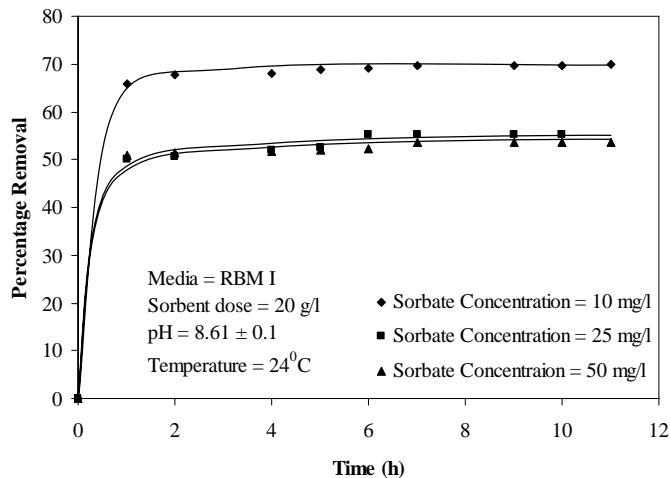


Fig. 2 Percentage removal of Cr(VI) on RBM I for different concentrations.

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

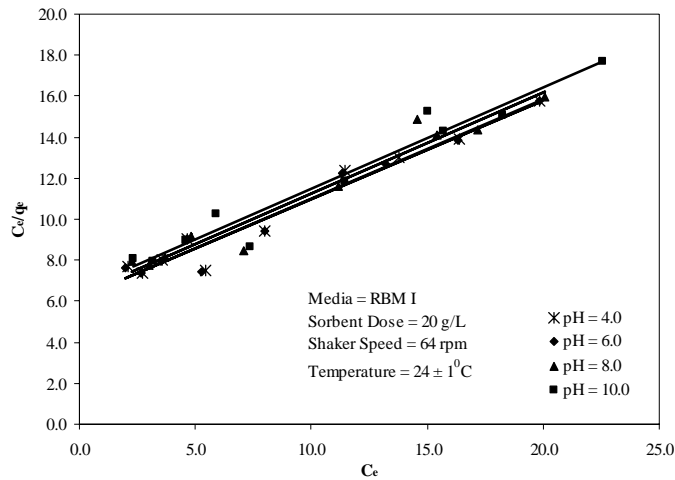


Fig. 3 Linearised Langmuir isotherms for Cr(VI) adsorption for different pH.

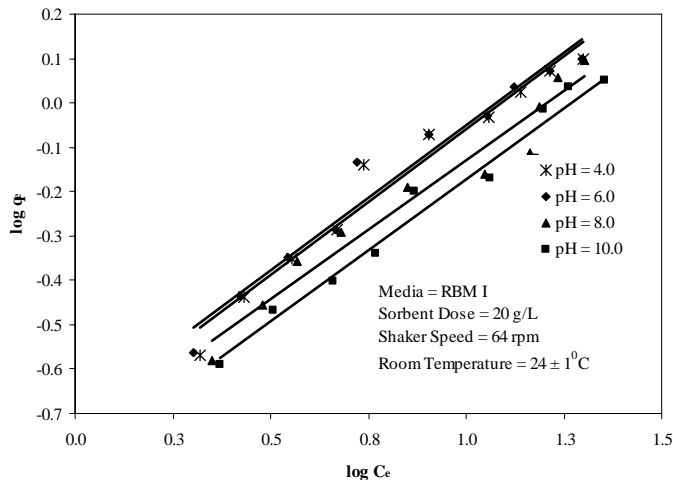
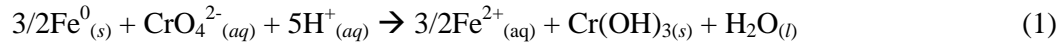


Fig. 4 Linearised Freundlich isotherms for Cr(VI) adsorption for different pH.

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 the 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 & Gilmore, 2002):



The removal mechanism may also be explained based on surface complexation theory. When placed in solution, the reactive barrier material (RBM) forms a hydrous oxide layer 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 surface material, the surface sites may be >FeOH_2^+ and >FeOH^{+2} . The surface complexation of chromate (HCrO_4^-) is:



Here $\text{S} - \text{OH}$ 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 depicts the effect of pH on Cr(VI) and total Cr by RBM I. The mechanism for removal of Cr(VI) can be explained by equation (2). The decrease in Cr(VI) removal in the pH range 6–10, may be result of negative charge on the RBM media ($>\text{pH}_{\text{zpc}}$). The dominant species of chromium in the pH range is $\text{Cr}(\text{OH})^{2+}$ and $\text{Cr}(\text{OH})_3$, disfavour adsorption on media surface.

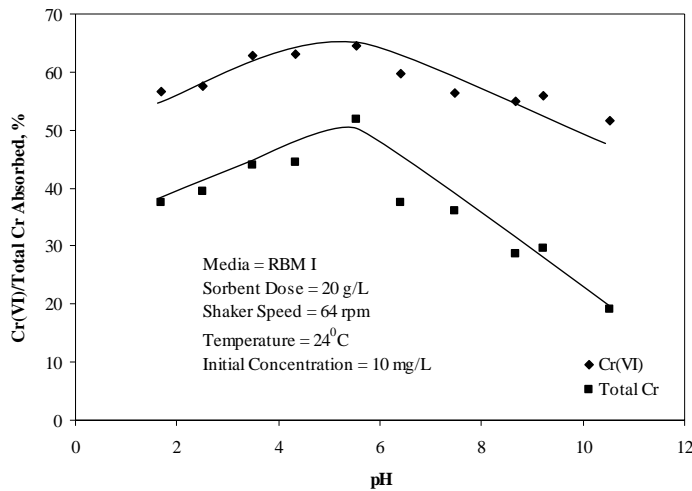


Fig. 5 Adsorption of Cr(VI)/Total Cr on RBM I as a function of pH.

Column experiments

Figure 6 shows breakthrough curves for three FBRs, which were packed with iron oxide coated sand and kaolin. The shapes of the breakthrough curves suggest Cr adsorption is taking place on the iron oxide coated sand and kaolin.

Column bed design by Wolborska & Pustelnik model

The Wolborska & Pustelnik (1996) model was used for modelling of Cr(VI) adsorption from aqueous solution on the RBM columns. The fundamental concept of this model is formation of a low concentration region in the column. The formation of the low concentration region takes place in the initial stage of process dynamics and the initial concentration distribution is translocated along the column in steady-state process

conditions. The low concentration regions that contain the so-called breakthrough concentrations have shown behaviour similar to that obtained during experimental fixed bed studies (Fig. 6).

This similarity provides the reason for using the Wolborska & Pustelnik model. This model is also based on Wicke's law, which is applicable for convex adsorption isotherms (Freundlich-Langmuir-BET-type). Since the batch experimental data were applicable for both Langmuir and Freundlich isotherms, the Wolborska & Pustelnik model was used. The experimental breakthrough curves (Fig. 7) seems to be rectilinear and can be described by the following equation.

$$\ln \frac{C}{C_0} = Av + B \quad (3)$$

where A and B are constants, C is the solution phase concentration of Cr(VI) at time t

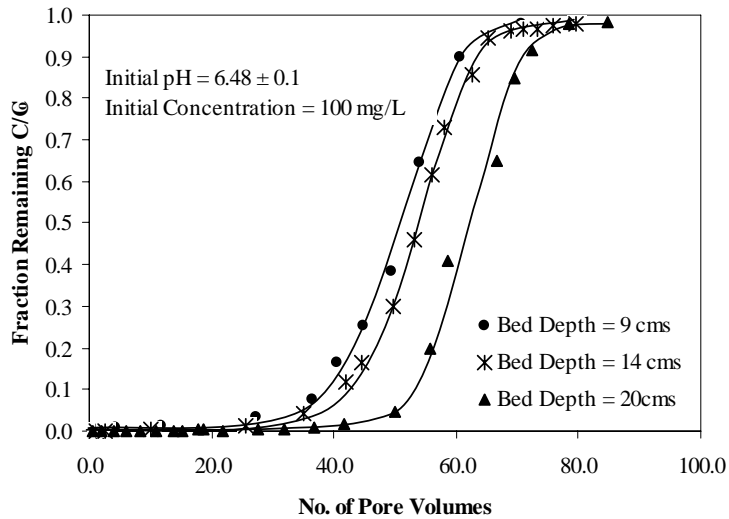


Fig. 6 Breakthrough curves for Cr(VI) adsorption by RBM I at different bed depths.

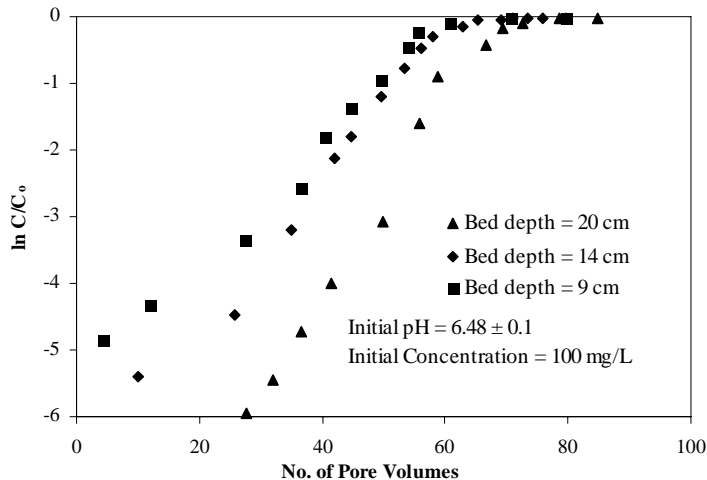


Fig. 7 Experimental breakthrough curves at various bed-depths.

(mg/L), and C_0 is the initial Cr(VI) concentration (mg/L). Further, the relationships and coefficients were determined using this model. The constants A and B were determined using least squares methods taking points that fall on the straight line for a particular breakthrough curve for given effluent concentrations. These constants and the coefficients of correlation (C_c) are given in Table 1. The observed and predicted values of breakthrough time in Table 1 are based on the mean value of constant B . The form of correlation obtained is in agreement with an equation derived by Wolborska & Pustelnik (1996) for the initial segment of the breakthrough curve. Figure 8 presents the relation between constant B and the bed depth.

Table 1 Comparison of calculated and predicted values of breakthrough number of pore volumes (Wolborska & Pustelnik Model).

Bed depth (cm)	Constants in equation (3)		Coefficient of correlation (C_c)	Kinetic coefficient $\beta_a \times 10^{-3}$ (s^{-1})	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

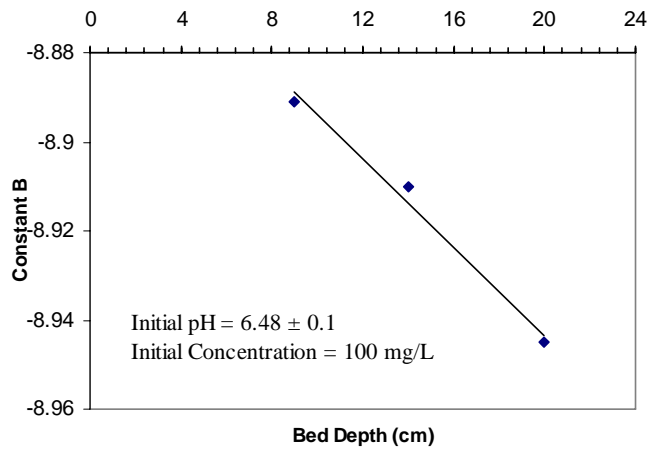


Fig. 8 Relation between constant B and the bed depth (h).

Kinetic coefficient of the process

The constant B determines the relative concentration of the first batch of the solution leaving bed ($t \rightarrow 0$). 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:

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

In the above equation, u is solution flow rate ($m^3/m^2/h$) and h is bed depth of column (cm). Kinetic coefficients β_a , were calculated using the constant B , for each breakthrough curve and are presented in Table 1. The proportionality of constant B to bed height was confirmed by a series of experiments carried out at constant flow. From the data

correlation in the system (B, h) a mean value of kinetic coefficient $\beta_a = 0.760 \times 10^{-3} \text{ s}^{-1}$ 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.

CONCLUSIONS

A good chromium sorption potential exists in the 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 the proposed reactive material will convert heavy metals into immobile form, thereby preventing potential groundwater contamination. It will be almost the same as *in situ* treatment of leachate. Precipitation occurred on kaolin during the experimentation, indicating 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 data from column studies by the Wolborska & Pustelnik model results in good reproducibility of the pore volumes observed during different treatments and predicted values. The IOCS-kaolin RBM may be a viable alternative material to use in landfill liners.

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