

## DEVELOPMENT OF 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 reactive media that consists of treatment mixtures of iron oxide coated sand (IOCS) and kaolin (K), known as Reactive Barrier Material (RBM), to use as liner or barrier material for effective containment of toxic hexavalent chromium (Cr(VI)). A series of batch kinetic experiments show that at equilibrium time, the percentage removal of Cr(VI) varies from 65 to 70% tested at initial pH of  $8.61 \pm 0.1$ . The percentage removal of Cr(VI) was decreased from 49 to 54% as sorbate concentrations in the solute were 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 the Cr removal was negligible by RBM; however, the maximum sorption occurred at about pH 5.0 - 6.0 under the experimental conditions. The effective removal of Cr(VI) by RBM under dynamic flow conditions (column studies) suggests 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).

### 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,  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$  (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, 1989). This approach can be ineffective. 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 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 prescreen potential candidates for further study using column tests.

### EXPERIMENTAL METHODOLOGY

#### Materials:

All glass and plastic equipment was soaked in 2N  $\text{HNO}_3$  for at least 24 h and then rinsed several times in distilled water before use. Analytical reagent grade chemicals (Merck) and distilled water were used for all solutions. Stock Cr(VI) solution was prepared as per standard methods (Chesceri et al., 1989). Quartz sand of geometrical mean (GM) size of 505  $\mu\text{m}$  by IS sieves was procured from the bank of river Yamuna at Allahabad (India) and 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.

**Batch Experiments:**

Laboratory batch sorption studies were conducted to investigate kinetic uptake of Cr(VI) by RBM at room temperature in an end-to-end rotary shaker at  $64 \pm 2$  rpm. The pH of each solution was measured before and after sorption experiments by the use of pH meter, Elico India Li 120 make. Resultant solution concentrations were determined for Cr(VI) using spectrophotometer (Model Genesys-20, Thermo Spectronic, USA) and Atomic Absorption Spectrophotometer (AAS) (Model Analysts-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 HCl or NaOH. Experiments were conducted at room temperature over a period of about 15 days.

**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  $8.61 \pm 0.1$ .

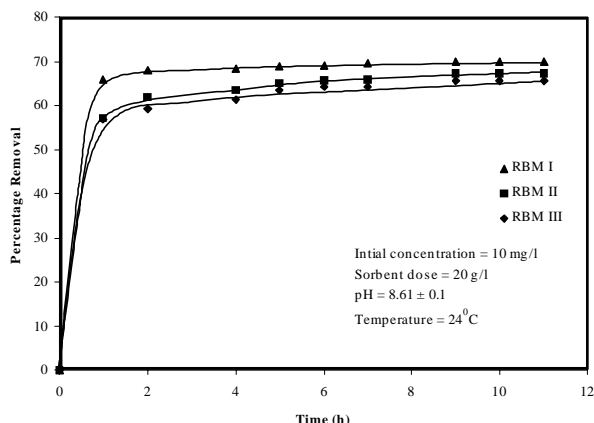


Figure 1: Percentage removal of Cr(VI) on reactive barrier material with different compositions

But, percentage removal of total chromium varies from 35 to 45% for RBM I (Figure 2). Figure 3 show the percentage removal of Cr(VI) was decreased from 49 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 increases the surface area of solids, leading to higher Cr removal as compared that observed 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.

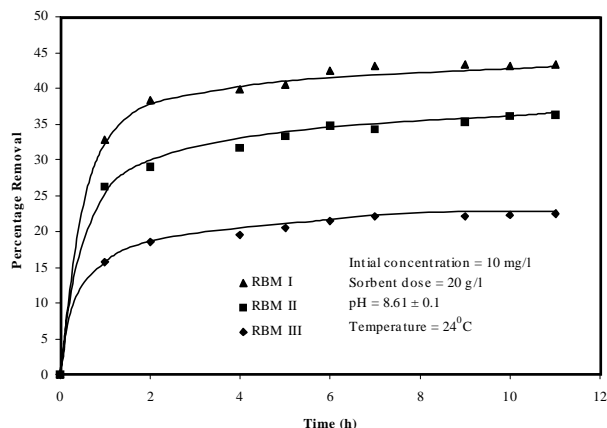


Figure 2: Percentage removal of total Cr on reactive barrier material with different compositions

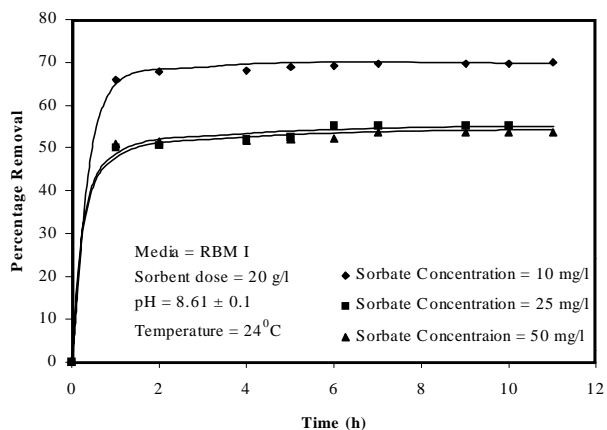


Figure 3 Percentage removal of Cr(VI) on RBM I for different concentration

Therefore, due to large surface area chromium adsorption on RBM I was more as compared to RBM II and RBM III. The obtained data from isothermal studies conducted on RBM I were fitted to Freundlich (Figure 4) and Langmuir isotherm models (Figure 5). The slight departures of experimental data points from line of best fit indicates less than perfect fit into Langmuir and Freundlich isotherms.

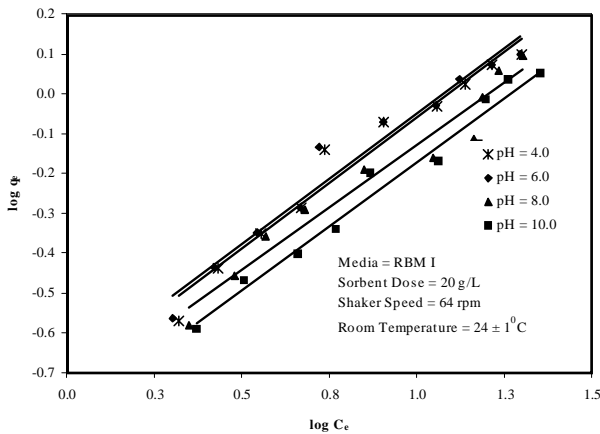
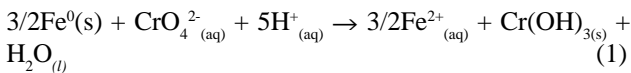
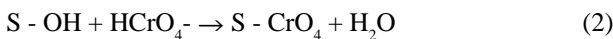


Figure 4 Linearised Freundlich isotherms for Cr(VI) adsorption for different pH

The ultimate sorption capacity for Cr(VI) was found to be 2.067 mg/g as per Langmuir isotherm and 0.191 mg/g as per Freundlich isotherm models. However, the value of this was 1.367 mg/g as per Langmuir isotherm and 0.191 mg/g as per Freundlich isotherm models for total chromium. The adsorption capacity of reactive barrier material increases with decreasing pH. Thus the co-precipitation mechanism of Cr(VI) is that of adsorption on Fe(III) hydroxide. According to one hypothesis reduction of Cr(VI) to Cr(III) by reaction with 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  $>\text{SOH}_2^+$  and  $>\text{SOH}$  representing positive and neutral charged sites. Since Fe is present in reactive barrier material surface, therefore surface sites may be  $>\text{FeOH}_2^+$  and  $>\text{FeOH}^{+2}$ . The surface complexation of chromate ( $\text{HCrO}_4^-$ ) 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 6 depicts 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 ( $>\text{pH}_{\text{zpc}}$ ). The dominant species of chromium in the pH range is  $\text{Cr}(\text{OH})_2^+$  and  $\text{Cr}(\text{OH})_3$ , disfavor adsorption on media surface.

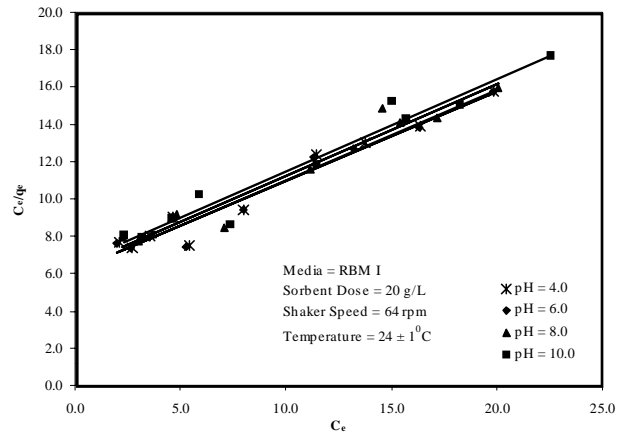


Figure 5: Linearised Langmuir isotherms for Cr(VI) adsorption for different pH

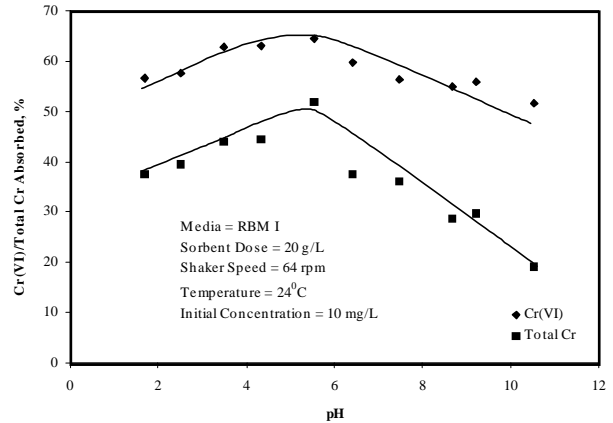


Figure 6: Adsorption of Cr(VI)/Total Cr on RBM I as a function of pH

**Column Experiments:**

Figure 7 shows breakthrough curves for the columns, which was packed with iron oxide coated sand and kaolin. Cr breakthrough occurred after about 50 pore volumes for RBM I (75% IOCS and 25% kaolin). In the composition range of the experimental solutions where  $\text{pH} < 6$ , thermodynamics predicts the predominant Cr(VI) species to be  $\text{HCrO}_4^-$ .

The shapes of the breakthrough curves suggest Cr retardation results from anion adsorption, probably to the iron oxide coated sand and kaolin. Comparison of breakthrough curves shown in Figure 7 proves that Cr mobility is significantly retarded in the presence of Fe. The developed breakthrough curves for three FBRs have been shown in Figure 8.

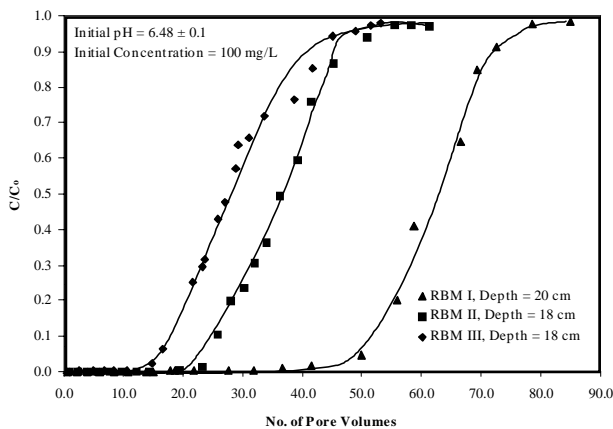


Figure 7: Breakthrough curves for Cr(VI) adsorption for different RBM

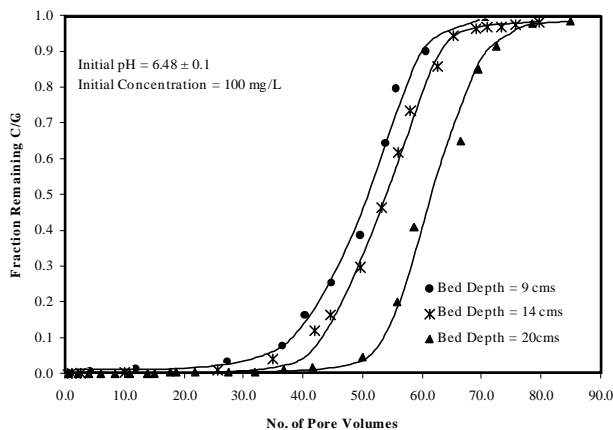


Figure 8: Breakthrough curves for Cr(VI) adsorption by RBM I at different bed depth

## 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. Proposed reactive material will achieve a low permeability ( $< 10^{-4}$  cm/sec), thereby reduce the advective flux. In addition, due to the presence of iron, the reactive material will transform organic contaminants into nontoxic end products or convert heavy metals into immobile form, thereby preventing potential groundwater contamination. It will be almost like in-situ treatment of leachate. Precipitation on kaolin means 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.

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