

Investigating colloid-associated transport of cadmium and lead in a clayey soil under preferential flow conditions

Wenjie Zhang ^a, Fengyong Jiang^a and Wenjing Sun ^{b,*}

^a School of Mechanics and Engineering Science, Shanghai University, Shanghai 200444, China

^b Department of Civil and Energy Engineering, College of Environmental Science and Engineering, Donghua University, Shanghai 201620, China

*Corresponding author. E-mail: wjsun@dhu.edu.cn

 WZ, 0000-0002-1645-562X; WS, 0000-0001-5074-337X

ABSTRACT

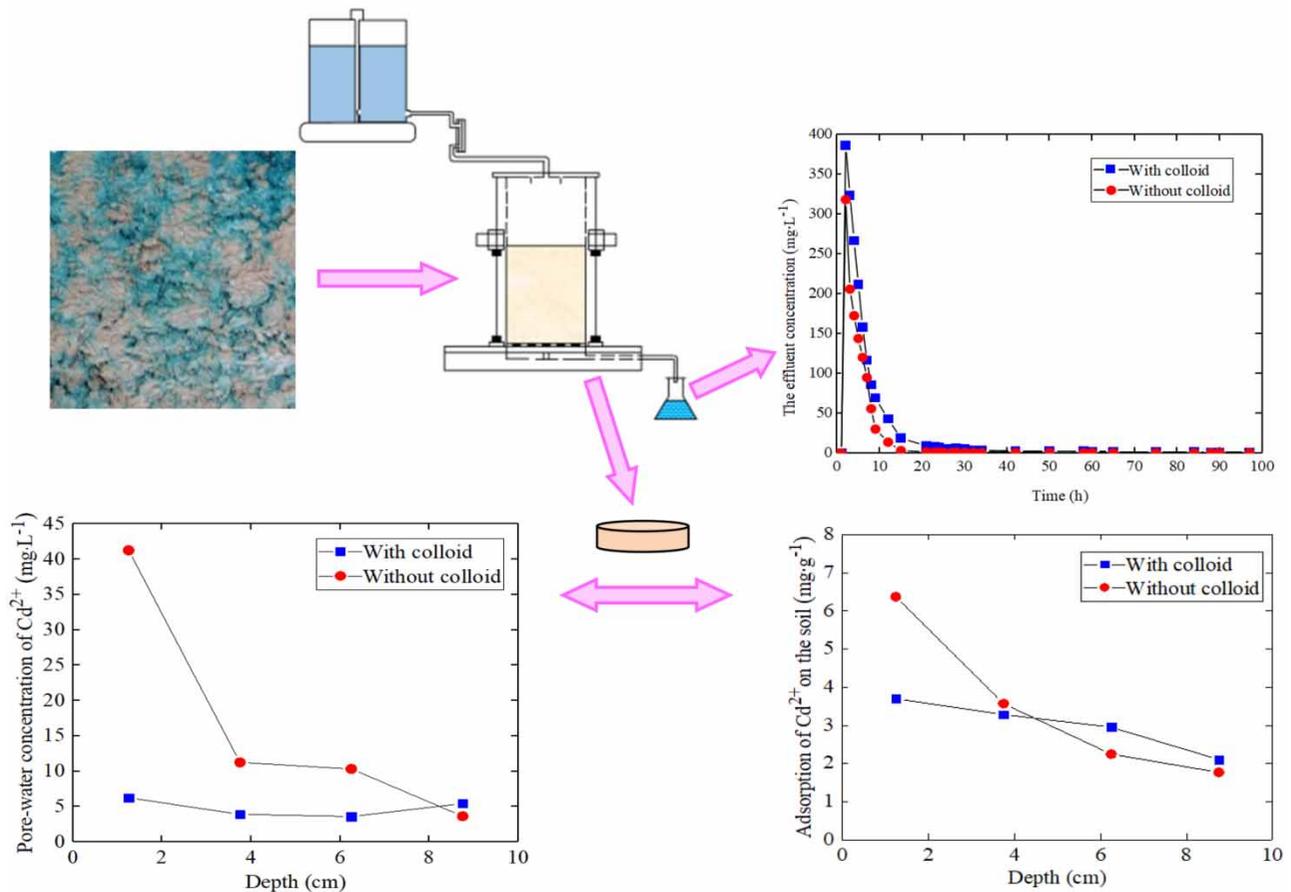
Colloids have a high adsorption capacity and can be mobile under preferential flow, and so may facilitate heavy metal migration. Heavy metal migration with soil colloids in a clayey soil under preferential flow conditions was investigated through experiments. Adsorption tests were carried out to determine the adsorption of Cd^{2+} and Pb^{2+} to the clay and colloids. The preferential flow characteristics in the soil column were investigated by dye tracing tests. The mobility of soil colloids in the soil column was studied by breakthrough tests. Leaching tests of cadmium and lead with and without colloids were carried out. The adsorption tests showed that soil colloids adsorbed more cadmium and lead than the silty clay. The dye tracing tests showed that moderate preferential flow in the soil column can be obtained by choosing clod-size distribution and dry density. The co-leaching test showed that the outflow of cadmium and lead was 1.49 and 33.88 times greater with colloids than without, respectively. The heavy metals adsorbed onto clay and the pore concentrations were both lower with colloids than without, indicating more heavy metals migrated downward with colloids. The migration of cadmium and lead was greatly enhanced by colloids under preferential flow conditions.

Key words: co-leaching, heavy metals, preferential flow, soil colloid

HIGHLIGHTS

- Soil columns with preferential flow path were constructed with soil clods.
- Preferential flow in the soil column was investigated by dye tracing tests.
- The mobility of soil colloids in the soil column was studied.
- Leaching tests of Cd^{2+} and Pb^{2+} with and without colloids were carried out.
- Breakthrough curves, the adsorbed heavy metals and pore solution concentrations were analyzed.

GRAPHICAL ABSTRACT



INTRODUCTION

There is growing public concern over soil pollution caused by heavy metals in recent decades. In areas with intensive anthropogenic activities, the problems are more serious (Gu *et al.* 2016). Most of the heavy metals in soils come from external human production activities (Qiao *et al.* 2013). In recent years, heavy metal pollutions from the relocation sites of heavy industrial enterprises have got a lot of attraction (Wei *et al.* 2021). Various factors, such as adsorption and precipitation of heavy metals in topsoil, play an important role in the migration of heavy metals (Qiao *et al.* 2019). The adsorption of heavy metals in soil has also been widely studied (Wang *et al.* 2016; Xie *et al.* 2017). As most heavy metals are prone to be adsorbed to the surface of soil material, heavy metals theoretically should be mainly confined to the shallow surface of the topsoil (Kim *et al.* 2008); in practice, however, heavy metals can migrate to considerable depths in some areas (Banks *et al.* 2006). The presence of large pores and cracks in topsoil is an important factor that caused pollution at deeper depths. Large pores and cracks may be caused by animals, plants or structural cracking, and become preferential channels through which migration of heavy metals can be enhanced. Further, soils generally contain large numbers of colloids with particle sizes ranging from 1 nm to 2 μm that have a strong ability to adsorb heavy metals. Under suitable physical and chemical conditions, colloids can be separated from the soils and act as heavy metal carriers, thus aggravating the heavy metal pollution (Arab *et al.* 2014).

Migrations of most heavy metals in soil are usually slow, and they rarely pass through homogeneous soils into groundwater (Behbahania *et al.* 2008; Antonkiewicz & Pelka 2014). For example, Dregulo & Bobylev (2021) found that concentrations of Pb, Cu, Ni and Co increased slightly with depth and that the highest concentrations were found in the upper horizons of only 0–5 cm. However, the migration ability of heavy metals can be significantly enhanced by preferential flow through macropores (Beven & Germann 2013). Preferential flow refers to the rapid transport of water or solutes through pathways

in soils that bypass a part of the soil matrix, and is usually facilitated by the intrinsic macro-pore characteristics of the soil (Zhang & Lin 2019). The influence of preferential pathway on the migration of heavy metals has been investigated by *in situ* or laboratory tests. For example, Kim *et al.* (2008) investigated the movement of Cd, Cu, and Pb through preferential flow paths in undisturbed soil columns and found that, despite their highly sorptive nature, some heavy metals were transported as rapidly as Cl^- under preferential flow conditions. Garrido & Helmhart (2012) found in an *in situ* dye tracer test that there were differences in the Pb distribution between different matrix domains, and that preferential flow and the low mobility of Pb might have been responsible for the high concentrations of Pb detected in the preferential flow paths. *In situ* tests can provide useful information that contributes to an improved understanding of the preferential flow characteristics in natural soils; however, preferential pathways are not distributed uniformly throughout surface soils, meaning that it is very difficult to reproduce experimental data. As a result, large man-made holes are usually used in laboratory column tests to mimic natural macropores. For example, Kohne & Mohanty (2005) used a metal tube to produce a macropore with a diameter of 2.4 cm in a soil column, into which they poured coarse sand. They chose this diameter to facilitate measurements of pressure head and water content inside the macropore domain. Zhou *et al.* (2013) performed laboratory column tests to investigate how large artificial holes affected the transport and distribution of solutes in a sandy soil in which straight large holes with a square cross-section of 1×1 cm were constructed using a steel screen (with 40 holes/cm²). Experimental data can be reproduced by introducing large artificial holes, however, pore sizes, connectivity properties and distribution of man-made holes differ considerably from natural macropores, so the test results may be much different from those in soils with natural preferential pathways. Soil samples with repeatable and representative preferential pathways are important to investigate the influence of preferential flow on solute transport, but this still needs further study.

Metal-bearing colloids can also cause potential environmental pollution due to their migration and the relatively stable adsorption to heavy metals (Mikhlin *et al.* 2016). Colloids could be highly mobile because of size exclusion effects and their mobility was influenced by the pore distribution, water saturation, and ionic strength (Gamerding & Kaplan 2001; Chen & Flury 2005). Kheirabadi *et al.* (2016) reported that colloids could enhance the migration of heavy metals by reducing retardation factor. Liu *et al.* (2019) investigated the co-migration of Cd with soil particles of different particle sizes and found that more Cd accumulated in the effluent when the particle size of the soil colloids was smaller than 0.2 μm . Through tests on sand columns, Móri *et al.* (2003) found that the presence of bentonite colloids could give rise to considerable increases in the migration of some radioactive elements (¹³⁷Cs, ²⁴¹Am, and ²³⁸Pu). Won *et al.* (2019) performed sand column experiment and found that kaolinite facilitated the transport of Pb and Cu under both low and high flow rate, because the presence of mobile kaolinite colloids delayed the sorption of heavy metals to the sand. Sen & Khilar (2006) concluded in a review paper that colloid fines can facilitate or retard contaminant transport in porous media, depending on the mobility of the colloids. The mobility of colloids partly depends on the pore size and connectivity of the soil. For fine-grained soil layers (e.g., clay), colloids can hardly move without preferential pathways. As mentioned previously, sand or glass beads were usually used as porous media when performing laboratory experiments to study preferential flow or cotransport of heavy metal with colloids. The adsorption capacity of clay to heavy metals is obviously different from that of sand/glass beads. So far, researches about the migration of heavy metals associated with colloids in a clayey soil under preferential flow conditions are still lacking.

This paper presents an experimental investigation on heavy metals migration in association with soil colloids under preferential flow conditions. Instead of introducing large artificial holes, preferential pathways in the tested column were developed in a novel way; that is, filling the columns with dried clay clods with a known clod-size distribution and dry bulk density. The preferential flow in the soil column was verified by dye tracing tests. Heavy metals Cd and Pb, of which the adsorption properties are different, were tested. Leaching tests were carried out in the column in the absence and presence of colloids, respectively. The solute concentrations in the soil pores and the amounts of heavy metals adsorbed on the soil were determined to show how the migration of heavy metals was enhanced in the presence of soil colloids under preferential flow conditions.

MATERIALS AND METHODS

Soils

The soil used in this study was collected to a depth of about 1 m from a construction site in Pudong District, Shanghai, China. This soil belongs to silty clay and is widespread in this area. Sand, silt, and clay particles accounted for about 5, 62, and 33%,

respectively. The soil had a pH of 6.5 to 7.5, a liquid limit of 38.1%, a plastic limit of 24.3%, and a specific gravity of 2.71. Cation exchange capacity (CEC) of the soil is 6.5 cmol/kg. There was almost no organic matter in this soil. Analysis of the mineral composition by X-ray diffraction (XRD) showed that the soil comprised 64.7% quartz, 24% muscovite, and 11.3% seraphinite. The contents of Pb and Cd (target heavy metals in this study) were 0.041 and 0.033 mg/kg respectively (XRF-1800, Shimadzu Limited, Japan).

The oven-dried silty clay was crushed into clods of different sizes, mixed uniformly, and filled into an acrylic mold with a height of 10 cm to form a soil column. As the clod size was much larger than soil particles, there will be large pores and hence preferential flow in the soil column. To ensure preferential flow will occur, dye tracing tests were carried out in soil columns with different clods-size distribution and different dry densities.

Solutions

Solutions of $\text{Cd}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ were used in the study. Stock solutions containing 1 g/L of Cd^{2+} and Pb^{2+} were prepared by dissolving analytical reagent grade $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 1 L deionized water. The desired working solutions were then prepared by diluting the stocks. In the batch tests, the Cd^{2+} and Pb^{2+} concentrations (C_0) ranged from 25 to 500 mg/L. In the leaching test with colloids, 30 mL of $\text{Cd}(\text{NO}_3)_2$ solution with Cd^{2+} concentration of 167 mg/mL (containing 5 g of Cd^{2+}), and 30 mL of $\text{Pb}(\text{NO}_3)_2$ solution with Pb^{2+} concentration of 333 mg/mL (containing 10 g of Pb^{2+}), were used.

Colloid preparation

The bentonite, obtained from Beishan area in Gaomiaozi County in the Inner Mongolia autonomous region of China, was used to prepare the inorganic soil colloids for the adsorption and leaching experiments. The bentonite has already been extensively studied and was selected preferentially as a component of the buffer-backfill materials for repositories in China (Ye *et al.* 2013). The bentonite comprised 75.4% montmorillonite, 11.7% quartz, 4.3% feldspar, and 7.3% cristobalite. The bentonite had a liquid limit of 276%, a plastic limit of 37%, a specific gravity of 2.66, a total specific surface area of 597 m²/g, and a CEC of 77.3 cmol/kg.

The <2 μm soil colloids were obtained using the sedimentation and siphoning methods, as follows: 50 g of bentonite and 150 mL of deionized water were mixed in a flask to create a bentonite suspension and placed in a shaking water bath for 30 min. The upper portion of the bentonite suspension was then drained into a 15-cm high beaker, made up to a volume of 1,000 mL with deionized water, and stirred with a magnetic stirrer for another 30 min. The resulting suspensions were allowed to settle for a period of 24 hours. Then, the colloids were siphoned from the upper 5 cm of the suspension and transferred to a clean beaker. The colloid concentration in the siphoned suspension was measured gravimetrically by allowing 10 mL aliquots to dry in an oven overnight at 60 °C. The aliquots from the siphoned suspension were diluted to 200 mg/L and the resulting colloid suspensions were kept in motion with a magnetic stirrer until they were ready to use.

Adsorption tests

Batch tests were carried out to determine how much Cd^{2+} and Pb^{2+} could be adsorbed to the silty clay and soil colloids. The silty clay was oven dried at 105 °C for 24 h, and sieved through a 0.25 mm mesh. The 200 mg/L colloid suspension prepared earlier was used. The adsorbent-water ratio for the Cd^{2+} adsorption tests was 1:100. As Pb^{2+} is more prone to be adsorbed onto soils, the adsorbent-water ratio for Pb^{2+} was 1:250. The adsorbents and solutions were mixed in polypropylene tubes to obtain suspensions of 50 mL and oscillated at 180 rpm in a thermostatic water bath for 24 h. In order to avoid the influence of pH on the measured adsorption, the adsorption process was adjusted with 0.01 mol/L HNO_3 and NaOH solution to maintain the pH of the reaction system at 6.0 ± 0.1 (Wang & Zhang 2021). The suspension was centrifuged at 3,000 rpm for 30 minutes. The concentrations of metal ions in the supernatant were measured by inductively coupled plasma atomic emission spectrometry (PerkinElmer Optima 7300 V ICP, USA). The amount of metal ions adsorbed per unit mass of adsorbent was obtained as (Xie *et al.* 2017):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e is the amount of metal ions adsorbed per unit mass of adsorbent (mg/g), C_0 and C_e are the initial and equilibrium concentrations (mg/L), V is the volume of the solution (L), and m is the mass of the adsorbent (g).

The adsorption isotherm curves of Cd^{2+} and Pb^{2+} were fitted to the Langmuir equation to describe the adsorption behavior (Langmuir 1918).

$$q_e = q_{\max} K_L C_e / (1 + K_L C_e) \quad (2)$$

where q_{\max} and K_L are Langmuir constants associated with the sorption capacity (mg/g) and sorption energy (L/mg), respectively.

Procedures for dye tracing tests

Dye tracing test was used in this paper to directly visualize and characterize the preferential flow in the soil column, which was prepared previously using soil clods of different clod sizes. A square prism acrylic mold (Figure 1) with the inner size of $0.1 \times 0.1 \times 0.1$ m was used for the dye tracing tests. For the convenience of sectioning, the mold was cut vertically into three equal parts and fastened with steel bar hoops. After filling soil clods into the mold, 125 mL brilliant blue solution, with a concentration of 4 g/L, was sprayed onto the upper surface of the column. A hand-held sprayer was operated carefully to achieve a well-distributed spraying. The soil column was left to stand for 30 min for further taking up of the brilliant blue (Zhang & Yuan 2019). Then, the molds were dismantled and the soil column was sectioned along the vertical seams. The sections were photographed using a digital camera. Correction of the images was made to eliminate the distortion caused by edge deformation and varied light environment. After adjusting color tolerance, lightness, and hue value, the dyed area was replaced with black color and the undyed area was replaced with white. The black and white image was converted into a gray scale image, and the threshold value was adjusted and binary processing was performed. After that, the binary image was denoised in Image-Pro 6.0 using the Erode algorithm and Dilate algorithm. Finally, pixel quantities of the dyed area and the undyed area were calculated and the dyed area ratio in every 1-cm height was then calculated. For each column, two sections were obtained and the average value of dyed area ratio in every depth was used. In order to ensure that there is moderate preferential flow in the column, different soil clod distributions and dry densities of the column were tried.

Leaching tests of colloids

In order to investigate the mobility of colloids, leaching tests were carried out. The leaching apparatus (Figure 2) was made up of a cylindrical container that included a rainfall simulator on the top. The container was made up of acrylic with a diameter of 0.1 m and a height of 0.2 m. The height of the soil column is 0.1 m. The 0.1 m space on the top of the soil column is designed for the rainfall simulator to achieve a well-distributed spraying. The turbidity value of the colloid suspension was measured using a turbidimeter. The relationship between the colloid concentration and the turbidity value was calibrated (Figure 3).

Two soil columns were tested: one was a soil column with preferential flow, and the other was a uniform soil column prepared using crushed soils. The dry densities of soils in the two columns were controlled as the same. The soil columns were first leached with deionized water until a steady-state flow was reached and the effluent absorbance was less than 0.002 to eliminate the influence of any background colloids in the soil. Then colloid suspension with a concentration of 200 mg/L was sprayed uniformly on the column surface by the rainfall simulator and the effluent turbidity value was measured regularly. Based on the linear relationship (Figure 3) and the measured effluent turbidity value, the effluent colloid

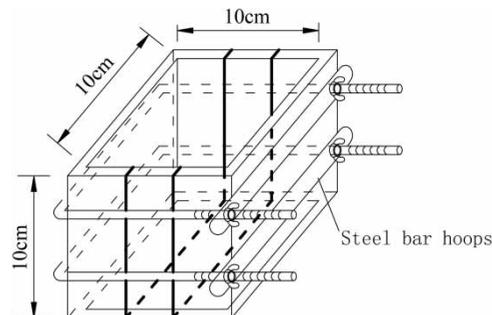


Figure 1 | Set-up of the mold used in dye tracing tests.

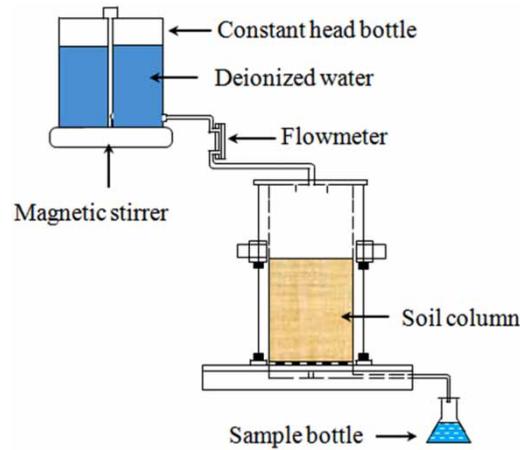


Figure 2 | Diagram of the setup for the leaching tests.

concentration was obtained. During the leaching process, the colloid suspension was stirred by a magnetic stirrer to prevent colloid coagulation.

Co-leaching tests under preferential flow conditions

Cd^{2+} and Pb^{2+} leaching tests were carried out in the presence and absence of colloids. This test used the same apparatus as the leaching tests of colloids. For the co-leaching test, the soil column was first leached with deionized water to eliminate the influence of background colloids in the soil. Then, either the Cd^{2+} or Pb^{2+} solution was sprayed uniformly on the column surface at an applied intensity of 10 mm/h. After that, the 200 mg/L colloid suspension was applied on the column at the same intensity to explore the colloid facilitated migration of heavy metals. For the scenario without colloids, deionized water was used for leaching. During the colloid leaching process, a magnetic stirrer was used to prevent colloid coagulation. The concentrations of heavy metals in the effluent were measured at regular intervals. Finally, the soil column was sliced and the pore-water concentrations were measured and the amounts of heavy metals adsorbed in each layer were calculated.

RESULTS AND DISCUSSION

Results of the isothermal adsorption tests

The adsorption isotherm curves of Cd^{2+} and Pb^{2+} fitted with the Langmuir equation are shown in Figure 4 and Table 1. The adsorption of Cd^{2+} and Pb^{2+} to the silty clay reached the saturated adsorption capacity at C_e of about 200 mg/L; however, the adsorption to the soil colloids did not reach saturation in the tested concentration range. The heavy metal absorption capacity of soil colloids was therefore much greater than that of the silty clay, because of the large specific surface area and high ion

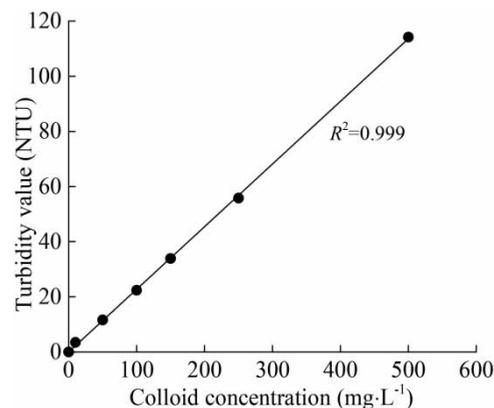


Figure 3 | Relationship between the colloid concentration and the turbidity value.

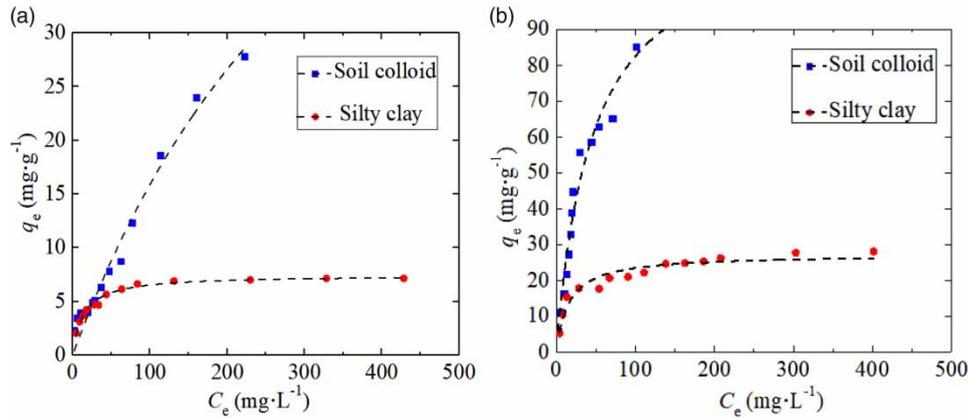


Figure 4 | Adsorption curves for (a) Cd²⁺; and (b) Pb²⁺ fitted by the Langmuir equation.

Table 1 | Adsorption model parameters of Cd²⁺ and Pb²⁺ for silty clay and soil colloids

Equation	Heavy metal adsorption	Parameter	Silty clay Estimated value	Soil colloid Estimated value
Langmuir	Cd ²⁺	q_{max} (mg/g)	7.45	82.32
		K_L (L/mg)	0.528	0.197
		R^2	0.981	0.973
	Pb ²⁺	q_{max} (mg/g)	27.17	120.06
		K_L (L/mg)	1.72	2.64
		R^2	0.929	0.970

exchange capacity of the soil colloids. As a result, soil colloids, when transported in flowing water, can act as carriers of heavy metals, thereby enhancing risk to the environment.

Results of the dye tracing tests

Three soil clod distributions were considered when preparing the soil column. Figure 5 gives the clod-size distributions together with the soil particle distributions, in which clod-size number 1 consists of more small-sized clods whereas number 3 consists of more large-sized clods.

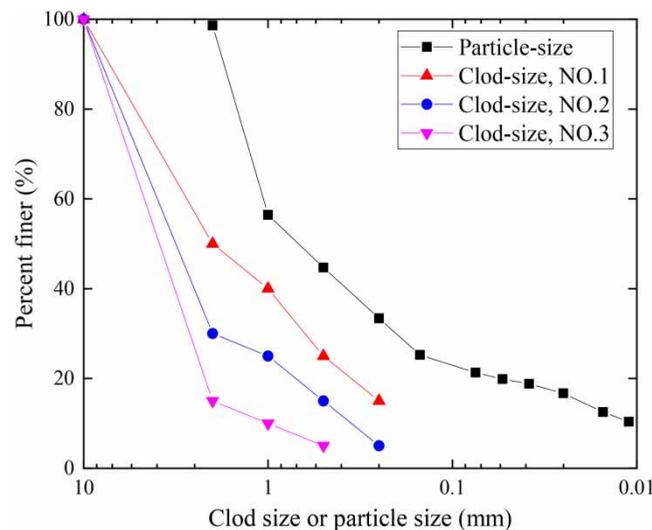


Figure 5 | Particle-size distribution of the soil and clod-size distributions in the soil column.

The photographs of the dyed sections corresponding to the three clod-size distributions are shown in Figure 6. For column number 1, only soil in the top 4 cm was dyed and the preferential flow is not obvious. This is because there are a lot of finer clods in the column and hence a lack of large pores. For the other two columns, dyed parts were observed throughout the whole depth, and obvious preferential flow was found. This is because a large amount of large-sized clods in these columns formed large pores connected to each other, which acted as preferential pathways for the brilliant blue solution. For column number 3, the content of large-sized clods was the highest and the solution flowed out from the bottom quickly, so it was not considered for use in the following tests. Further investigations were carried out on columns with clod distribution of number 2 and dry densities of 1.15, 1.25 and 1.35 g/cm³.

According to the procedures mentioned previously, the dyed area ratios corresponding to the three dry densities were obtained and are shown in Figure 7. It can be seen that the dyed area ratios decrease with depth. For the column with the dry density of 1.35 g/cm³, the dyed area ratio decreases fast and reach 0 at the depth of 8.5 cm, reflecting the fact that the downward flow of the brilliant blue solution is slow and much of the solution was taken up in the upper part of the soil column. For columns with the dry densities of 1.25 and 1.15 g/cm³, the dyed area ratios decrease slowly, means that more preferential flow occurs in these two columns. The dyed area ratios illustrate that preferential flow increases with a decreasing dry density. Therefore, clod-size distribution of number 2 and a dry density of 1.15 g/cm³ were determined to be the best scheme to ensure the existence of preferential flow in the soil column. For the subsequent leaching tests, soil columns were prepared according to these parameters.

Results of the colloids leaching tests

After being leached continuously for 300 hours, no colloid was detected in the effluent of the uniform column. Though soil in the column was loosely filled with a dry density of only 1.15 g/cm³, the test result showed that colloid can not pass through

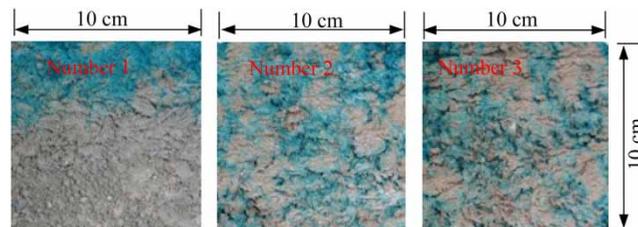


Figure 6 | Dyed sections for different clod-size distributions.

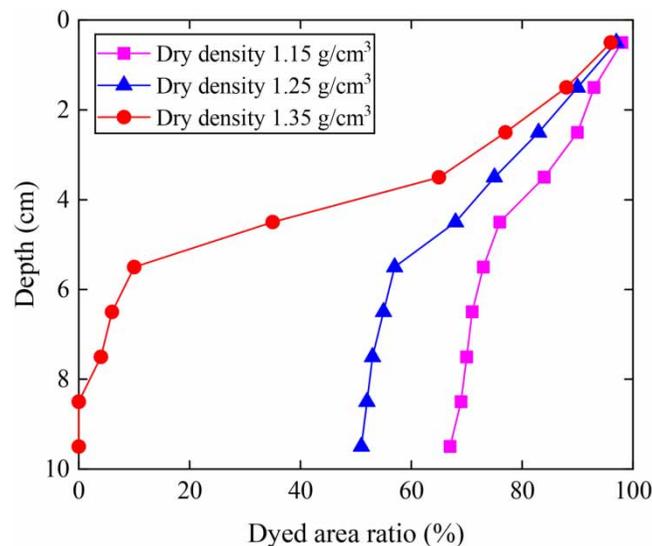


Figure 7 | Dyed area ratios at different depths under different dry densities.

the 10-cm thick uniform clay. The reason lies in interception and deposition of colloids in the small soil pores of the uniform column.

The colloid breakthrough curve of the column with preferential flow is shown in Figure 8. On the whole, the effluent colloid concentration increased with time and reached the source concentration at the 200th hour. Then the effluent concentration decreased gradually due to the interception and accumulation of colloids in the flow pathway. Compared with the uniform column, it is concluded that colloid can easily be transported in the preferential pathway and therefore acts as a heavy metal carrier. It should be noted that the test durations of the following co-leaching test of heavy metal and colloid were all shorter than 200 hours and the deposition colloid process after 200 hours is beyond the topic of this paper.

Transport of Cd^{2+} facilitated by colloids under preferential flow conditions

The Cd^{2+} leaching tests in the presence and absence of colloids both lasted 100 hours, until the effluent concentration was lower than 0.5 mg/L. The measured concentration of Cd^{2+} in the effluent peaked after leaching for about 2 hours, then decreased gradually (Figure 9). For a steady-state flow, the applied intensity equals the Darcy velocity; that is, 10 mm/h, so the peaks that appeared after 2 hours are because of preferential flow. The reasons for the decrease of effluent concentration afterwards are the outflow of Cd^{2+} and adsorption. During the whole leaching process, the effluent concentrations were higher in the presence of colloids than without colloids, and the peak concentrations with and without colloids were 386.98 and 318.54 mg/L, respectively. The total mass of Cd^{2+} in the effluent with colloids was 1.49 times higher than without colloids. This shows that the colloids enhanced the migration of Cd^{2+} .

The soil column was cut horizontally into 4 layers that were each 2.5 cm thick. The profiles of Cd^{2+} adsorbed on each layer and the pore-water concentrations of Cd^{2+} are shown in Figure 10. In the upper part of the soil column, the Cd^{2+} adsorption without colloids (Figure 10(a)) was close to the adsorption capacity of the soil (7.45 mg/g, Table 1). However, when there were colloids, the adsorption in the upper part was obviously lower, because of the competitive adsorption of colloids. The Cd^{2+} adsorption in the lower part of the soil column was higher with colloids than without colloids, which shows that colloids can act as Cd^{2+} carriers and transport more Cd^{2+} to the lower part. The Cd^{2+} concentrations of pore-water that remained in the column (Figure 10(b)) were noticeably lower with colloids than without colloids, which demonstrates that more Cd^{2+} was transported out of the soil column with colloids than the one without. This coincides well with Figure 9 and again shows that the migration of Cd^{2+} can be facilitated by colloids.

Transport of Pb^{2+} facilitated by colloids under preferential flow conditions

The Pb^{2+} leaching tests lasted 200 hours, until the effluent concentration was lower than 0.01 mg/L. The breakthrough curves in Figure 11 show that the effluent concentration was much higher in the presence of colloids than without colloids. The total outflow of Pb^{2+} was 33.88 times higher with colloids than without colloids, which shows that the migration of Pb^{2+} was greatly enhanced in the presence of colloids. Although the source concentration of Pb^{2+} (333 mg/mL) was higher than the source concentration of Cd^{2+} (167 mg/mL), the concentration of Pb^{2+} in the effluent (Figure 11) was much lower

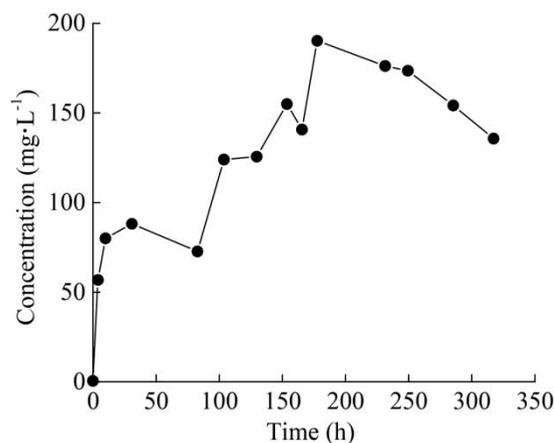


Figure 8 | The effluent colloid concentration under the preferential flow condition.

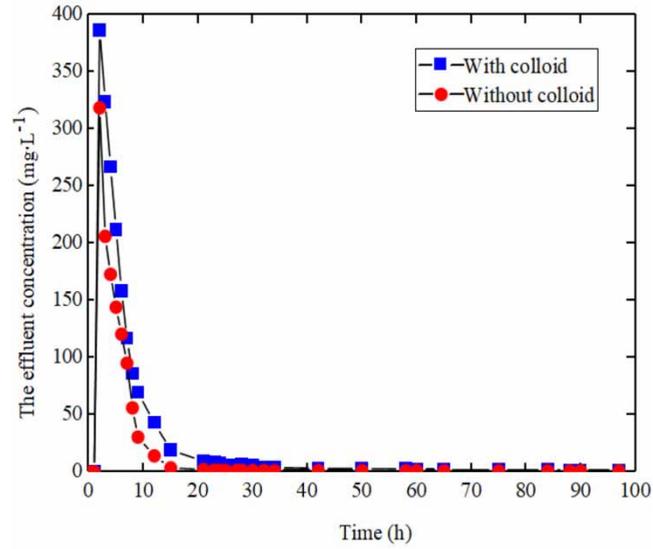


Figure 9 | The concentrations of Cd²⁺ in the effluent with and without colloids.

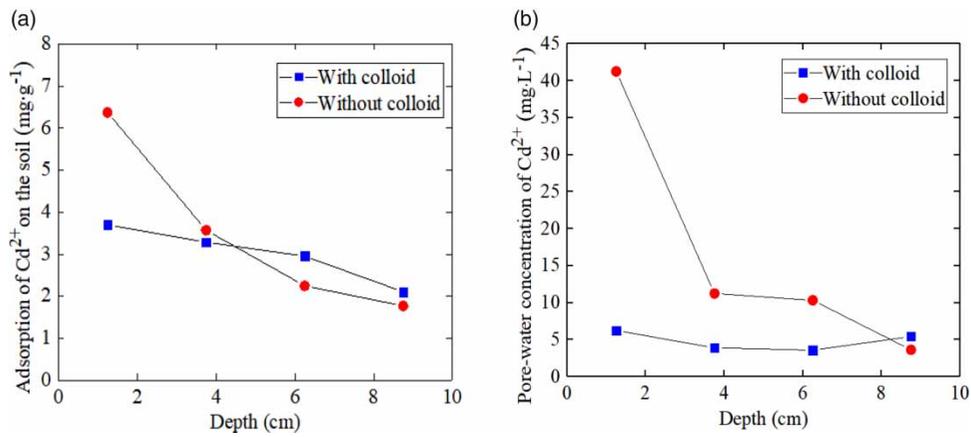


Figure 10 | Concentration profiles of (a) adsorption of Cd²⁺ on the soil and (b) pore-water concentration of Cd²⁺.

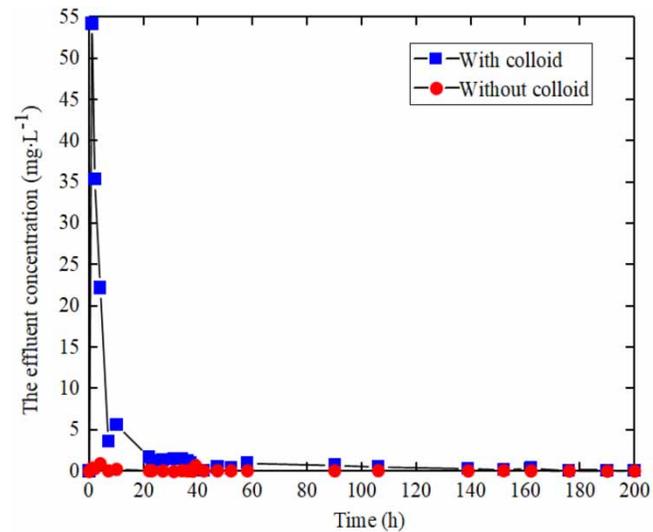


Figure 11 | The concentrations of Pb²⁺ in the effluent with and without colloids.

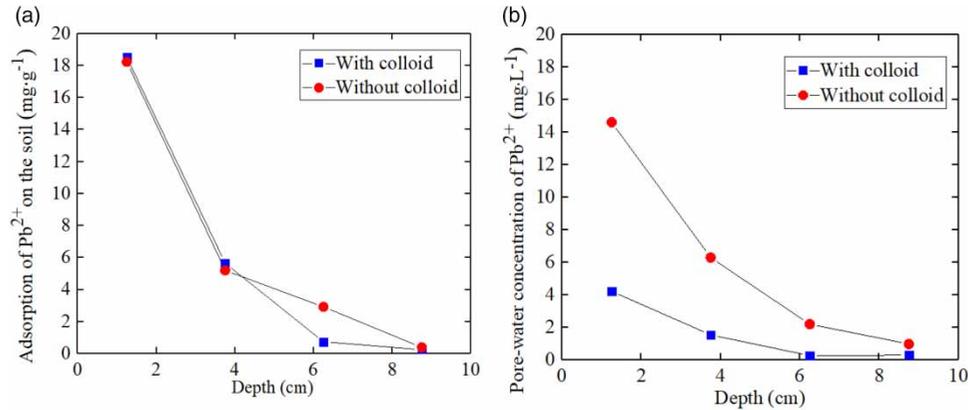


Figure 12 | Profiles of (a) Pb²⁺ adsorption on the soil and (b) Pb²⁺ concentrations in pore water.

than that of Cd²⁺ (Figure 9), and the cumulative Pb²⁺ outflow was only 1/13 of the cumulative Cd²⁺ outflow. This is because Pb²⁺ is more likely to be adsorbed by the clay during leaching, resulting in a much lower migration ability than Cd²⁺.

The amounts of Pb²⁺ adsorption and the Pb²⁺ concentrations in soil pore-water at different depths of the soil column are shown in Figure 12. As Pb²⁺ is easily adsorbed to soil, there was generally little difference between the amounts of adsorption in the presence and absence of colloids, except that the adsorption was noticeably less with colloids than without colloids at the depth of 6.25 cm (Figure 12(a)). Less adsorption means that more Pb²⁺ was transported downwards with colloids. The Pb²⁺ concentrations that remained in soil pore-water (Figure 12(b)) were obviously lower with colloids than without, indicating that more Pb²⁺ had migrated out of the soil column with colloids. The migration ability of Pb²⁺ was greatly enhanced by colloids. The test results here were consistent with those of Won *et al.* (2019). In their study, sand columns were used. It was found that kaolinite reduced the adsorption of Pb on sand and hence accelerated the migration of Pb.

DISCUSSION

Contaminant migration associated with colloids in saturated porous material has been studied by many researchers (Yan *et al.* 2019; Yang *et al.* 2019). As colloidal sorption capacity for heavy metals is usually high, colloids can act as heavy metal carriers. However, the transport of heavy metals can either be facilitated or retarded by colloids, depending on the mobility of colloids (Sen & Khilar 2006). Colloids can hardly transport through fine-grained uniform soil due to entrapment or plugging of pore constrictions. Under the preferential condition, mobility of colloids can be enhanced greatly and therefore transport of heavy metals can be facilitated to a great extent. This paper focused on Cd²⁺ and Pb²⁺ transport associated with inorganic soil colloid in a clayey soil with preferential flow pathway. It is challenging to reproduce the natural preferential flow pathways in a laboratory because they are in fact irregularly distributed. In this study, the soil columns were constructed with poorly-graded soil clods to ensure the presence of preferential flow. The specific porous structure of soil is still different from natural preferential flow pathways; however, the pore structure is more nearing to reality than other man-made large pores. This method is to some extent novel and is of reference value for researchers in this field. The colloids used in the tests are obtained from natural bentonite using the sedimentation and siphoning methods, representing inorganic fines that can be released from natural soils. Bentonite was not used directly as colloidal fines because it contains some large particles. In the co-leaching test, the presence of colloids reduced the adsorption of heavy metals in the soil column, and increased the effluent concentration. These results clearly demonstrated that colloids facilitated the transport of heavy metals, which is consistent with the existing literatures (e.g., Möri *et al.* 2003; Wan *et al.* 2018). The co-migration of colloids and heavy metal is a complex process, which is influenced by many factors such as type and concentration of heavy metal, pH, soil type, and colloid type. These factors need to be studied further. In this paper, the influence of heavy metal on the transport of colloids was not investigated. This is also an important issue and needs further study.

CONCLUSIONS

The objective of this paper was to investigate whether colloids facilitated the transport of Cd²⁺ and Pb²⁺ under preferential flow conditions. The following conclusions can be drawn.

1. The adsorption test showed that soil colloids had a much greater ability to absorb Cd^{2+} and Pb^{2+} than silty clay. The colloid breakthrough tests showed that colloid could not pass through the uniform clay column whereas it can easily migrate in the column with preferential pathway. Soil colloids transported in preferential pathways can therefore act as heavy-metal carriers.
2. The dye tracing tests showed that clod-size distribution and dry density can obviously influence the preferential flow characteristic in the soil column. Preferential flow is obvious in the clayey-soil columns prepared by using clod-size distribution of number 2 and controlling the dry density at 1.15 g/cm^3 .
3. The co-leaching tests showed that cumulative outflows of Cd^{2+} and Pb^{2+} were 1.49 and 33.88 times higher with colloids than without colloids, respectively. Colloids enhanced the transport ability of Cd^{2+} and Pb^{2+} . The pore-water concentrations and the amounts of heavy metals adsorbed on soil were all lower in the presence of colloids than without colloids. The movement of heavy metals therefore was significantly accelerated when transported along with colloids under preferential flow conditions. For heavy-metal migration analysis or pollution control in soils with mobile colloids, attention must be paid to the co-migration of heavy metal and colloids.
4. Lead had a higher source concentration and leaching time than cadmium; however, the outflow of lead was only about 1/13 of the outflow of cadmium. As Pb^{2+} is more prone to be adsorbed by the clay, the migration ability of Pb^{2+} with colloids under preferential flow conditions was much lower than that of Cd^{2+} .

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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