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Zero-Valent Iron (ZVI) as Permeable Reactive Barrier: Chromium (VI) removal by fixed bed column of ZVI

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Abstract-Recent industrial and urban activities have led to elevated concentrations of a wide range of contaminants in groundwater and wastewater, which affect the health of millions of people worldwide. Zero-valent Iron was the first material to be used in permeable reactive barriers (PRBs) for groundwater remediation.This report aims to provide an overview of fulfillment of all the requirements of permeable reactive barrier by zero valent iron. To support this aim, a fixed bed column was studied in which chromium (VI) was removed. A column was prepared by filling 4 cm thick layer of ZVI-Sand media (ZVI: Sand is 1:1 v/v), sandwiched between 1 cm thick layer of sand. Chromium feed was given in downward direction. The Adams–Bohart, Thomas and Yoon–Nelson models were applied to the adsorption to predict the breakthrough curves. Kinetic models were also applied and best curve fit model was determined.

Keywords- Adsorption, wastewater, chromium

INTRODUCTION

Groundwater is a limited ecological resource representing a small percentage of the total water distribution. Urban residents increasingly rely on groundwater due to unreliable and inadequate municipal water supplies. Ground water contamination is the presence of certain pollutants in ground water that are in excess of the limits prescribed for drinking water. The commonly observed contaminants include arsenic, fluoride, nitrate, chromium and iron, which are geogenic in nature. According to the data of the World Health Organization (WHO), the scarcity of water resources has created challenges for over 40% of the world population, i.e., more than 2 billion people have no access to enough or clean water.

Traditional groundwater remediation methods such as pump and treat are of questionable utility: a 1994 study found that 69 of 77 treatment sites using pump and treat had not met clean up goals [1]. PRBs are a relatively new technology; the oldest full-scale PRB has been in operation for just over a decade. Original work using reduced metals for the treatment of chlorinated organic built on studies of the corrosive effects of chemicals on metals [2]. The concept of PRBs is relatively simple. A permeable reactive barrier material consisting of permanent, semi-permanent or replaceable reactive media is placed in the subsurface across the flow of path of a plume of contaminated groundwater, which must move through it as it flows, typically under its natural gradient, thereby creating a passive treatment system.

MATERIAL AND METHODS

The materials used for the all experiments were commercial iron filings (size 60-35 mesh) of *Fizmerk India Chemicals*, sand and sulphuric acid. Iron filling and sulphuric acid were purchased from *The Scientific shop, Lucknow.*

Instrumentation- Absorbance was recorded using UV-Vis Spectrophotometer. pH measurements were recorded using pH meter.

Preparation of column- The fixed-bed column was prepared using a laboratory scale glass column with an internal diameter of 2 cm and total length of 100 cm. Glass wool was inserted at the bottom of column to support the bed material. The column was wet-packed through incremental addition of sand (and ZVI). This was done carefully to ensure that columns were free of air bubbles. The column consisted of a 4 cm layer of 1:1 (v/v) ZVI-sand mix sandwiched by two 1 cm layers of cleaned sand, giving an overall ZVI content of 24.56% (v/v, solid basis). The iron filing was measured to 10g and mixed with equal volume (4.629 cm^3) of sand. The column bed volume was 18.849 cm^3; the corresponding porosities were approximately 36% for sand columns and 29% for ZVI columns.

Adsorption Study- Columns were operated under saturated and continuous down-flow conditions at a rate of 2± 0.03 mL/min, prior to use, four bed volumes of 0.01N sulfuric acid was passed through the column to remove any iron oxides. Several bed volumes of model groundwater were then passed through the column prior to collecting reported data.

Feed water of Cr (VI) with 80mg/l was prepared by diluting 80ml of stock solution (concentration of stock solution was 1000mg/l Cr (VI)) in 1000ml distilled water. Effluent samples were collected at regular time intervals to determine the metal concentration in the effluent solutions. The flow to the column was continued until there was no further adsorption, i.e. the Cr (VI) concentration at the influent and effluent remained unchanged. Amount of adsorbed Cr (VI) was measured spectrophotometrically following the diphenylcar-bazide method [3]. Diphenylcarbazide reacts with Cr (VI) ions in acidic medium forming Cr (III) – diphenylcarbazone complex [4].The absorbance of the coloured solution was measured at 540 nm in a UV–vis spectrophotometer and the amount of Cr (VI) was measured with the help of a calibration curve.

RESULTS AND DISCUSSION

Successful design of a column adsorption process requires prediction of the breakthrough curve for the effluent [5]. Over the years, several simple mathematical models have been developed for describing and analysing the lab-scale column studies for the purpose of industrial applications [5-7].

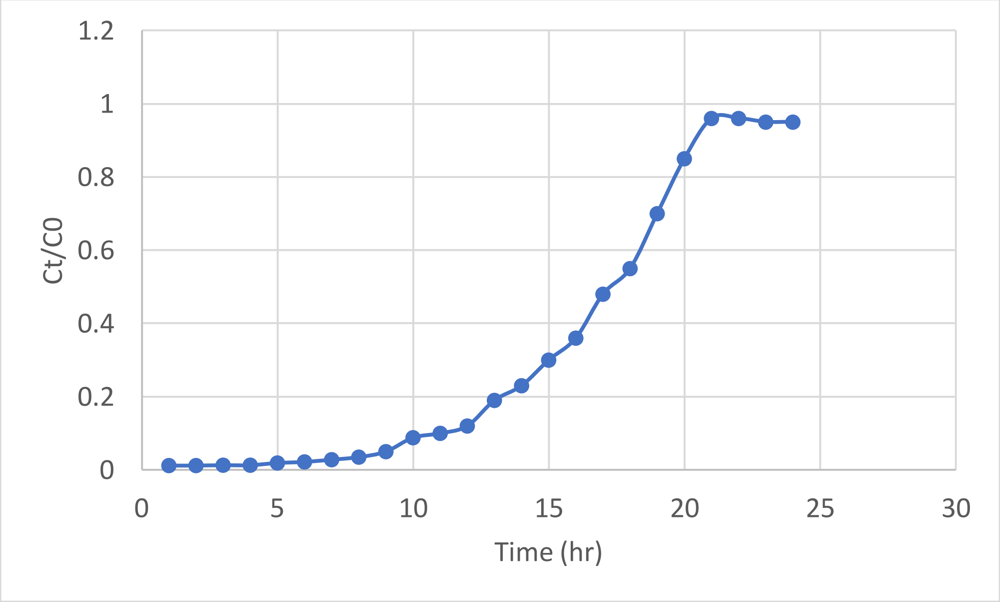

Figure1. *Break through Curve*

In this study, Adams–Bohart, Thomas and Yoon models were developed to identify the best model for predicting the dynamic behaviour of the column.

Bohart and Adams [8] based on the surface reaction theory established a fundamental equation, which describes the relationship between C_t/C_0 and t in a continuous system. This model assumes that that equilibrium is not instantaneous. It is used for describing the initial part of the breakthrough curve. The expression is as follows:

$$\ln\frac{C_t}{C_0} = k_{AB}C_0 - k_{AB}N_0\frac{Z}{U_0}$$

where C_0 and C_t are the influent and effluent concentration (mg/L), respectively; k_{AB} is the kinetic constant (L/mg min), N_0 is the saturation concentration (mg/L), Z is the bed depth of the fix-bed column (cm) and U_0 is the superficial velocity (cm/min) defined as the ratio of the volumetric flow rate Q (cm^3/min) to the cross-sectional area of the bed A (cm^2). The range of t was taken into consideration from the beginning to the end of breakthrough. The parameters k_{AB} and N_0 can be calculated from the linear plot of $\ln(C_t/C_0)$ against t.

Thomas model [10] assumes plug flow behaviour in the bed. This model is one of the most general and widely used to describe the performance theory of the sorption process in fixed-bed column. The linearized form of this model can be described by the following expression,

$$\ln\left(\frac{C_0}{C_t}-1\right)=\frac{k_{Th}q_0m}{Q}-k_{Th}C_0t$$

Where k_{Th} is the Thomas model constant (L/min mg), q_0 is the adsorption capacity (mg/g), and t stands for total flow time (min). The values of k_{Th} and q_0 can be determined from the linear plot of $\ln[(C_0/C_t) - 1]$ against t.

Yoon and Nelson [10] developed a model to investigate the breakthrough behaviour of adsorbate gases on activated charcoal. The Yoon–Nelson model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent [11-13].The linearized Yoon–Nelson model for a single component system can be expressed as:

$$\ln\left(\frac{C_t}{C_0-C_t}\right)=k_{YN}t-\tau K_{YN}$$

Where k_{YN} is the rate constant (min^{-1}) and τ is the time required for 50% adsorbate breakthrough (min). A linear plot of $\ln[C_t/(C_0\text{-}C_t)]$ against t determined the values of k_{YN} and τ from the intercept and slope of the plot.

Table 1.
Data showing the values of breakthrough models obtained for adsorption of Cr (VI) ions onto ZVI.

Models	Parameters
Adams–Bohart	
k_{AB} (L/mg hr)	-0.0636
N_0 (mg/L)	3.915
R^2	0.986
Thomas model	
k_{Th}(L/hr mg)	4.275×10^{-3}
R^2	0.942
Yoon–Nelson model	
k_{YN} (hr^{-1})	0.342
τ (hr)	16.56
R^2	0.940

KINETIC MODELS

Simple first order model-

The sorption kinetics of metals removal may be described by a simple first order rate expression as evident from literature. The change in bulk concentration of the system with time can be described using the following simple first order rate expression:

$$\frac{dC}{dt}=-k'_1C$$

Above equation can be integrated with initial condition at t=0, $C=C_0$ and rearranged to obtain a linear as follows:

$$\log C=\frac{k'_1}{2.303}t+\log C_0$$

Where C and Co are the concentration of Cr (VI) in mg/l at anytime t and initially respectively, k'_1 is the first order rate constant, (time^{-1}).

Pseudo first order kinetic model-

In order to investigate the controlling mechanism of adsorption process such as mass transfer and Chemisorption, the pseudo first and second order equations are applied. Lagergren, proposed a pseudo first order kinetic model, which is expressed as follows:

$$\frac{dq}{dt} = k''_1(q_e - q)$$

Where q the amount of Cr sorbed mg/g at time t, q_e is the amount of Cr sorbed at equilibrium, (mg/g) and k_1" is the first order rate constant (min^{-1}).

On integration and by applying the initial conditions i.e. q_t=0 at t=0, above equation can be written in linear form as:

$$\log(q_e - q) = \log q_e - \frac{k''_1}{2.303}t$$

This model equation has found applications in describing adsorption kinetics of metal removal by different adsorbent.

Second order kinetic model-

Second order rate equation can be expressed as:

$$\frac{dC}{dt} = k_2C^2$$

In linear form, the second order rate equation is typically expressed as:

$$\left(\frac{1}{C} - \frac{1}{C_0}\right) = k_2t$$

Where C is the residual concentration of Cr at any time t (mg/l), C_o is the initial Cr concentration (mg/l), t is the time (min), and k_2 is the second order rate constant (L/mg/min).

Weber and Morris model-

It is always important to predict the rate limiting step in an adsorption process to understand the mechanism associated with the phenomena. For a solid liquid adsorption process, the solute transfer is usually characterized by either external mass transfer or intra-particle diffusion or both. Generally three types of mechanism are involved in the adsorption process, mentioned as follows:

1. Film diffusion.
2. Particles diffusion.
3. Adsorption of the adsorbate molecules on the interior of the porous adsorbent.

The rate constant of intra-particle diffusion (k_3, mg/g $\text{min}^{0.5}$) at different temperatures were determined by the following equation:

$$Q = k_3t^{1/2}$$

Where, q is the amount adsorbed at time t and $t^{1/2}$ is the square root of the time. The value of k_3 were determined from the slope of plots between adsorption capacity q and square root of time $(t)^{1/2}$ under different experimental conditions.

Table 2.
Kinetic parameters for the adsorption of Cr (VI) onto ZVI.

Kinetic Models	Parameters
Simple first order	
k'_1 (hr^{-1})	0.2487
R^2	0.9869
Pseudo first order kinetic	
k_1'' (hr^{-1})	0.2372
R^2	0.8011
Second order kinetic	
k_2 (L/mg/hr)	-0.055
R^2	0.8228
Weber and Morris	
k_3 (mg/g $hr^{0.5}$)	4.299
R^2	0.9891

CONCLUSION

In this study, we have seen that how ground water contamination can be stopped by permeable reactive barriers (PRBs) and zero valent iron is an excellent material for that purpose. The table 1 clearly shows that the breakthrough curve of removal of Cr(VI) by ZVI follows Adams-Bohart model as the R^2 Value is the highest i.e. 0.9869 among the three models studied. In kinetic study removal of Cr(VI) from the ZVI follows Webber and Morris model with the R^2 value of 0.9891 (Table 2).

We have also found that mixing zero valent iron filings with sand gives good water permeability. Zero valent iron has proved to be excellent material for permeable reactive barrier. This study also shows the removal of Cr (VI) having removal capacity of 14.47 mg of Cr (VI)/g of ZVI.

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