Testing Soil Accumulation of Cd from Reclaimed Water

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Abstract: The reuse of wastewater improves the comprehensive utilization of water resources, and reduces the shortage of water resources. In this paper, the accumulation of heavy metal Cd risk in reclaimed water irrigated soil to human health was analysed through experiments and simulations. Firstly, according to the static adsorption experiment of sandy clay loam, the fitting effect of Freundlich equation on Cd is better for the certainty coefficient $R^2$ reaches 0.97. Then, use the more accurate DEM model of CXTFIT2.1 software to fit the $Cl^-$ penetration curve. Finally, made the heavy metal leading experiment, found that the TSM model has a good fitting effect on the penetration curve of Cd, with a determination coefficient close to 1 and a small standard error coefficient. Based on the results of the above experiments, the HYDRUS-1D was used to analyze and predict the cumulative risk of Cd in reclaimed water irrigated soil. The results showed that: after 100 years under current situations, the predicted concentration of Cd in soil may reach 0.742 mg/kg, which exceeded the national soil environmental quality standard, may be a serious health hazard. Measures should be taken to reduce the risk of human health by ingestion and accumulation of crops and vegetables.

Keywords: reclaimed water irrigated soil; heavy metal Cd; human health; cumulative risk

1. Introduction

The reuse of wastewater improves the comprehensive utilization of water resources and reduces the shortage of water resources [1-3]. However, there are many problems in the application process. When the wastewater was used in agricultural irrigation, heavy metal ions in reclaimed water may be enriched into vegetables and crops. Heavy metal Cd has strong mobility transfer from soil to vegetable [4-10], and may be combined with phosphate groups or chlorine containing bases in DNA and RNA after entering the human body [11-13]. Excessive accumulation of Cd in the body can cause lung and kidney dysfunction and may be harmful to human health through food intake [14].

In recent years, the accumulation of heavy metal Cd in soil and its impact on agricultural product safety has become a major concern of the scientific community, government and society, and the sustainable development of the environment [15-17]. Many scholars at home and abroad have carried out a great deal of research on the transport rule of heavy metal ions in soil. Scuntjens et al. studied the aging effects on Cadmium transport in undisturbed contaminated sandy soil columns [18]. Daniel et al. studied the migration behavior of Cd in soil under different concentration conditions using sequential extraction, batch, and miscible displacement experiments [19]. Gu et al. collected soil of different levels and depths, measured the content of CD, Pb and Ni in the soil, and discussed the enrichment characteristics and migration rules of CD, Pb and Ni in the soil [20]. Lu et al. studied the effects of exogenous organic acids on soil pH, enzyme activity, and cadmium migration and transformation [21]. Pang et al. [22], through indoor soil column penetration test, studied the migration rule of Pb/Cd/Zn under 3-60m/d pore water velocity, and used CXTFIT software to fit experimental data to obtain migration parameters. Dube et al. summarized the model methods of soil adsorption and migration of

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modern heavy metals, including soil column experiment method and artificial neural network based on data fitting [23]. In addition, there are many studies on the accumulation characteristics and rules of heavy metals from soil to plants. Ru et al., [24] studied the migration and accumulation of heavy metal Cu, Zn, Pb and Cd in the soil radish system using greenhouse soil culture pot experiments. Wei, et al. [15], studied the accumulation and distribution characteristics of soil heavy metal Cd in cassava, and discussed the safety critical value of cassava in the environment polluted by Cd. There are also many studies on the migration of heavy metal Cd in the soil plant system [25,26]. In Japan's Minamata disease event, inorganic mercury in seawater into methyl-mercury, fish intake is cumulative, people food poisoning, the heavy metal bioaccumulation, may cause human health risk [27]. Y.X. Zhang, et al. also showed that Cd is one of the main factors of soil pollution. Trace Cd$^{2+}$ not only has a toxic effect on plant growth, but also has great harm to human health [28].

However, there is relatively little research on the long-term accumulation of heavy metal Cd in soil. In China, the time of using reclaimed water for irrigation is still short, and the study of target heavy metals concentration in the soil and grain of the reclaimed water can't reflect the human health risk under the long-term irrigation of reclaimed water. Therefore, it is necessary to establish a model to predict the harm of accumulated heavy metals to the human health.

In this study, reclaimed water from Beijing was taken as the research object. Relevant experiments were carried out and the corresponding soil accumulated Cd concentration was predicted by HYDRUS-1D software for 100, 300 and 500 years of reclaimed water irrigation.

2. Materials and methods
2.1. The material
The tested soil is sandy loam (International), which was dried by indoor air and 2 mm screened to remove impurities. The soil column is made of plexiglass tube, 10cm high and 5cm the inner diameter. Before filling the soil column, the column and hemispherical funnel need to be washed by dilute acid solution to wash away the heavy metals which may be adsorbed, and the residual acid is washed with deionized water. Then, spread a 100-mesh screen over the perforated panel and cover the 1 cm thick 2-3 mm quartz sand. When filling the soil column, pack 2 times and each filling 5 cm according to the actual soil bulk density and the initial soil moisture content. The soil column is compacted with a plastic compactor to reach the required height and ensure that the bulk density of the soil column is the same as or comparable to the bulk density of the natural soil.

2.2. Experimental devices

2.3. Soil column transport experiments
With 2 L large beaker and constant flow pump as the water supply device, the water column was injected slowly into the saturated soil column to sufficiently remove air from the soil column. Then adjust the direction of the inflow fluid, so that it flows through the soil column from top to bottom, and the CdCl$_2$ solution was input to the soil column at the speed of 0.05 mL/min. Finally, the flow liquid was collected by 50 mL centrifuge tube and the concentration of Cd ion in the liquid was determined. The experimental installation is shown in Figure 1.
2.4. Cd Static Adsorption Test

Batch equilibrium adsorption method was used to prepare cadmium nitrate solution with concentration gradients of 5, 10, 20, 40, 60, 100, 200, 300, 400 mg/L, using reclaimed water as mother liquor and adding cadmium nitrate (analytical purity). Then add NaOH or HNO₃ to regulate pH same as the reclaimed water. Weigh accurately 2.00 g soil sample 9 times in 50 mL with round bottom plug plastic centrifuge tube, according to the 1:10 soil water ratio, pour into heavy metal solution 20 ml with different concentration gradient, sealing stopper. In the constant temperature oscillator, keep the temperature of 25°C with 24 h shaking. Centrifuges were centrifuged at 3000 r/min and filtered after 10min, then the supernatant was collected. Determine the concentration of heavy metals by atomic absorption spectrophotometer.

Calculation formula of heavy metal adsorption amount:

\[ q = \frac{(C_i - C_e)V}{m} \]  

In the formula, \( q \) is the amount of heavy metal adsorption, mg/kg; \( C_i \) and \( C_e \) are added heavy metal concentration and equilibrium solution concentration, mg/L; \( V \) is the volume of liquid at equilibrium, L; and \( m \) is soil weight, g.

In order to evaluate the adsorption of heavy metals in soil, Langmuir and Freundlich adsorption isotherms were used to fit them:

Freundlich: 
\[ S = K_f C^\beta \]  

Langmuir: 
\[ S = \frac{K_d C}{1 + \eta C} \]  

In the formula, \( S \) is adsorption capacity (mg/kg), \( C \) is concentration of solution (mg/L), \( K_d, K_f, \beta, \eta \) are adsorption constant.

2.5. Cl- Tracer Test

The breakthrough curves of heavy metals with different treatments were obtained by a hybrid displacement experiment facility. After filling the soil column, open the peristaltic pump from the soil at the bottom of the column at a slower rate from input deionized water solution to saturated soil, to exclude the air in the soil column, and then adjust the flow into the liquid flow as the top-down
through the soil column, thereby forming a stable flow field. The CdCl₂ solution, 0.06 mol/L concentration, is used as the inflow liquid, and injected into the soil column from the top of the soil column. The effluent was collected at regular intervals until the Cl⁻ concentration in the effluent was close to the inlet liquid, and then stop the tracer test.

2.6. Heavy Metal Leaching Experiment

Because the concentration of heavy metals in reclaimed water was very low, in order to shorten the breakthrough time, heavy metals were added to the reclaimed water as the inflow liquid: Cd was 500 mg/L. The process is similar to tracer test. The leachate collected at each time was stored in a plastic bottle (after pickling and removing heavy metals adsorbed on the surface) and stored in storage at 4 degrees.

2.7. Software

Origin 9.0, to compile the isotherm adsorption equation and fit the data of static adsorption experiment;

CXTFIT2.1, developed by American saline soil laboratory, to solve the inverse problem of convection dispersion equation for one-dimensional solute transport;

HYDRUS-1D, to predict the distribution and accumulation trend of heavy metal Cd in soil under the condition of reclaimed water irrigation.

3. Results and discussions

3.1. Adsorption Test

The two isothermal adsorption equations of self-defining function Freundlich and Langmuir were compiled by Origin 9.0 software, and the static adsorption test data of heavy metal Cd under pH=7 condition were fitted. The result was shown in Figure 2.

![Freundlich Isothermal adsorption model](image1)

![Langmuir Isothermal adsorption model](image2)

**Figure 2.** The isothermal adsorption data and fitting curves of soil Cd when pH=7
From the above data, we can see that the fitting effects of Freundlich and Langmuir equations are good, and all of them are related to Cd. However, the certainty coefficient of Freundlich equation reaches 0.97, so its equation is chosen as the soil adsorption parameter, which provides parameter support for the numerical simulation of soil movement.

### 3.2. Cl\textsuperscript{-} tracer test

Based on CXTFIT 2.1 algorithm, the breakthrough curve of mixed displacement experiment is optimized by nonlinear least square method based on Levenberg-Marquardt algorithm, and the inverse problem of advection dispersion equation of one-dimensional solute transport is solved. For tracer Cl\textsuperscript{-}, assuming that it does not react with the soil medium, given the R=1, the deterministic equilibrium model is used to estimate D and V, as shown in Table 2 and Table 3.

#### Table 2. Fixed R, the parameters of Cl\textsuperscript{-} BTC with the DEM model

<table>
<thead>
<tr>
<th>Soil texture</th>
<th>V (cm/min)</th>
<th>D (cm\textsuperscript{2}/min)</th>
<th>R</th>
<th>r\textsuperscript{2}</th>
<th>D</th>
<th>MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>sandy clay loam</td>
<td>0.0715</td>
<td>0.0457</td>
<td>1</td>
<td>0.9922</td>
<td>0.9922</td>
<td>0.0009637</td>
</tr>
</tbody>
</table>

V- mean pore flow velocity; D- Fitted dispersion coefficient; R- Retardation factor; r\textsuperscript{2} - Coefficient of determination; MSE- Mean square error.

Fixed V invariant, using deterministic equilibrium model to estimate D and R, as shown in Table 3.

#### Table 3. Fixed V, the parameters of Cl\textsuperscript{-} BTC with the DEM model

<table>
<thead>
<tr>
<th>Soil texture</th>
<th>V (cm/min)</th>
<th>D (cm\textsuperscript{2}/min)</th>
<th>R</th>
<th>r\textsuperscript{2}</th>
<th>MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>sandy clay loam</td>
<td>0.0711</td>
<td>0.0454</td>
<td>0.995</td>
<td>0.9922</td>
<td>0.0009637</td>
</tr>
</tbody>
</table>

V- Mean pore flow velocity; D- Fitted dispersion coefficient; R-Fitted retardation factor; r\textsuperscript{2} - Coefficient of determination; MSE- Mean square error

Fixed R and V values, and used physical non-equilibrium TRM model to fit the breakthrough curve to estimate D, \(\beta\), and \(\omega\), as shown in Table 4.

#### Table 4. Fixed V and R, the parameters of Cl\textsuperscript{-} BTC with the DEM model

<table>
<thead>
<tr>
<th>V (cm/min)</th>
<th>D (cm\textsuperscript{2}/min)</th>
<th>R</th>
<th>(\beta)</th>
<th>(\omega)</th>
<th>r\textsuperscript{2}</th>
<th>MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0711</td>
<td>0.0462</td>
<td>1.0</td>
<td>0.983</td>
<td>100</td>
<td>0.9921</td>
<td>0.00104</td>
</tr>
</tbody>
</table>

V- measured mean pore flow velocity; D-fitted dispersion coefficient; \(\beta\)-fitted partition coefficient; \(\omega\)-fitted mass transfer coefficient.

According to Tables 2-4, compared with the DEM model, TRM estimation of D value is not significantly different, but DEM model is more accurate. Therefore, it is suggested that the deterministic DEM equilibrium model be used to fit the breakthrough curves of Cl\textsuperscript{-}.

### 3.3. Heavy Metal Leaching and the Fitting of BTC

In this experiment, the inversion function of HYDRUS-1D software and the chemical non-equilibrium two-point mathematical model (TSM) were used to fit the breakthrough curve of heavy metal Cd. The result was shown in Figure 3.
The parameters obtained by Cd- BTC fitting with the TSM model

<table>
<thead>
<tr>
<th>soil texture</th>
<th>element</th>
<th>f</th>
<th>α</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>sandy clay loam</td>
<td>Cd</td>
<td>0.472</td>
<td>0.03811</td>
<td>0.99974</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.001096)</td>
<td>(0.00034353)</td>
<td></td>
</tr>
</tbody>
</table>

where f means the equilibrium adsorption point total adsorption point ratio; α means first-order kinetic rate coefficient; R² means coefficient of determination, the closer to 1, the better of fitting effect; the amount of value in brackets is the standard error coefficient, the smaller the better.

The Table 5 shown that: the effect of using the deterministic chemical non-equilibrium two-point model (TSM) to fit the breakthrough curve of Cd is very well, the coefficient of determination is close to 1 and the standard error coefficient is very small. The BTC is used to obtain soil transport parameters f and α, which provided parameter support for prediction of heavy metal accumulation in reclaimed water under long-term irrigation conditions.

According to the experimental results and the mathematical model established, combined with the soil water parameters and movement parameters, using HYDRUS-1D software to predict the reclaimed water irrigation condition, distribution of heavy metal Cd in agricultural soils and accumulation trend. Tables 6 and 7 are the soil moisture parameters and soil transport parameters used in the HYDRUS-1D model, respectively. The predicted irrigation conditions are shown in Table 8.

### Table 6. Soil moisture parameters

<table>
<thead>
<tr>
<th>soil texture</th>
<th>Qr (cm³/cm³)</th>
<th>Qs (cm³/cm³)</th>
<th>Α (cm⁻¹)</th>
<th>N</th>
<th>Ks (cm/h)</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>sandy clay loam</td>
<td>0.0569</td>
<td>0.531</td>
<td>0.0152</td>
<td>1.46</td>
<td>86.38</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### Table 7. Soil movement parameters

<table>
<thead>
<tr>
<th>soil texture</th>
<th>Bulk.D (g/cm³)</th>
<th>Disp (cm)</th>
<th>Kf (L/kg)</th>
<th>B</th>
<th>f</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>sandy clay loam</td>
<td>1.15</td>
<td>0.64</td>
<td>89.40</td>
<td>0.59</td>
<td>0.472</td>
<td>0.0381</td>
</tr>
</tbody>
</table>

### Table 8. Irrigation water quality

<table>
<thead>
<tr>
<th>Reclaimed water process</th>
<th>pH</th>
<th>Cd mg/L</th>
<th>Pb mg/L</th>
<th>Cu mg/L</th>
<th>Zn mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculation sedimentation sand filtration</td>
<td>6.4-9</td>
<td>0.0013</td>
<td>0.0012</td>
<td>0.0017</td>
<td>0.013</td>
</tr>
</tbody>
</table>
According to the cross-sectional area of the tested soil column (diameter 5 cm), each column designed annual irrigation water consumption is 2 L, irrigation flow is 0.5 mL/min, the actual amount of irrigation for one year is equivalent to HYDRUS-1D in the simulation of 66.67 h irrigation. The predicted irrigation years are 100, 300 and 500 years, and the corresponding HYDRUS-1D simulation time is 6667 h, 20000 h, 33333 h, respectively. The predicted soil depth is 0~40 cm. The numerical simulation results are shown in Figure 4.

![Figure 4. Distribution of Cd in soil solution during 100, 300 and 500 years of reclaimed water irrigation](image)

Blue represents 100 years, green represents 300 years and the turquoise represents 500 years. In the simulation process, the density of the mesh of the soil profile is closely related to the stability of the prediction results. When the grid line in the concentration prediction of 251 below the large, unstable, but in more than 351 is basically stable, so there are 451 grid lines to discretize the soil profile, the relationship between the quantity and stability of grid line prediction results are shown in Table 9.

Applied those parameters to the adsorption isotherm of Freundlich, the amount of heavy metals adsorbed by soil can be obtained. Heavy metals are easily adsorbed by soil matrix when they enter the soil, they are difficult to migrate in the soil profile and accumulate mainly in 0~20 cm top soil [29,30]. The concentration of soil solution is calculated from the average value of 0~20 cm. The results are shown in Table 10.

### Table 9. Meshing and stability relationship

<table>
<thead>
<tr>
<th>Predicted irrigation time</th>
<th>The migration depth of Cd corresponding to the number of mesh lines (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>151</td>
</tr>
<tr>
<td>100 year</td>
<td>2.1</td>
</tr>
<tr>
<td>300 year</td>
<td>5.8</td>
</tr>
<tr>
<td>500 year</td>
<td>8.8</td>
</tr>
</tbody>
</table>

### Table 10. Accumulation of heavy metals in soil during simulated irrigation at 100, 300, and 500 years

<table>
<thead>
<tr>
<th>Predicted irrigation time</th>
<th>HYDRUS-1D Simulation time(h)</th>
<th>Heavy metal elements</th>
<th>Soil accumulated concentration(mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 year</td>
<td>6667</td>
<td>Cd</td>
<td>0.742</td>
</tr>
<tr>
<td>300 year</td>
<td>20000</td>
<td>Cd</td>
<td>1.419</td>
</tr>
<tr>
<td>500 year</td>
<td>33333</td>
<td>Cd</td>
<td>1.783</td>
</tr>
</tbody>
</table>

The national standard HJ 332-2006 specifies the limits of Cd in soil environment, \(\leq 0.30 \text{ mg/kg (pH} \leq 6.5)\);\(\leq 0.30 \text{ mg/kg (pH} 6.5 < \text{pH} \leq 7.5)\);\(\leq 0.60 \text{ mg/kg (pH} > 7.5)\). From the data available in Table 11, the predicted content of soil heavy metal Cd may reach 0.742 mg/kg, exceeded the limit value after 100 years of simulated irrigation. The accumulated concentration of heavy metal Cd in soil is
relatively high after long-term irrigated by reclaimed water. In relevant research [31-36], also shown that long-term use of sewage irrigation, heavy metal pollutants like Cd, Cr, As et al in sewage are easy to deposit in the soil, which pollute the soil to a certain extent. Effective prevention and control measures should be taken. Furthermore, it is possible to enter the plant, food intake, accumulated in body, thus endangering human health [37-43] and also for some drug interferences [44,45].

4. Conclusions
In this paper, the cumulative risk of Cd in reclaimed water irrigated soil was analyzed and predicted. Firstly, according to the static adsorption experiment of sandy clay loam, the fitting effect of Freundlich equation on Cd is better for the certainty coefficient R² reaches 0.97. Then, use the more accurate DEM model of CXTFIT2.1 software to fit the Cl⁻ penetration curve. Finally, made the heavy metal leading experiment, found that the TSM model has a good fitting effect on the penetration curve of Cd, with a determination coefficient close to 1 and a small standard error coefficient. Based on the results of the above experiments, the prediction of heavy metal accumulation in soil under the condition of long-term irrigation of reclaimed water was predicted by HYDRUS-1D. The results shown that the predicted concentration of Cd in soil may reach 0.742 mg/kg, 1.419 mg/kg, 1.783 mg/kg, after 100 years, 300 years, 500 years, respectively, which exceeded the national standard for soil environmental quality. Measures should be taken to reduce the risk of human health. How the heavy metals in soil migrate to human body through plants and animals and pose health risks to human body will be the focus of next research.

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