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Finite element modeling of Cr(VI) reduction by *Shewanella oneidensis* MR-1 employing the dual-enzyme kinetic model

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Abstract

Chromium (VI) (Cr(VI)) contamination of soil and groundwater is considered a major environmental concern. Bioreduction of Cr(VI) to chromium (III) (Cr(III)) can be considered an effective technology in remediating Cr(VI) contaminated sites. Among the Cr(VI) reducing bacteria, *Shewanella oneidensis* MR-1 (MR-1) is relatively effective. Reduction of Cr(VI) by MR-1 is defined by the dual-enzyme kinetic model. Existing models are not able to simulate bioreduction of Cr(VI) by employing the dual-enzyme kinetic model. The objective of this paper is to present a finite element model capable of simulating bioreduction of Cr(VI) by employing the dual-enzyme kinetic model and compare its prediction with experimental results. The model developed is accurate and can provide oscillation-free results for Peclet number $Pn \leq 20$ and Courant number $Cn \leq 1$. The model prediction compares well with the experimental results.

Keywords: Modeling; Cr(VI); Bioreduction; Dual-enzyme

1. Introduction

Chromium (Cr) has a wide range of industrial use (Stern, 1982). Consequently, soil and groundwater contamination by Cr is frequently encountered at some industrial sites. In fact, at most of the US Department of Energy's (DOEs) sites, Cr contamination of soil and groundwater is a major environmental concern (Riley et al., 1992).

Chromium can occur at several different oxidation states ranging from −2 to 6. However, only Chromium (III) (Cr(III)) and Chromium (VI) (Cr(VI)) are the stable forms in the natural environment. Cr(III) is naturally occurring. It is essential in trace amounts for humans, contributing to the glucose tolerance factor necessary for insulin-regulated metabolism (Mertz, 1975). Further, Cr(III) is only slightly soluble in water and is adsorbed very strongly by soils (Davis et al., 1993). Cr(VI), on the other hand, is rarely naturally occurring and is found in the subsurface environment, almost exclusively, as a result of anthropogenic activities (Barnhart, 1997). It is relatively soluble in aqueous systems and is readily transported in groundwater (Dragun, 1988). Additionally, it is significantly toxic. It is reported that Cr(VI) constitutes more than 90% of the total Cr present at many contaminated sites in the US (Riley et al., 1992).

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In situ bioremediation is considered a viable alternative for the remediation of Cr(VI) contaminated soil and groundwater (Shen and Wang, 1994; Fujie et al., 1996). A significant volume of literature is available in support of bioreduction of Cr(VI) to Cr(III) (Romanenko and Koren'kov, 1977; Horitsu, 1987; Bopp and Ehrlich, 1988; Wang et al., 1989; Chen and Hao, 1996).

Cr(VI) reducing bacteria are found abundantly in the subsurface environment and in the natural ecosystem (Wang and Shen, 1995; Turick et al., 1996; Chen and Hao, 1997; Schmieman et al., 1998). Among the Cr(VI) reducing bacteria, the *Shewanella* species are perhaps the most widely studied (Venkateswaran et al., 1999). Viamajala et al. (2002) report that *Shewanella oneidensis* MR-1 (MR-1) can effectively reduce Cr(VI) for a wide range of concentrations under anaerobic conditions and the reduction is accomplished by two enzymes acting simultaneously.

Viamajala et al. (2003) developed a nonlinear dual-enzyme kinetic model to simulate the multi-mechanism reduction of Cr(VI) by MR-1. The model is based on the assumption that two enzymes—a fast acting but quickly deactivating and a slow acting but stable—are responsible for reducing Cr(VI) to Cr(III). The dual-enzyme kinetic model proposed by Viamajala et al. (2003) can be summarized by the following parallel reactions.

$$\mathrm{Cr(VI)} + \mathrm{E_d} \rightarrow \mathrm{E_d^*} + \mathrm{Cr^*}, \tag{1}$$

$$\mathrm{Cr(VI)} + \mathrm{E_s} \rightarrow \mathrm{E_s} + \mathrm{Cr^*}. \tag{2}$$

In Eqs. (1) and (2), E_d is the "deactivating enzyme" which is fast acting but converts to the inactive form E_d^* while reacting with Cr(VI); Cr^* is the reduced product of Cr(VI) and is assumed to be Cr(III); and E_s is the slow acting "stable enzyme". The rate expression for this reaction scheme is zero order and can be expressed as follows:

$$r_{cr} = -\frac{dCr}{dt} = \alpha + \beta\, e^{-\gamma t}. \tag{3}$$

In Eq. (3), r_{cr} is the rate of Cr(VI) reduction, Cr is the Cr(VI) concentration at any time, t is the time, α is rate constant for the stable enzyme, and β, γ are rate constants for the deactivating enzyme.

An examination of Eq. (3) indicates that Cr(VI) reduction rate by MR-1 is independent of its concentration and is zero order. When a zero-order rate expression is incorporated in advective–dispersive transport equation to mathematically describe the fate and transport of a contaminant, Cr(VI) in this context, in the subsurface, it may violate the continuity equation, i.e., conservation of mass may not be maintained. Additionally, the deactivating-enzyme-induced rate is time dependent. It is necessary to keep track of the rate induced by the deactivating enzyme as a function of time.

There are a number of numerical models available for simulating the fate and transport of contaminants in the subsurface. These models, however, are not designed to predict bioreduction of Cr(VI) by employing the dual-enzyme kinetic model. Either finite differences (FDs) or finite elements (FEs) are the underlying bases of the available models. Finite element models (FEMs), however, are becoming increasingly popular in modeling contaminant transport in groundwater. The FEMs are based on the Galerkin minimization principle. The Galerkin FEM (GFEM) provides results of higher-order spatial accuracy than the widely used finite difference models (FDMs) (Donea et al., 1987).

Therefore, the principal objective of this paper is to present a GFEM, utilizing the fourth-order Runge–Kutta integration method, to evaluate the fate and transport of Cr(VI) in the subsurface by employing the dual-enzyme kinetic model and compare its predictions with experimental results. Additionally, criteria for numerical accuracy of the model will also be investigated.

2. The mathematical model

For one-dimensional (1D) flow, the equation to describe the fate and transport of Cr(VI) by employing the dual-enzyme kinetic model can be written as follows:

$$\frac{\partial Cr}{\partial t} = -v\frac{\partial Cr}{\partial x} + D\frac{\partial^2 Cr}{\partial x^2} - r_{Cr}, \tag{4}$$

$$t \geq 0, \quad x = 0, \quad Cr = Cr_0, \tag{5}$$

$$t \geq 0, \quad x = L, \quad \frac{\partial Cr}{\partial x} = 0, \tag{6}$$

$$t = 0, \quad 0 < x \leq L, \quad Cr = 0. \tag{7}$$

In these equations, r_{cr} is the Cr(VI) reaction rate represented by the dual-enzyme kinetic model given in Eq. (3), v is the velocity of flow, D is the dispersion coefficient, x is the distance along the direction of flow, Cr_0 is the Cr(VI) concentration at the source, and L is the length of the flow domain of interest.

Eq. (4) can be solved for a variety of boundary and initial conditions. However, the conditions presented by Eqs. (5)–(7) constitute the most challenging numerical problem. An accurate and stable model for these conditions will remain stable and accurate for other conditions.

3. Solution technique

The zero-order reaction rate makes the solution of Eq. (4) difficult and challenging. First, it may violate the

conservation of mass and can result in negative concentrations when reduction due to the reaction is greater than the concentration at a given point in time and space. Removal by the reaction can never be greater than the concentration at a given point. Second, rate induced by the deactivating enzyme is time dependent and nonlinear. Tracking reaction time can be difficult for the reason that reaction time begins when Cr(VI) first comes in contact with MR-1 which is different for different points in a flow domain of the subsurface.

Therefore, Eq. (4) with the associated boundary and initial conditions was first solved without reaction employing the GFEM and the fourth-order Runge–kutta integration routine. The solution thus obtained was then corrected for the reaction. When concentration at a point was equal to, or, smaller than the removal due to reaction, it was set to zero. Otherwise, concentration after the reaction was taken to be equal to the difference between concentration without reaction and the removal due to reaction. Removal due to reaction is equal to $r_{\mathrm{Cr}}\Delta t$ where Δt is the time step.

4. GFEM Formulation

The FE solution of the transport equation begins with the construction of a trial solution. If $\overrightarrow{\mathrm{C}}\mathrm{r}$ is the trial solution of Eq. (4) without the reaction term then it can be expressed as follows:

$$\overrightarrow{\mathrm{C}}\mathrm{r} = \mathrm{Cr}_0(t)\varphi_0(x) + \sum_{i=1}^{N} \mathrm{Cr}_i(t)\varphi_i(x), \tag{8}$$

where $\mathrm{Cr}_i(t)$ is the magnitude of Cr at any node i and is a function of time only, φ_i is the basis function, and N is the number of FEs.

The piece-wise linear basis functions (PLBFs) are usually preferred to construct the trial solution for computational simplicity. Additionally, the PLBFs provide the required continuity and fulfill the compatibility and the completeness requirements. The PLBF for a typical element i, φ_i, is given in the following equation:

$$\varphi_i = 0 \quad \text{if } x \le x_{i-1}, \tag{9a}$$

$$\varphi_i = \frac{x - x_{i-1}}{x_i - x_{i-1}} \quad \text{if } x_{i-1} \le x \le x_i, \tag{9b}$$

$$\varphi_i = \frac{x_{i+1} - x}{x_{i+1} - x_i} \quad \text{if } x_i \le x \le x_{i+1}, \tag{9c}$$

$$\varphi_i = 0 \quad \text{if } x_{i+1} \le x. \tag{9d}$$

The trial solution may not exactly satisfy the transport Eq. (4) without reaction. There will be some residual as given:

$$R = \frac{\partial \overrightarrow{\mathrm{C}}\mathrm{r}}{\partial t} + v\frac{\partial \overrightarrow{\mathrm{C}}\mathrm{r}}{\partial x} - D\frac{\partial^2 \overrightarrow{\mathrm{C}}\mathrm{r}}{\partial x^2}. \tag{10}$$

The GFEM minimizes the residual R over the domain by making it orthogonal to the basis functions. Application of the Galerkin minimization principle to the residual R and some mathematical manipulations lead to the following matrix equation:

$$[A]\left\{\frac{\mathrm{dCr}}{\mathrm{d}t}\right\} = -v[A^a]\{\mathrm{Cr}\} - D[A^d]\{\mathrm{Cr}\} + \{B\}, \tag{11}$$

where

$$a_{ij} = \int \varphi_i(x)\varphi_j(x)\mathrm{d}x \quad i, j = 1, 2, 3, \ldots, N, \tag{12}$$

$$a^a_{i,j} = \int \frac{\mathrm{d}\varphi_i(x)}{\mathrm{d}x}\varphi_j(x)\mathrm{d}x, \quad i, j = 1, 2, 3, \ldots, N, \tag{13}$$

$$a^d_{i,j} = \int \frac{\mathrm{d}\varphi_i(x)}{\mathrm{d}x}\frac{\mathrm{d}\varphi_j(x)}{\mathrm{d}x}\mathrm{d}x, \quad i, j = 1, 2, 3, \ldots, N, \tag{14}$$

$$b_i = \left[\frac{v}{2} + \frac{D}{\Delta x}\right]\mathrm{Cr}_0 \quad \text{if } i = 1, \tag{15a}$$

$$b_i = 0 \quad \text{if } i \neq 1. \tag{15b}$$

Here Δx is the element length. The semi-discrete Eq. (11) can be written as follows:

$$\left\{\frac{\mathrm{dCr}}{\mathrm{d}t}\right\} = -v[A]^{-1}[A^a]\{\mathrm{Cr}\} - D[A]^{-1}[A^d]\{\mathrm{Cr}\} + [A]^{-1}\{B\}, \tag{16a}$$

$$\left\{\frac{\mathrm{dCr}}{\mathrm{d}t}\right\} = \left[-v[A]^{-1}[A^a] - D[A]^{-1}[A^d]\right]\{\mathrm{Cr}\} + [A]^{-1}\{B\}, \tag{16b}$$

$$\left\{\frac{\mathrm{dCr}}{\mathrm{d}t}\right\} = [G]\{\mathrm{Cr}\}[A]^{-1}\{B\}, \tag{16c}$$

where $[G] = -v[A]^{-1}[A^a] - D[A]^{-1}[A^d]$.

Eq. (16c) was solved numerically by employing a fourth-order Runge–Kutta integration method as mentioned earlier. Concentrations after the reaction was obtained by evaluating the value of $\mathrm{Cr}_i(t) - \Delta t\, r_{\mathrm{cr}}$. If $\mathrm{Cr}_i(t) - \Delta t\, r_{\mathrm{cr}} \le 0$, concentration after reaction was taken to be zero, otherwise, it was set to $\mathrm{Cr}_i(t) - \Delta t\, r_{\mathrm{cr}}$.

5. Stability and criteria for accuracy

The stability of the model was investigated by computing the eigenvalues of the matrix $[G]$ in Eq. (16c) for a variety of v, D, and Δx values. Real parts of the eigenvalues of $[G]$ were found to be negative even for purely advective transport for which the Peclet

number $Pn = \frac{v\Delta x}{D}$ is infinity. Unconditional stability is guaranteed when real parts of the eigenvalues of $[G]$ are negative.

The model, although unconditionally stable, may provide oscillatory results if the eigenvalues of $[G]$ are complex. Eigenvalues of $[G]$ were found to be real and negative for $Pn \leq 1.25$. Extremely fine spatial discretization is, therefore, needed for oscillation-free predictions when the criterion based on the eigenvalue is used. Further numerical experimentation led to the conclusion that oscillation-free accurate results are obtained when $Pn \leq 20$ and the Courant number $Cn = \frac{v\Delta t}{\Delta x} \leq 1$.

6. Results and discussions

6.1. Model parameters

Predictive ability of the model developed was tested by employing data obtained from the literature. Continuous-flow soil column experiment data was obtained from Alam (2004). Pertinent information of the soil column experiment is presented in Table 1. Dual-enzyme kinetic parameters were obtained from Viamajala et al. (2003). Viamajala et al. (2003) reported the average stable rate constant α to be $0.988\,\mathrm{mg\,L^{-1}h^{-1}}$ with a standard deviation of $0.104\,\mathrm{mg\,L^{-1}h^{-1}}$. The mean of the maximum deactivating rate constant β was reported be $13.00\,\mathrm{mg\,L^{-1}h^{-1}}$ and the standard deviation was $3.12\,\mathrm{mg\,L^{-1}h^{-1}}$. The rate constant γ was reported to be $9.68 \pm 1.5\,\mathrm{h^{-1}}$.

The stable-enzyme-induced reaction rate remains constant as a function of time according to the dual-enzyme kinetic model. A rate of $0.988 \times \mathrm{mg\,L^{-1}h^{-1}}$ corresponds to a capacity of $0.988\,\mathrm{mg\,L^{-1}h^{-1}} \times 22.5\,\mathrm{h} = 22.2\,\mathrm{mg\,L^{-1}}$ for the continuous-flow column employed by Alam (2004). Therefore, even if the increase in the reaction rate due to the action of the deactivating enzyme is not considered, the column will have a breakthrough only if Cr(VI) in the influent is greater than $22.2\,\mathrm{mg\,L^{-1}}$ which is contrary to the observation of Alam (2004). A breakthrough was obtained for average influent concentration as low as 1.94 mg/L as shown in Fig. 1.

Therefore, reaction kinetics obtained by utilizing batch data may not be considered appropriate for a continuous-flow dynamic column system that represents the subsurface condition with greater accuracy. A careful examination of Fig. 1 reveals that breakthrough may occur only after the depletion of the deactivating enzyme. Reduction of Cr(VI) after the breakthrough is due to the steady action of the stable enzyme. The stable-enzyme-induced reaction rate determined from the removal after the breakthrough was found to be $0.04\,\mathrm{mg\,L^{-1}h^{-1}}$. The time period for which the deactivating enzyme remains active can be found from the ratio of the time at breakthrough and the column residence time and was found to be 11.48 h. Therefore, at 11.48 h, the deactivating-enzyme-induced reaction rate at a given point $\beta e^{-\gamma t} = \beta e^{-11.48\gamma}$ should approach zero. A plot of $e^{-11.48\gamma}$ as function of γ is presented in Fig. 2. It can be seen that for $\gamma = 0.70\,\mathrm{h^{-1}}$, $e^{-11.48\gamma}$ and $\beta e^{-11.48\gamma}$ approach zero. A γ of $0.70\,\mathrm{h^{-1}}$ is much smaller than $9.68\,\mathrm{h^{-1}}$ reported for a batch reactor. The parameter β can be determined during the model calibration.

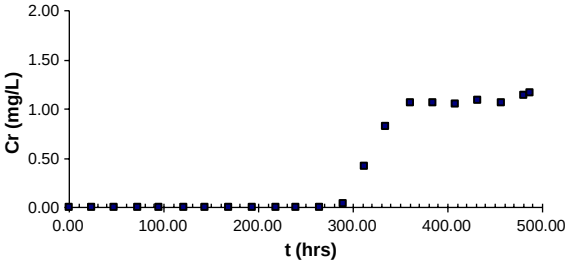

Fig. 1. Breakthrough profile for average influent Cr(VI) concentration of 1.94 mg/L (Alam, 2004).

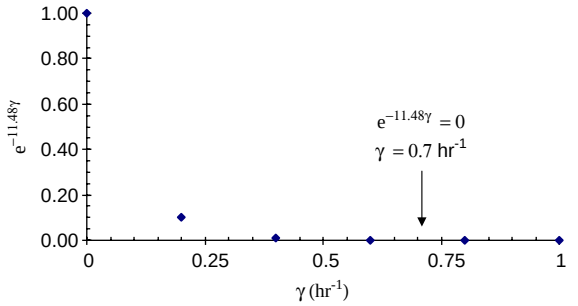

Fig. 2. Rate constant γ for deactivating enzyme.

Table 1
Pertinent hydraulic parameters of soil column employed by Alam (2004)

Parameter	Value
D	$0.05\,\mathrm{cm^2\,h^{-1}}$
τ	22.5 h
V	$0.67\,\mathrm{cm\,h^{-1}}$

6.2. Model calibration

Hydraulic parameters contained in Table 1 and the kinetic parameters presented in the preceding section were utilized to calibrate the model. The calibration parameter, as discussed, was the deactivating-enzyme-induced rate constant β. The best fit presented in Fig. 3 was obtained for $\beta = 13.5\,\mathrm{mg\,L^{-1}h^{-1}}$. It is to be noted

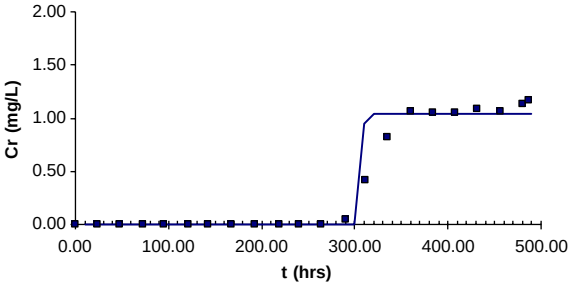

Fig. 3. Calibrated model prediction vs. experimental data.

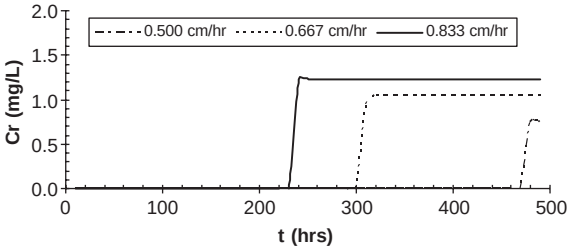

Fig. 4. Effect of varying transport velocity on model prediction.

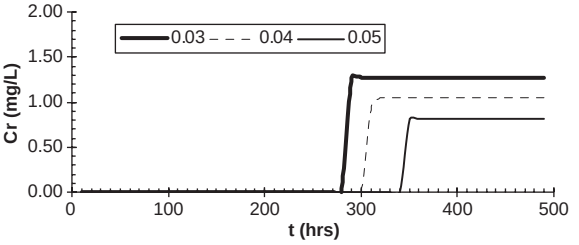

Fig. 5. Effect of varying α, in mg $L^{-1}h^{-1}$, on model prediction.

Table 2
Pertinent kinetic parameters of soil column

Parameter	Value
α	0.04 mg $L^{-1}h^{-1}$
β	13.5 mg $L^{-1}h^{-1}$
γ	0.70 h^{-1}

that this value of β is similar in magnitude to that reported in the literature for batch reactors. Kinetic parameters approximated by using column data are summarized in Table 2.

The calibrated model can be used for predicting reduction of Cr(VI) by MR-1 for concentrations in the neighborhood of 1.94 mg/L.

6.3. Sensitivity analysis

Sensitivity of the model prediction to changing parameters was evaluated both for hydraulic parameters and for kinetic parameters. Hydraulic parameters of primary concern are the transport velocity and the dispersion coefficient. Kinetic parameters are the stable-enzyme-induced reaction rate constant α and the deactivating-enzyme-induced reaction rate constants β and γ.

6.3.1. Sensitivity to hydraulic parameters

Transport velocity was varied from 0.500 to 0.833 cm h^{-1} with an intermediate value of 0.667 cm h^{-1}. Hydraulic residence time τ of the column decreases with increasing transport velocity. Consequently, reduction due to the stable enzyme $\alpha\tau$ decreases resulting in higher steady-state effluent concentrations when transport velocity increases as shown in Fig. 4. A change of $\pm 25\%$ in transport velocity can bring about a change in breakthrough time of at least ∓ 30 h. The steady-state effluent concentration was found to be equal to $Cr_0-\alpha\tau$. The dispersion coefficient was varied from 0.025 to 0.100 $cm^2 h^{-1}$ with an intermediate value of 0.050 $cm^2 h^{-1}$. Earlier breakthrough, as expected, was observed for higher values of the dispersion coefficient. However, mean residence time remained the same. Therefore, the steady-state effluent concentration $Cr_0-\alpha\tau$ also remained the same.

6.3.2. Sensitivity to kinetic parameters

The stable-enzyme-induced rate α was varied by $\pm 10\%$ from the base value of 0.04 mg $L^{-1}h^{-1}$ which was determined from experimental data. The effect of varying α is presented in Fig. 5. An increase in α reduces the steady-state effluent concentration proportionally by $\alpha\tau$, which is significant.

The maximum reaction rate due to the deactivating enzyme was varied from 10.8 to 16.2 mg $L^{-1}h^{-1}$ with an intermediate value of 13.5 mg $L^{-1}h^{-1}$ for a constant γ of 0.70 h^{-1}. Fig. 6 presents the effect of changing β on model prediction. Increasing β is observed to delay the breakthrough. An increase in β increases the reaction rate $\beta e^{-\gamma t}$ leading to more reduction of Cr(VI) and breakthrough cannot occur until the deactivating enzyme has been consumed entirely. An examination of Fig. 6 indicates that a change of $\pm 25\%$ in β brings about change of approximately $\mp 17\%$ in breakthrough time. Therefore, increasing β is expected to delay the breakthrough of Cr(VI) because of an increase in the reaction rate.

The rate constant γ determines the length of time for which the deactivating enzyme remains active. A larger γ implies a shorter life span of the enzyme. Therefore, when β is constant, increasing γ leads to reduced

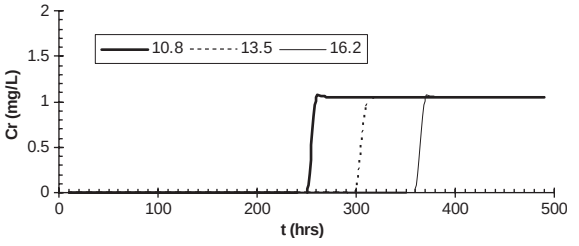

Fig. 6. Effect of varying β, in mg $L^{-1}h^{-1}$, on model prediction.

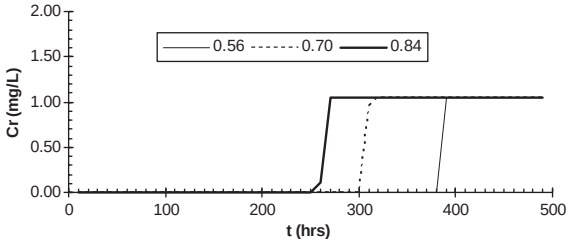

Fig. 7. Effect of varying γ, in h^{-1}, on model prediction.

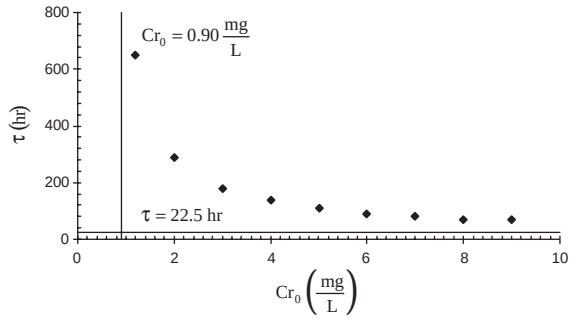

Fig. 8. Effect of influent concentration on residence time τ.

reduction causing an early breakthrough of Cr(VI) as seen in Fig. 7. A change of $\pm 20\%$ in γ brings about a change in the breakthrough time by at least $\mp 17\%$.

Therefore, changes in kinetic parameters can significantly effect the model predictions. It is essential that the kinetic parameters are determined as accurately as possible.

6.4. Effect of influent concentration on breakthrough

Higher influent concentration of Cr(VI) can quickly consume the deactivating enzyme. Therefore, higher influent concentration should lead to earlier breakthrough of Cr(VI) as shown in Fig. 8. However, no breakthrough will be observed when the influent concentration Cr_0 is less than $\alpha\tau$ which is the stable-enzyme-induced removal capacity of the column. Consequently, the τ vs. Cr_0 curve becomes asymptotic at $Cr_0 = \alpha\tau = 0.90\,mg\,L^{-1}$. As the influent concentration is increased, even though the breakthrough occurs quicker, the residence time, however, cannot be shorter than τ. The curve, therefore, becomes asymptotic to $\tau = 22.5\,h$ at high Cr_0.

Alam (2004) did not observe any breakthrough for influent concentration of 0.57 mg/L for at least 53 days. Therefore, when the stable-enzyme-induced removal capacity is larger than or equal to the influent or source concentration of Cr(VI), it will all be removed.

7. Conclusions

The model developed can simulate bioreduction of Cr(VI) by employing the dual-enzyme kinetic model. It is unconditionally stable and provides accurate results for $Pn \leq 20$ and $Cn \leq 1$. The accuracy of the model prediction is a function of the kinetics of Cr(VI) reduction by MR-1. Therefore, the kinetic parameters should be determined as accurately as possible. When Cr(VI) concentration is less than stable-enzyme-induced removal capacity of MR-1, all the Cr(VI) will be reduced.

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