Mass transport model of Cr(VI) through contaminated soil under the effect of external electric field

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Abstract: Based on diffusion and absorption-desorption process in soil-water environment, an equilibrium mathematical model was developed to simulate the behavior of Cr(VI) in contaminated soil layer under external electric field. Bench-scale experiment was designed to investigate effective diffusion coefficients of hexavalent chromium through contaminated soil layer without external electric field and further to obtain mass transport flux of Cr(VI) through contaminated soil layer under electric field. The effects of reference concentrations, soil layer thickness and applied electric field density in the model were studied to compare and analyze the theoretic results calculated by the equilibrium mathematical mode. It provides theoretical evidence for studying Cr(VI) transport through contaminated soils, as well as for soil environmental quality assessment, pollution prediction and pollution control in soil.

Keywords: soil-water environment, Cr(VI) transport, mathematical model, external electric field.

1. INTRODUCTION

Contamination of soil and ground water by hazardous wastes is a widespread problem and has caused a serious threat to public health. During the past decade, the need to develop cost effective and efficient techniques for remediation of contaminated soil has grown.

Waste chromium sludge, arising from many diverse fields such as metallurgy, electroplateing, leather tanning, chemical catalysts, pigments, corrosion inhibitors, printing inks, etc, is primarily present in hexavalent form such as divalent oxyanions, chromate (CrO₄²⁻) and dichromate(Cr₂O₇²⁻). Cr(VI) is highly soluble in water and toxic to most organisms due to its strong oxidizing nature[1]. In contrast, trivalent chromium [Cr(III)] is less toxic and forms insoluble oxides and hydroxides at above pH 5.0 and is impermeable to biological membranes[2]. Many earlier works focused on transformation of Cr(VI) to Cr(III) under various environmental conditions[3-8] and understanding of the effects of advection, dispersion, adsorption and geo-chemical processes on the remediation in different soils[9–11]. Electro-kinetics offers the possibility of transport enhancement and in-situ remediation of Cr(VI) in cases where conventional techniques are not feasible [12,13]. However, there has been no report considering the mathematical modeling of hexavalent chromium transport through different soils, especially the transport enhancement by external electric field, which is very essential for making the decision of the treatment option(whether in situ or ex situ) and for designing the optimal in situ remediation.

In this paper, the theoretical considerations underlying the transport of hexavalent chromate under external electric field were experimentally investigated. The objective was to gain a better understanding of the process through modeling so that effective means can be taken to remediate the soil. The model predictions are compared with the experimental date from laboratory scale studies.

2. MATERIALS AND METHODS

2.1. Soil and chemicals

The original soils were collected from the unsaturated zone in Yima, Henan province, China. Before mass transport measurement, the soils were grinded, sifted with sieves(passed through 0.6mm and retained in 0.425mm sieves) and sterilized. Having been cooled to room temperature, the pretreated soils were preserved in clean plastic containers for subsequent use. All the chemicals were of analytical grade and purchased from Beijing Chemical Works(Beijing, China). All solutions were prepared with Milli-Q water, and the glassware was cleaned using 10N HNO₃ and rinsed with Milli-Q water before use.

2.2. Batch adsorption studies

Cr(VI) sorption equilibrium measurement was conducted to estimate the adsorption coefficients of Cr(VI) in the soil. Adsorption kinetic study was conducted using 1g of sterilized soil and 100mL of synthetic chromium contaminated water with 50 mg/L of Cr(VI) in various reaction bottles. The reaction bottles were kept in a shaker at 140 rpm. The samples were withdrawn at time intervals of 5, 10, 15, 30, 60, 120, 180, 360, 420 and 480 minutes respectively, then filtrated solid and analyzed residual Cr(VI) concentration.

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For the isotherm sorption studies, 1 g of soil with 100 ml solution containing Cr(VI) was put in several reaction bottles and then kept in a shaker for 6 h at 140 rpm, respectively. The initial Cr(VI) concentrations employed were 2, 5, 10, 20, 30, 50, 100, 200, 300, 400 and 500 ng/L, respectively. At the end of 6 h (pseudoequilibrium time), the supernatant was separated and analyzed for Cr(VI) concentration.

For the study of the effect of pH value on sorption equilibrium, 1 g of soil with 100 ml solution containing Cr(VI) was put in several reaction bottles and then kept in a shaker for 6 h (pseudoequilibrium time) at 140 rpm. The pH values were 1, 3, 5, 6, 6.5, 7, 8, 9, 11 and 12, respectively. At the end of 6 h, the supernatant was separated for Cr(VI) concentration determination.

2.3. Estimation of transport parameters

2.3.1. Theory

Soil is porous media where void fraction and tortuosity factor have great effects on the mass transfer rate of Cr(VI) through pores in the soil[14,15]. Before modeling, the following hypotheses are made firstly:

1. The soil is composed of pores and inert substance.
2. The electric field between the soil layer and electrolyte is uniform.
3. No heterogeneous chemical reactions occur in the soil and electrochemical reactions are ignored in the system[17].
4. The physical, transport and electrokinetic parameters are constant throughout the soil layer.
5. The electro-osmotic velocity in the soil is assumed to be zero resulting from its very low surface charge and zeta potential.

Under an effect of external electric field, the ions in the soil pores will move in the possible fashion of electromigration, diffusion and convection. The overall mass transport flux \( J_s \) can be formulated as below[18]:

\[
J_s = -U_s^* C \cdot \nabla V - D_s \cdot \nabla C + v C
\]

where \( U_s^* \) is ionic mobility in soil, \( C \) is the concentration of ions, \( \nabla V \) is the voltage in soil and \( v \) is the apparent velocity of water within soil. In most cases, water can be regard as static within soil pores, so eq. (1) can be simplified as follows:

\[
J_s = -U_s^* C \cdot \nabla V - D_s \cdot \nabla C
\]

The Cr(VI) diffusion coefficient in soil \( D_s \) can be formulated as[19]:

\[
D_s = \frac{\varepsilon}{\tau} D_w
\]

where \( D_w \) is Cr(VI) diffusion coefficient in water, \( \varepsilon \) is void fraction, and \( \tau \) is tortuosity factor.

\( \varepsilon \) in eq.(3) can be experimentally determined according to the following relationship[20]:

\[
\varepsilon = 1 - \frac{\rho_{\text{wet}} - \rho_0}{\rho_0}
\]

where \( \rho_{\text{wet}} \) and \( \rho_0 \) are wet and dry bulk density of soil respectively, \( \rho_{\text{wet}} \) is the density of water(1.00g/cm\(^3\)).

Based on geometric model[17], \( \varepsilon \) and \( \tau \) are accounted as follows:

\[
\varepsilon = \frac{\pi^4 r^2}{8 h} \left( 1 - A \frac{r}{h} \right)
\]

\[
\tau = \frac{\pi^2}{4} \left( 1 - A \frac{r}{h} \right)
\]

where \( r \) and \( h \) are average radius and length of pores in the geometric mode of the soil layer, \( A \) is ratio factor which can be drew through boundary conditions: \( \tau = 1 \) while \( \varepsilon = 1 \), and \( A = 1.32 \).

\( \tau \) can be calculated by combining eq.(3) with eq.(4), and \( D_s \) can be further calculated by eq.(3).

The relationship of ionic mobility in water \( (U_w^*)\) versus diffusion coefficient\( (D_w)\) in aqueous media is determined using Nernst-Eintein equation[21]:

\[
U_w^* = D_w \frac{zF}{RT}
\]

where \( z \) is the charge number of ion, \( F \) is the Faraday constant(96500 C·mol\(^{-1}\)), \( R \) is the universal gas constant(8.314 J·mol\(^{-1}\)·K\(^{-1}\)), \( T \) is temperature.

In soil layer, the ionic mobility \( U_s^* \) is determined by similar equation:

\[
U_s^* = D_s \frac{zF}{RT}
\]

Mass transport in the soil layer is due to migration in an electric field and diffusion in concentration gradient. In the condition that substrate only does unidimensional mass transport and the electrical field is even, eq.(2) can be further simplified:

\[
J_s = -D_s \frac{zF}{RT} C - D_s \frac{4C}{dx}
\]

where \( \frac{zF}{RT} \) is the electric field intensity in the soil.

2.3.2. Experimental facility

The schematic of the experimental facility used in this study is shown in Fig.1. The main body is composed of two compartments with different sizes, which are connected by a hole with the diameter of 60mm. The compartment A and B of the equipment were 80mm(l)×145mm(w)×145mm(h) and 80mm(l)×85mm(w)×85mm(h), respectively. The Soil \( (\rho_{\text{wet}}=1.63 \text{ g/cm}^3, \rho_0 = 0.94 \text{g/cm}^3)\) was fixed in the hole between two compartments by micro-filtration.

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membranes with apertures of 0.45 μm. Cr(VI) transports through the soil layer from compartment A filled with Cr(VI) solution to compartment B filled with Milli-Q water. The graphite flat electrodes in compartment A and B were used as negative and positive poles respectively. The samples were withdrawn at time of 2, 4, 6, 8, 10 and 12 hours from compartment B and analyzed Cr(VI) concentration.

The stable mass transport process of ions through the instrument shown in Fig 1 is illustrated in Fig 2. From the left (compartment A) to the right (compartment B), ions pass through the left micro-filtration membrane, soil layer, and the right micro-filtration membrane one by one. The overall effective mass transport flux $J_{s,e}$ can be formulated as below according to Fick’s law:

$$J_{s,e} = V_B \frac{dC_B}{dt} = -K(C_B - C_A)$$  \hspace{1cm} (8)

when Cr(VI) concentration in compartment A is much higher than that in compartment B, the Cr(VI) concentration in compartment A approximatively keeps invariant, so the rate equation can be simplified to:

$$C_B = K \frac{C_A}{V_B} t$$  \hspace{1cm} (9)

where $V_B$ is volume of compartment B; $C_A$ is Cr(VI) concentration in compartment A; $C_B$ is Cr(VI) concentration in compartment B; $t$ is transport time; $K$ is coefficient of mass transfer. It is clear that the plot of $C_B$ versus time is linear, and the slope of the linear plot is $K \cdot C_A / V_B$. The transport process is affected by two micro-filtration membranes and soil layer (Fig.2.), the effective mass transport flux through left micro-filtration membrane, soil layer and right micro-filtration membrane can also be respectively formulated according to Fick’s law:

$$J_{m,l} = -\frac{D_m}{d_m} \Delta C_l$$  \hspace{1cm} (10)

$$J_{m,r} = -\frac{D_m}{d_m} \Delta C_r$$  \hspace{1cm} (11)

where $D_m$ and $d_m$ are thickness of soil layer and micro-filtration membrane, respectively; $\Delta C_l$, $\Delta C_r$, $\Delta C_s$ are ion concentration differences in left micro-filtration membrane, soil layer and right micro-filtration membrane, respectively; $D_{s,e}$, $D_m$ are effective diffusion coefficients of soil layer and micro-filtration membrane, respectively. Combining eq.(8) with eq.(10) to eq.(14), $K$ can be expressed as:

$$\frac{1}{K} = \frac{d_m}{D_{s,e}} + 2\frac{d_m}{D_m}$$  \hspace{1cm} (15)

$D_{s,e}$ and $J_{s,e}$ can be further expressed as:

$$D_{s,e} = \frac{d_s}{\frac{1}{K} \cdot \frac{1}{K}}$$  \hspace{1cm} (16)

$$J_{s,e} = \frac{D_{s,e}}{d_s} C_B$$  \hspace{1cm} (17)

where $K_m = \frac{D_m}{d_m}$ is coefficient of mass transfer in micro-filtration membrane, which was experimentally determined (0.0102 m/h).

Fig.2. Transport process of Cr(VI) through soil layer. M: Micro-filtration membranes; S: Soil layer.

2.4. Analytical procedures

Cr(VI) concentration was determined by the diphenylcarbazide method by measuring the absorbance at 540 nm using a LabTech UV-2100 UV–vis spectrophotometer [22](Holliston, USA). The current and voltage were gained by a regulated DC power supply.

$$J_s = -\frac{D_{s,e}}{d_s} \Delta C_s$$  \hspace{1cm} (12)

In the condition that substrate only does unidimensional mass transport, the transfer process can be supported by the following equations:

$$J_{s,e} = J_s = J_{m,l} = J_{m,r}$$  \hspace{1cm} (13)

$$C_A - C_B = \Delta C_1 + \Delta C_r + \Delta C_s$$  \hspace{1cm} (14)

where $J_{m,l}$, $J_s$, $J_{m,r}$ are effective mass transport fluxes through left micro-filtration membrane, soil layer and right micro-filtration membrane, respectively; $\Delta C_1$, $\Delta C_r$, $\Delta C_s$ are ion concentration differences in left micro-filtration membrane, soil layer and right micro-filtration membrane, respectively; $D_{s,e}$, $D_m$ are effective diffusion coefficients of soil layer and micro-filtration membrane, respectively. Combining eq.(8) with eq.(10) to eq.(14), $K$ can be expressed as:

$$\frac{1}{K} = \frac{d_m}{D_{s,e}} + 2\frac{d_m}{D_m}$$  \hspace{1cm} (15)

$D_{s,e}$ and $J_{s,e}$ can be further expressed as:

$$D_{s,e} = \frac{d_s}{\frac{1}{K} \cdot \frac{1}{K}}$$  \hspace{1cm} (16)

$$J_{s,e} = \frac{D_{s,e}}{d_s} C_B$$  \hspace{1cm} (17)

where $K_m = \frac{D_m}{d_m}$ is coefficient of mass transfer in micro-filtration membrane, which was experimentally determined (0.0102 m/h).

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3. RESULTS AND DISCUSSION

3.1. Batch adsorption studies

Fig. 3 shows Cr(VI) adsorption in soil versus time at pH 5.5±0.2. It is observed that the adsorption process was very fast during the beginning 40 minutes and attained a pseudo-equilibrium state at approximately $t = 6h$. In the following studies, 6h is considered as pseudo-equilibrium time for all the transport studies without other declaration.

Fig. 3. Cr(VI) adsorption versus time at pH 5.5±0.2.

$A_{[Cr(VI)]}$: Adsorption extent of Cr(VI)($\times 10^{-3}$mg$\cdot$g$^{-1}$).

Fig.4 shows the adsorption isotherms for Cr(VI), with Freundlich isotherm, i.e. $\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e$. The result, $\ln Q_e = -2.4628 + 1.0537\ln C_r$ ($Q_e$:µgCr(VI)/g soil, $C_r$:µg/L,$R^2=0.9746$) was drawn with the experimental data.

Fig.4. Freundlich adsorption isotherm for Cr(VI) (pH 4.5–5.5,$C_0 = 2.0–500.0$ mg/L).

3.2. Estimation of transport parameters

The model presented in section 2.3.2 can be used to predict Cr(VI) concentration in compartment B as a function of time. The model was tested for different water contents by changing initial Cr(VI) concentrations in compartment A, soil layer thickness and applied electric field density(electrolyte solution:100 mg·L$^{-1}$ Na$_2$SO$_4$). These results are compared to the theoretic data(2.3.1) on Cr(VI) transport.

Data from batch adsorption studies indicates that the solution pH has a dramatic effect on Cr(VI) adsorption. Adsorption extent increased with the decrease in pH value (Fig.5). Mass transport in soil layer was supposed to be weakened by Cr(VI) adsorption of soil. To estimate the effect of adsorption on $D_{s,e}$ of Cr(VI) transport through soil layer, we monitored the average $D_{s,e}$ of different time at pH 2.0 and 5.5 through a 3mm wide soil layer. As shown in Fig.6, the average $D_{s,e}$ at pH 2.0 increased till the third day, and kept invariable, indicating Cr(VI) transport was weakened till the balance between adsorption and desorption achieved. The average $D_{s,e}$ at pH 5.5 kept invariable, and observed stable $D_{s,e}$ at pH 2.0 and 5.5 had neglectable difference, indicating the adsorption-desorption balance was achieved quickly at pH 5.5 and solution pH had no effect on Cr(VI) transport. In this work, the pH was settled 5.5±0.2 to eliminate the influence of adsorption process.

Fig.5. Effect of pH on Cr(VI) adsorption. $A_{[Cr(VI)]}$: Adsorption extent of Cr(VI)($\times 10^{-3}$mg$\cdot$g$^{-1}$).

Fig.6. Effect of pH on Cr(VI) transport:$D_{s,e}$ versus time at different pH value. $C_A=55$mg·L$^{-1}$, $d_s=3$mm

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3.2.1 Verification of the model

Measured was the mass transport of Cr(VI) of three different concentrations through a 3mm thick soil layer and 110mg/L Cr(VI) solution through soil layers of three different thickness without electric field. As shown in Figure 7a,b, Cr(VI) transport rate increases as \( C_A \) is increased and \( d_s \) is decreased. From Table 1, it is obvious that the experimental results and the calculated values is close without external electric field.

- **Table 1.** Cr(VI) transport parameters without external electric field: \( D_{s,e} \) and \( D_s \).

<table>
<thead>
<tr>
<th>( C_A )/mg·L(^{-1})</th>
<th>( d_s = \text{3mm} )</th>
<th>( d_s = \text{7mm} )</th>
<th>( d_s = \text{12mm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{s,e} )/×10(^{-9}) m(^2)·s(^{-1})</td>
<td>0.35</td>
<td>0.33</td>
<td>0.32</td>
</tr>
<tr>
<td>( D_s )/×10(^{-9}) m(^2)·s(^{-1})</td>
<td>0.34</td>
<td>0.34</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Experimental conditions: pH=5.5±0.2, temperature: 293±5K.

- **Table 2.** Cr(VI) transport parameters under external electric field: \( J_{s,e} \) and \( J_s \).

<table>
<thead>
<tr>
<th>( \Psi_s )/V·m(^{-1})</th>
<th>( C_A )/mg·L(^{-1})</th>
<th>( d_s )/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_s = \text{3mm},\ C_A = \text{55 mg·L}^{-1})</td>
<td>( d_s = \text{3mm},\ \Psi_s = \text{350 V·m}^{-1})</td>
<td>( C_A = \text{55 mg·L}^{-1},\ \Psi_s = \text{350 V·m}^{-1})</td>
</tr>
<tr>
<td>( J_{s,e} )/×10(^{-5}) g·m(^{-2})·s(^{-1})</td>
<td>0.57</td>
<td>2.19</td>
</tr>
<tr>
<td>( J_s )/×10(^{-5}) g·m(^{-2})·s(^{-1})</td>
<td>0.61</td>
<td>2.15</td>
</tr>
</tbody>
</table>

Experimental conditions: pH=5.5±0.2, temperature: 293±5K.
In order to verify the model under external electric field, the effects of reference concentrations, soil layer thickness and applied electric field density in the model were also studied under external electric field. As shown in Figure 8a,b and c, measured was the concentration of Cr(VI) in compartment B under different $\Psi_s$, $C_A$, and $d_s$. The results in Table 2 show that external electric field can enhance Cr(VI) transport through contaminated soil layer effectively, and the mathematical model above is reliable in determining effective diffusion fluxes under external electric field.

3.2.2 Improvement of the model

The relative errors of effective diffusion coefficient and flux between actual process and model results are probably explained by the following factors:

1. $D_w$ is accounted by the following equation[23]:

$$D_w = \frac{RT}{1/\lambda^+ + 1/\lambda^-}$$

where, $T$: temperature, K; $R$: universal gas constant, 8.314 J·mol$^{-1}$·K$^{-1}$; $\lambda^+$, $\lambda^-$ : conductance of $K^+$, $\text{CrO}_4^{2-}$, $A^2$·s$^{-3}$·m$^{-2}$·kg$^{-1}$; $n_+$, $n_-$: charge number of $K^+$, $\text{CrO}_4^{2-}$; $F$: Faraday constant, 96500 C·mol$^{-1}$. The $D_w$ applied is actually $K_2\text{CrO}_4$ diffusion coefficient in rare solution, however, the actual species of Cr(VI) existing in solution are $\text{CrO}_4^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$, $\text{HCrO}_4^-$ at pH 5.5±0.2. The diffusion coefficients of these species are different due to unique $\lambda^+$ and $\lambda^-$.  

2. $D_s$ was described using eq.(3), which is introduced from porous media system. The mathematical model used to determine the relationship of $\varepsilon$ versus $\tau$ needs to be improved due to the complex soil-water environment. 

3. The above modeling and experiment were carried on under the condition that ions concentration was very low. The more obviously error between the model results and actual process observed from Table 1 and 2 can be explained from electro chemical theory. The relation between the electric conductivity of ions in aqueous solution and their concentration was showed as below:

$$\lambda_i = \lambda_i^\infty - a\sqrt{C}$$

where $\lambda_i$ and $\lambda_i^\infty$ are conductivity and limiting conductivity of ion, $a$ is constant. Ionic mobility $U_i$ and $\lambda_i$ was interrelated:

$$U_i = \frac{\lambda_i}{z_iF}$$

Obviously, the error between the model results and actual process will be bigger and bigger with the increase of ions concentration.

4. CONCLUSION

The mathematical model developed to describe...
chromium transport through soil layer under external electric field shows that external electric field is an effective method to enhance Cr(VI) transport through contaminated soil. The good agreement between the model results and the experimental data demonstrates that the analysis is likely to be an accurate estimate of the physical situation, within the limits of the assumptions. The combined effects of reference concentrations, soil layer thickness and applied electric field density have been considered in the model. The model presented here may serve as a basis for simulating the behavior of Cr(VI) in contaminated soil layer. If physical data are available, utilizing a model described herein could be a cost-effective way to choose optimum conditions for further study. The model could also be useful in evaluating further possible destination of Cr(VI) in the decontamination process, such as uniform mixing of contaminants in sand and different flow patterns like electro-osmosis and convection for other types of soil.

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