

## Article

# Influence of Soil Colloids on Ni Adsorption and Transport in the Saturated Porous Media: Effects of pH, Ionic Strength, and Humic Acid

Zhanxi Wei <sup>1,2,†</sup>, Yidan Zhu <sup>3,†</sup>, Yuanyuan Wang <sup>4,\*</sup>, Zefeng Song <sup>5</sup>, Yuanzhao Wu <sup>1,2</sup>, Wenli Ma <sup>1,2</sup>, Yongxia Hou <sup>6</sup>, Wenqing Zhang <sup>4</sup> and Yuesuo Yang <sup>4</sup> 

- <sup>1</sup> Qinghai 906 Engineering Survey and Design Institute, Qinghai Bureau of Environmental Geology Exploration, Xining 810007, China; weizhanxi3014@163.com (Z.W.); wyz4060@163.com (Y.W.); Mw11\_283594902@126.com (W.M.)
- <sup>2</sup> Qinghai Research Center for Geo-Environment Protection and Disaster Prevention Engineering Technology, Xining 810007, China
- <sup>3</sup> Ningbo Shuiyi Membrane Technology Development Co., Ltd., Ningbo 315336, China; zyd202206@163.com
- <sup>4</sup> Key Laboratory of Ground Water Resources and Environment, Ministry of Education, Jilin University, 2519 Jiefang Road, Changchun 130021, China; zhangwenqing0826@jlu.edu.cn (W.Z.); yangyuesuo@jlu.edu.cn (Y.Y.)
- <sup>5</sup> Institute of Geological Survey, Hebei GEO University, Shijiazhuang 050031, China; songzefeng@sina.com
- <sup>6</sup> Key Laboratory of Regional Environment and Eco-Restoration, Ministry of Education, Shenyang University, Shenyang 110044, China; houyongxia@syu.edu.cn
- \* Correspondence: wang\_yuanyuan19@mails.jlu.edu.cn
- † These authors contributed equally to this work.



**Citation:** Wei, Z.; Zhu, Y.; Wang, Y.; Song, Z.; Wu, Y.; Ma, W.; Hou, Y.; Zhang, W.; Yang, Y. Influence of Soil Colloids on Ni Adsorption and Transport in the Saturated Porous Media: Effects of pH, Ionic Strength, and Humic Acid. *Appl. Sci.* **2022**, *12*, 6591. <https://doi.org/10.3390/app12136591>

Academic Editor: Chang-Gu Lee

Received: 17 May 2022

Accepted: 16 June 2022

Published: 29 June 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

**Abstract:** Natural colloids are widely distributed in soil and groundwater. Due to their specific characteristics, colloids can actively involve various transport contaminants, resulting in a complicated fate and the transport of heavy metals to the environment. This study investigated the effects of soil colloids on the adsorption and transport of Ni<sup>2+</sup> in saturated porous media under different conditions, including pH, ion strength (IS), and humic acid (HA), because these indexes are non-negligible in the fates of various organic or inorganic matters in the subsurface environment. The results indicate that Ni<sup>2+</sup> adsorption by soil colloids slightly increased from 17% to 25% with the increase of pH from 5.5 to 7.5 at the IS of 30 mmol·L<sup>-1</sup>, whilst it significantly reduced from 55% to 17% with the increase of IS from 0 to 30 mmol·L<sup>-1</sup> at a pH of 5.5. Both Langmuir and Freundlich models can fit the adsorption isotherms of Ni<sup>2+</sup> on soil colloids and quartz sand. According to the column experiment, the presence of soil colloids increased the initial penetration rate, but could not increase the final transport efficiency of Ni<sup>2+</sup> in the effluent. The presence of soil colloids has weakened the effect of IS on Ni<sup>2+</sup> transport in the sand column. Moreover, this experiment implies that HA remarkably decreased the Ni<sup>2+</sup> transport efficiency from 71.3% to 58.0% in the presence of soil colloids and that there was no significant difference in the HA effect on the Ni<sup>2+</sup> transport in the absence of soil colloids.

**Keywords:** soil colloids; Ni<sup>2+</sup> adsorption; Ni<sup>2+</sup> transport; ionic strength; pH; humic acid

## 1. Introduction

Recently, due to industrial and agricultural activities, various contaminants (especially heavy metals, such as Cd, Cr, Cu, Pb, Ni, Mn, etc.) have been detected in groundwater, significantly threatening the health of humans [1,2]. For the safety of water environments, it is necessary to prevent heavy metals in soils from contaminating the groundwater.

Colloids, generally defined as small particles with dimensions roughly between 1 nm and 10 μm, including inorganic colloids, organic colloids, and microorganisms, are ubiquitous in subsurface environments [3–5]. Some toxic colloids, such as bacteria, viruses, and

nanomaterials, can transport from soil to groundwater, resulting in groundwater contamination [6,7]. Generally, colloids have the characteristics of large specific surface areas and high activity, causing them to exhibit strong affinities to hydrophobic contaminants, heavy metals, and pharmaceuticals [8–12]. At the same time, these colloids can carry the adsorbed pollutants for long-distance transport, greatly enhancing the dispersion of pollutants in soil and water environments and increasing the ecological risk [13–16].

It was reported that heavy metals in groundwater are strongly associated with small-sized colloidal matter and organic molecules [17,18]. Moreover, as reported in the study, the colloids have the potential to promote the transport of heavy metals in soils and groundwater [19]. In recent years, the co-transport of colloids and contaminants has attracted widespread attention regarding environmental remediation due to its prevalence and efficient treatment in groundwater [20–22]. It was reported that colloids are well dispersed, which can provide highly potential adsorption material for heavy metal removal [23,24]. Based on the conclusion of the soil column experiment [19,25], it seems that colloids and heavy metals are discharged into the groundwater through the vadose zone. The presence of colloids may alter the propagation of heavy metals in contaminant plumes [26]. The effect of colloids on contaminant transport is dependent on hydrogeological conditions and physicochemical properties of the aquifers [27–30]. Both groundwater chemistry and site-specific conditions may promote or hinder the co-transport of heavy metals and natural colloids in the subsurface environment [20,28,29].

Clay colloid is one of the most significant colloidal carriers for many contaminants in the subsurface environment [11,31]. The facilitated transport of some heavy metal ions in porous media by clay colloid particles has been widely reported [32]. However, few studies have investigated the adsorption and transport of  $\text{Ni}^{2+}$  with natural colloids in soil and groundwater. The high toxicity of  $\text{Ni}^{2+}$  can result in serious ecological damage and cause disorders and diseases in humans due to long-term exposure. Therefore, it is necessary to understand the  $\text{Ni}^{2+}$  transport behavior with colloids in soil and groundwater.

Moreover, common experimental adsorbents are artificial and will inevitably have adverse impacts on water. To overcome this shortcoming, we selected  $\text{Ni}^{2+}$  to represent heavy metals; moreover, we investigated the influence of natural soil colloids on the adsorption and transport of heavy metals in groundwater. In this study, the typical slime soil of Wudalianchi in Heilongjiang Province was selected as the experimental material for soil colloid extraction. The purpose of this study was to investigate how the general (but neglected) soil colloids influence the adsorption and transport of  $\text{Ni}^{2+}$  in saturated porous media, considering pH, ionic strength, and humic acid (HA). These factors play significant roles in the transport of contaminants in subsurface environments [12,21,22]. This study is crucial in preventing groundwater from being contaminated by heavy metals and other colloid-associated pollutants.

## 2. Materials and Methods

### 2.1. Soil Samples

The soil samples used in this study were collected from the Wudalianchi area in Heilongjiang Province, buried below a surface depth of 0.2–0.8 m, with an average thickness of 0.499 m. The soil samples were black or gray–black, with high viscosity and strong adhesion, containing iron–manganese nodules and basalt gravel blocks, showing low water content and semi-solid states. The soil surface was covered with 0.2–0.8 m of black humus, containing abundant plant roots. The natural moisture content of the top soil was low, and the soil block was loose and brittle, with weak adhesion. The main elements of the soil were detected by an inductively coupled plasma mass spectrometer (ICP-MS).

The soil samples were dried at room temperature ( $20 \pm 5$  °C) and ground and sieved through a 2 mm nylon sieve to remove large particles. The particle size distribution and zeta potential of the soil colloids were measured using a dynamic light scattering analyzer (Zetasizer Nano ZS, Malvern Instruments, Worcester, UK). The main anion and cation content in the soil samples were determined by atomic absorption spectroscopy (AAS).

## 2.2. Soil Colloids Preparation

Soil colloid suspensions were prepared by adding 1.0 g of soil samples to a 50 mL centrifuge tube containing 30 mL of ultrapure water, then homogenized by stirring for 60 min and sonicating for 8 min. The soil colloids were kept stable for 24 h. After preparation, the resulting soil colloids were characterized using an energy dispersive X-ray detector (EDX) and scanning electron microscopy (SEM) for a morphological analysis.

## 2.3. Porous Media and Column Packing

Quartz sand was used as the porous media for all column experiments. The pure quartz sand (99.7% silica and trace amounts of metal oxides, Damao, Tianjin, China) was prepared by soaking in a 12 M hydrochloric acid (HCl) solution for 36 h to eliminate impurities on the surface, followed by rinsing with ultrapure water. Then, the clean quartz sand was dried in a hot air oven at 105 °C for 24 h.

Column experiments were conducted in a glass chromatographic column with a length of 10 cm and an inner diameter of 2.6 cm. The column was rinsed with excess 0.01 M HNO<sub>3</sub> and 0.01 M NaOH before packing. The column was wet-packed and the porosity was controlled to about  $0.42 \pm 0.02$ . After packing, the column was injected with around 10 pore volumes (PVs) of ultrapure water using a peristaltic pump in the bottom-up mode to keep the sand column saturated and stable.

## 2.4. Solutions Preparation

All Ni<sup>2+</sup> solutions were prepared with Ni(NO<sub>3</sub>)<sub>2</sub> using ultrapure water or soil colloid suspensions to adjust the concentrations of Ni<sup>2+</sup> from 0 to 2 mg·L<sup>-1</sup>. The initial pH was adjusted to be 5.5, 6.5, or 7.5, as required, using 0.1 mol·L<sup>-1</sup> HNO<sub>3</sub> or 0.1 mol·L<sup>-1</sup> NaOH. The ionic strength (IS) was adjusted to 0 mmol·L<sup>-1</sup>, 3 mmol·L<sup>-1</sup>, and 30 mmol·L<sup>-1</sup> by NaNO<sub>3</sub>. Humic acid (HA) at a concentration of 20 mg·L<sup>-1</sup> was selected to represent the organic matter.

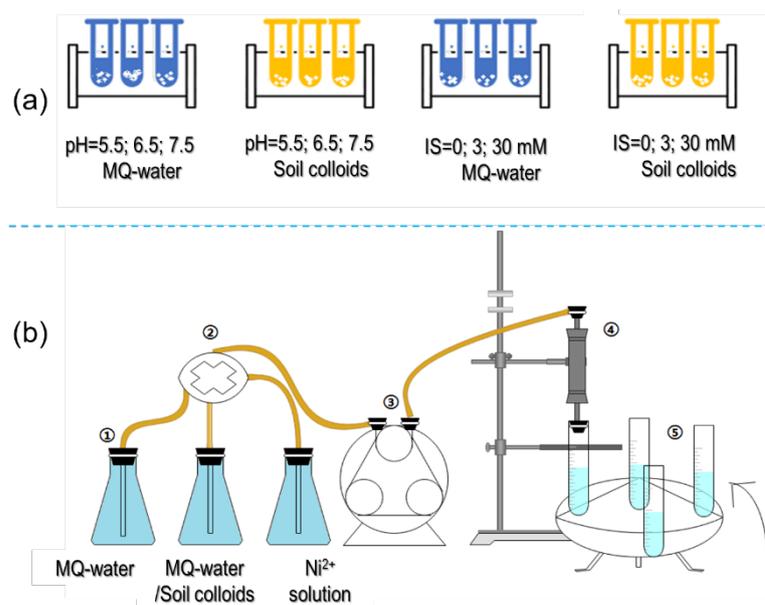
## 2.5. Experimental Method

### 2.5.1. Isothermal Adsorption

For the isothermal adsorption experiment, a 20 mL Ni<sup>2+</sup> solution with a concentration series of 0, 0.2, 0.5, 1, and 2 mg·L<sup>-1</sup> was mixed with 1.0 g of quartz sand or with soil colloids in several glass bottles. These glass bottles were placed in an incubator at 20 °C and then shaken at 150 rpm for 24 h. After equilibration, the solutions were centrifuged at 10,000 rpm for 1 h and the liquid supernatant was filtered through a polyether sulfone membrane with a 0.22 µm bore diameter. The filtered liquid was then acidified with 1 mol·L<sup>-1</sup> HNO<sub>3</sub> to render the pH < 2.0. Finally, the concentration of Ni<sup>2+</sup> in the equilibrium aqueous phase was then detected by ICP-MS. In addition, the solutions with different pHs (5.5, 6.5, 7.5) and IS (0, 3, 30 mmol·L<sup>-1</sup>) were used to study the effect of groundwater chemistry on the Ni<sup>2+</sup> adsorption by soil colloids and sand. The setup of the batch experiments is illustrated in Figure 1a.

### 2.5.2. Column Experiment

The sand column was first stabilized with around 10 PVs of ultrapure water using a peristaltic pump in the bottom-up mode and a flow rate of 1 mL·min<sup>-1</sup>. Then, ultrapure water or soil colloidal suspensions were injected into the sand columns at the same flow rate in the top-down mode. After the sand column was saturated with ultrapure water or soil colloidal suspensions, the Ni<sup>2+</sup> solution (with a specific concentration) was injected into the sand columns for 10 PVs. The effluent was collected at regular intervals and the concentrations of Ni<sup>2+</sup> in the effluent were tested by ICP-MS after acidification. In addition, the soil colloid suspensions with IS (0 mmol·L<sup>-1</sup>, and 3 mmol·L<sup>-1</sup>) and HA (20 mg·L<sup>-1</sup>) were also applied to study the effect of IS and HA on Ni<sup>2+</sup> transport with or without soil colloids. The experimental facility of the column experiments is illustrated in Figure 1b.



**Figure 1.** Schematic illustration of experimental setup (a) batch experiments (b) column experiments; ① experimental solutions; ② a three-way valve; ③ peristaltic pump; ④ a column containing the porous medium; ⑤ fully automatic partial collector.

## 2.6. Mathematical Models

The Langmuir model represents the monolayer adsorption that assumes the adsorbent surface is homogeneous, and there is no transfer movement between the adsorbed metal ions. The Freundlich model describes the heterogeneous adsorption behavior of the adsorbent surface. The  $\text{Ni}^{2+}$  adsorption by the soil colloids and sand was simulated by the Langmuir model Equation (1) and Freundlich model Equation (2); the related equations are shown below:

$$Q = \frac{bC_e Q_m}{1 + bC_e} \quad (1)$$

$$Q = K_f C_e^{1/n} \quad (2)$$

where  $Q$  ( $\text{mg}\cdot\text{g}^{-1}$ ) and  $C_e$  ( $\text{mg}\cdot\text{L}^{-1}$ ) are the solid-phase and solution-phase equilibrium concentrations, respectively;  $b$  is the Langmuir constant ( $\text{L}\cdot\text{mg}^{-1}$ );  $Q_m$  is the maximum adsorption capacity ( $\text{mg}\cdot\text{g}^{-1}$ );  $K_f$  ( $\text{mg}\cdot\text{kg}^{-1}\cdot\text{mg}^{-n}\cdot\text{L}^n$ ) is the Freundlich affinity coefficient, and  $n$  is the Freundlich adsorption strength parameter.

The value of  $Q$  can be calculated by the equation as follows; Equation (3):

$$Q = \frac{(C_0 - C_1) V_0}{m} \quad (3)$$

where  $C_0$  is the initial  $\text{Ni}^{2+}$  concentration ( $\text{mg}\cdot\text{L}^{-1}$ );  $C_1$  is the final concentration after the equilibrium of  $\text{Ni}^{2+}$  in the solution ( $\text{mg}\cdot\text{L}^{-1}$ );  $V_0$  is the solution volume (mL), and  $m$  is the dry weight of the soil colloids (g).

## 3. Results and Discussion

### 3.1. Characterization of Soil Samples and Soil Colloids

The basic physicochemical characteristics of soil samples and soil colloids are shown in Table 1 [33]. It is obvious that the pH of the soil colloids was lower than the soil samples, indicating that the colloid extraction process changed the pH of the soil. Moreover, the cation exchange capacity (CEC) was 34 meq/100 g for soil samples. The main mechanical composition of the soil samples was in the range of 0.02–0.002 mm since the proportion

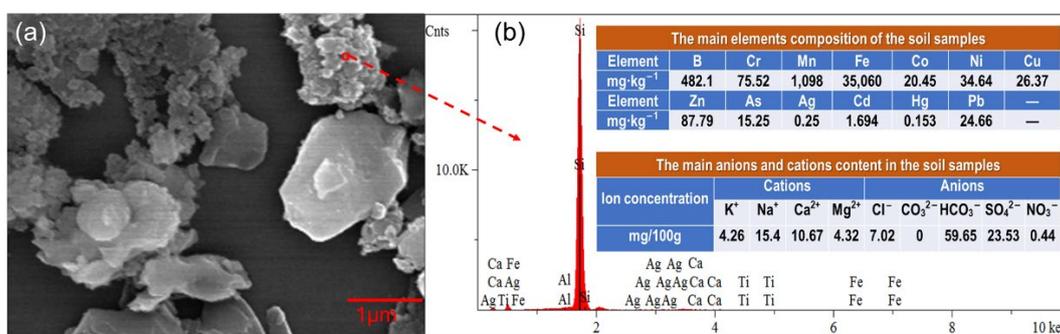
was more than 50%. There is a difference in the average particle sizes between soil colloids and soil samples, but the Zeta potential of the two samples was similar. Moreover, the mass concentration of the soil colloids was detected to be 220 mg·L<sup>-1</sup>. The total organic carbon of the soil samples was higher than that of the soil colloids, indicating that the colloid extraction process led to the loss of organic carbon, which may influence the adsorption capacity of the two kinds of materials for contaminants in groundwater.

**Table 1.** The basic physicochemical characteristics of soil samples and soil colloids.

Materials	pH	CEC <sup>a</sup>	Mechanical Composition (mm%)		Average Particle Size (nm)	Zeta Potential (mV)	Mass Concentration of Soil Colloid (g·L <sup>-1</sup> )	TOC <sup>b</sup>
Soil colloids	5.81	—	—	—	433.3	−26.23	0.22	5.72 mg/L
Soil samples	7.32	34	2–0.02	32.94	1270	−25.7	—	27.17%
			0.02–0.002	55.72				
			<0.002	11.34				

<sup>a</sup> CEC: cation exchange capacity (meq/100 g); <sup>b</sup> TOC: total organic carbon.

As shown in Figure 2, the EDX result indicates that the composition of soil colloids was complicated and mainly contained Si, Ca, Fe, Ti, Ag, etc. The shapes of the single colloidal particles are diverse in the SEM image, e.g., circular, irregular polygon, and aggregates of nanoparticles. Generally, the soil colloidal particles were considered to be mineral particles coated with organic matter. The embedded tables in Figure 2b exhibit the main element compositions and the main ion content in the soil samples. It is obvious that the contents of Fe and Mn in soil are higher than in other elements. Moreover, some toxic heavy metals (i.e., Cr, Ni, Cu, Zn, Cd, Pb) were detected in the soil, indicating that the soil was polluted by heavy metals, which cannot be ignored. It is obvious that HCO<sub>3</sub><sup>-</sup> is dominant in all the anions. The detection of Ca<sup>2+</sup> was consistent with the EDX result.



**Figure 2.** (a) SEM images of soil colloids; (b) EDX of soil colloids and the embedded tables are the main element compositions and the ion content in the soil samples.

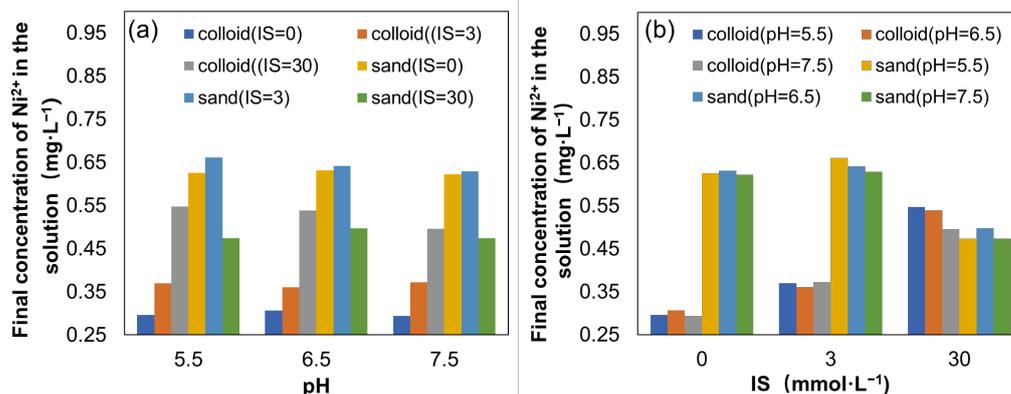
### 3.2. Ni<sup>2+</sup> Adsorption on Sand and Soil Colloids

#### 3.2.1. pH Effect

Figure 3a shows that there were no significant changes in the adsorption behaviors of Ni<sup>2+</sup> on quartz sand under different pH values (because the adsorption of Ni<sup>2+</sup> on quartz sand was weak due to the small surface area (only 10 m<sup>2</sup>·g<sup>-1</sup>) of sand). Although the high pH values of the solution may decrease the zeta potential of sand, the weak sorption capacity of sand leads to no significant effect of pH on Ni<sup>2+</sup> adsorption on a small scale.

Noticeably, the Ni<sup>2+</sup> adsorption by soil colloids had no significant changes with different pHs when the IS was 0 or 3 mmol·L<sup>-1</sup>. However, the Ni<sup>2+</sup> adsorption by soil colloids slightly increased with the increase of pH from 5.5 to 7.5 when the IS was 30 mmol·L<sup>-1</sup> since the final concentration of Ni<sup>2+</sup> in the solution slightly decreased from 0.55 to 0.50 mg·L<sup>-1</sup> with an increase of the pH from 5.5 to 7.5. Some studies reported that the increase in pH led to more negative charges on the surfaces of soil particles, indicating the high pH was

favorable for heavy metal adsorption by soil colloids in porous media [34,35]. Generally, the surfaces of soil colloids were predominantly negatively charged, implying that most  $\text{Ni}^{2+}$  adsorption occurred through electrostatic attraction. The increasing pH in the amount of  $\text{H}^+$  became low, which further reduced the  $\text{H}^+$  competitive adsorption between  $\text{H}^+$  and  $\text{Ni}^{2+}$  in the presence of soil colloids [36]. In addition, the amount of cation at the bonding sites of the soil colloids was also reduced with high pHs; therefore, the number of negative sites increased to contribute to  $\text{Ni}^{2+}$  adsorption.



**Figure 3.** Effect of pH and ion strength (IS) on the adsorption of  $\text{Ni}^{2+}$  on the soil colloids and quartz sand (a) pH effect; (b) IS effect. The initial concentration of  $\text{Ni}^{2+}$  was  $0.6628 \text{ mg}\cdot\text{L}^{-1}$ , different ISs were adjusted with  $\text{NaNO}_3$ , the concentration of soil colloids was  $220 \text{ mg}\cdot\text{L}^{-1}$ , different pHs were adjusted with  $0.1 \text{ M HNO}_3$  or  $0.1 \text{ M NaOH}$ , the equilibrium time was 24 h.

High  $\text{H}^+$  concentration can produce compression of the electric double layer and repulsive surface interaction energy, which is why the corresponding zeta potential of the soil colloids and sand decreased with the increase of pH [37]. The hydroxides of most heavy metals are insoluble; therefore, the  $\text{OH}^-$  in the solution could precipitate with heavy metal ions, which may further adsorb heavy metal ions in the precipitation process when the pH increases [36]. Moreover, the adsorption affinity of soil to heavy metal hydroxyl ions is greater than that of free ions and the proportion of hydrated ions will increase with pH increasing, indicating more heavy metals will be adsorbed by soil colloids.

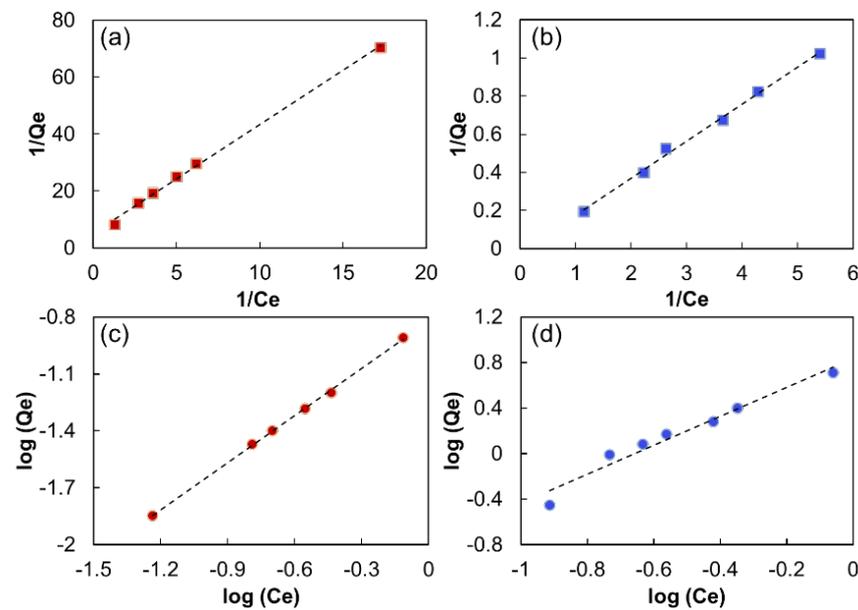
### 3.2.2. Ionic Strength Effect

In the presence of soil colloids, it was found (see Figure 3b) that the concentration of  $\text{Ni}^{2+}$  in the solution increased when the IS increased from 0 to 30 mM, indicating that  $\text{Ni}^{2+}$  adsorption by soil colloids decreased as the IS increased. Increasing IS can make the zeta potential of soil colloids more positive, which may be harmful to positively-charged  $\text{Ni}^{2+}$  adsorption by soil colloids [38,39]. There is a strong cationic bridging effect between clay colloids and metal cations, which can explain the decrease of the  $\text{Ni}^{2+}$  adsorption by the soil colloids with the increased IS [32]. The metal cations were adsorbed through an ion-exchange reaction to form outer-sphere complexes; these reactive sorption sites can be defined as variable charge sites. On the contrary, it was said that if the metal ion adsorption on the soil particles increased or had no change with the IS increasing, these reactive sorption sites can be treated as permanent charge sites, which generally have difficulty exchanging with other cations in the aqueous phase [40]. It was reported that the increase of ionic strength inhibited the transport and release of clay colloids in porous media [41,42], affecting the adsorption behavior of heavy metals in groundwater. Moreover,  $\text{Na}^+$  in the solution increased with the increased IS (which may reduce the  $\text{Ni}^{2+}$  adsorption through competitive adsorption for the reactive sites on the soil colloids). However, in the absence of soil colloids, it was found that the concentration of  $\text{Ni}^{2+}$  in the solution decreased when the IS increased from 3 to 30 mM, indicating that  $\text{Ni}^{2+}$  adsorption by sand increased as the IS increased; this may be attributed to the increasing  $\text{Na}^+$  concentration increasing the attraction between  $\text{Ni}^{2+}$  and the surface of sand.

In addition, it was obvious that the Ni<sup>2+</sup> adsorption was much larger on the surface of soil colloids than that on the surface of sand when the IS was 0 or 3 mM. However, the Ni<sup>2+</sup> adsorption was slightly larger on the surface of sand than that on the surface of soil colloids when the IS was 30 mM. These results indicate that high IS has significantly negative and positive effects on Ni<sup>2+</sup> adsorption by soil colloids and by sand, respectively.

### 3.2.3. Isothermal Adsorption of Ni<sup>2+</sup>

Both Langmuir and Freundlich models were used to fit the adsorption isotherms of Ni<sup>2+</sup> on quartz sand and soil colloids (Figure 4), and the related parameters are shown in Table 2. It was obvious that the adsorption capacity of quartz sand and soil colloids for Ni<sup>2+</sup> increased with the increase of initial concentrations of Ni<sup>2+</sup> at the range of 0–2 mg·L<sup>-1</sup>. Both Langmuir and Freundlich models fit well with the adsorption isotherms of Ni<sup>2+</sup> on quartz sand and soil colloids since the correlation coefficients (R<sup>2</sup>) were larger than 0.95. In addition, both models fit better for Ni<sup>2+</sup> adsorption on sand than that on soil colloids, which may be because the composition of soil colloids is more complex than quartz sand.



**Figure 4.** Langmuir model for Ni<sup>2+</sup> adsorption on (a) sand and (b) soil colloids; Freundlich model of Ni<sup>2+</sup> adsorption on (c) sand and (d) soil colloids.

**Table 2.** Parameters of Langmuir and Freundlich models for Ni<sup>2+</sup> adsorption.

Materials	Langmuir Equation			Freundlich Equation		
	<i>Q<sub>m</sub></i>	<i>b</i>	<i>R</i> <sup>2</sup>	<i>K<sub>f</sub></i>	<i>n</i>	<i>R</i> <sup>2</sup>
Sand	0.1973	1.3259	0.9976	0.1503	1.2077	0.9993
Soil colloid	57.1429	0.0938	0.9911	6.8391	0.7874	0.9604

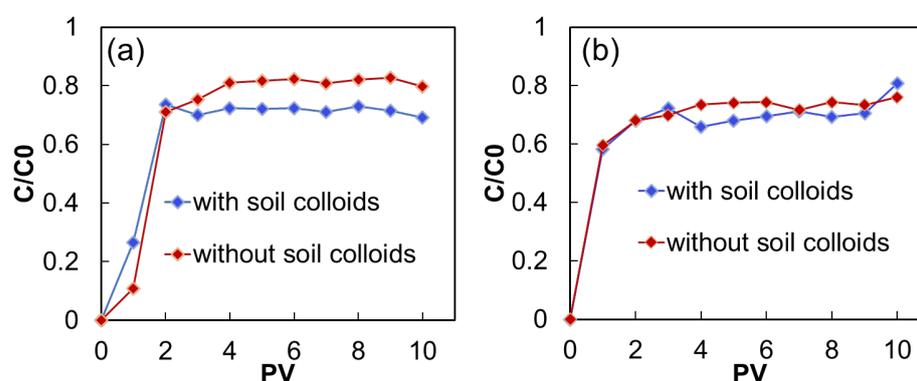
According to the parameters shown in Table 2, the *Q<sub>m</sub>* values fitted by the Langmuir model for Ni<sup>2+</sup> adsorption by soil colloids were larger than the Ni<sup>2+</sup> adsorption on the sand. This result indicated that the adsorption capacity of Ni<sup>2+</sup> on soil colloids was much stronger than that of Ni<sup>2+</sup> adsorption on the sand, which is consistent with the previous study [43,44]. Moreover, it was also reported that soil colloids had a large specific surface area and could be bound with exchangeable cations to a greater extent than sand. Thus, Ni<sup>2+</sup> could not only be adsorbed on quartz sand, it could be adsorbed much more on soil colloids. The Freundlich model assumes that the sorption of Ni<sup>2+</sup> occurs on a heterogeneous surface. The *K<sub>f</sub>* value of Ni<sup>2+</sup> adsorption by soil colloids is approximately 45 times higher than that on the sand. It may be because soil colloids have greater specific surface areas

and CEC than sand, resulting in a better adsorption capacity for  $\text{Ni}^{2+}$ . As a result, it can be speculated that heavy metal ions could be adsorbed on the colloids or fixed on the solid particles in the soil environment to reduce heavy metal contamination in groundwater.

### 3.3. $\text{Ni}^{2+}$ Transport in the Saturated Porous Media

#### 3.3.1. Effect of Soil Colloids

The column breakthrough curves (BTCs), i.e., the normalized  $\text{Ni}^{2+}$  concentrations in the column effluent ( $C/C_0$ ) plotted as a function of PV, are presented in Figure 5. The concentration of  $\text{Ni}^{2+}$  increased quickly at the initial phase of transport and reached the maximum value at about 2 PV, which was then maintained at a steady concentration. The normalized  $\text{Ni}^{2+}$  concentrations are less than 1, indicating that  $\text{Ni}^{2+}$  was retained in the sand column by adsorption on the surface of the sand or adsorption on the soil colloids being caught in the sand column together during transport.



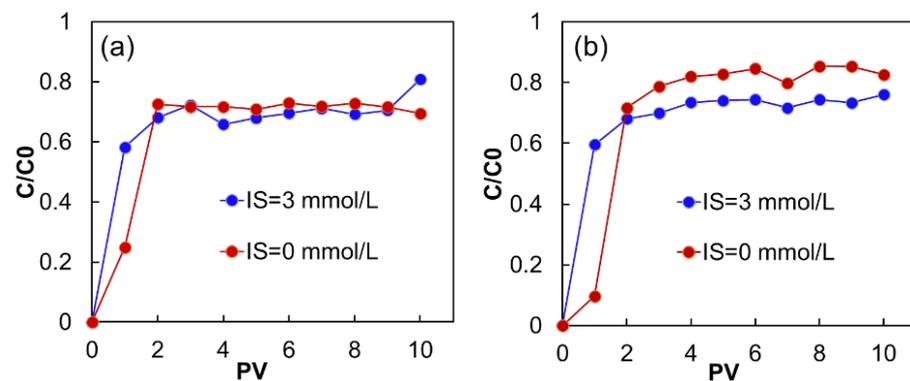
**Figure 5.** The effect of soil colloids on  $\text{Ni}^{2+}$  transport in the sand column. (a)  $\text{IS} = 0$ ; (b)  $\text{IS} = 3 \text{ mmol}\cdot\text{L}^{-1}$ . The initial concentration of  $\text{Ni}^{2+}$  was  $0.6628 \text{ mg}\cdot\text{L}^{-1}$ , the different ISs were adjusted with  $\text{NaNO}_3$ , the concentration of soil colloids was  $220 \text{ mg}\cdot\text{L}^{-1}$ .

Compared to the breakthrough curve of the  $\text{Ni}^{2+}$  transport without soil colloids, the retention of  $\text{Ni}^{2+}$  in the sand column increased in the presence of soil colloids. Moreover, the migration rate of  $\text{Ni}^{2+}$  with soil colloids in the initial phase was slightly faster than that of  $\text{Ni}^{2+}$  transport without soil colloids; the IS was  $0 \text{ mmol}\cdot\text{L}^{-1}$  (Figure 5a). This phenomenon can be explained by the following mechanisms [13]: The motion rates of large molecules may be greater than the average velocity of the average groundwater flow line in fine granular soil or aquifers, caused by the volume exclusion effect. When the particle sizes of molecules or ions are too large to pass through smaller pores, they are limited to a larger velocity than the average velocity of the groundwater flow line. The size of the colloid is larger than that of the soluble  $\text{Ni}^{2+}$  and the colloid-associated  $\text{Ni}^{2+}$  may be trapped in the sand column due to the blocking effect in the late transport [45], causing the transport efficiency of  $\text{Ni}^{2+}$  to decrease.

Moreover,  $\text{Ni}^{2+}$  could act as a bridge to reduce the repulsive forces between the quartz sand and soil colloids and, therefore, have an inhibiting effect on  $\text{Ni}^{2+}$  as well as soil colloid transport in the sand column [46,47]. It can be seen from Figure 5 that, despite the presence of soil colloids resulting in a faster penetration rate of  $\text{Ni}^{2+}$  at the initial phase of transportation, the final transport efficiency of  $\text{Ni}^{2+}$  was suppressed. It can be speculated that a part of  $\text{Ni}^{2+}$  was retained in the sand column due to the direct adsorption by quartz sand, and the other part of  $\text{Ni}^{2+}$  was retained in the sand column just because the colloid-associated  $\text{Ni}^{2+}$  was captured by the sand column. The effect of colloid on the transport of pollutants in porous media is two-sided [48]. On the one hand, colloids can move faster than that of solute in porous media due to size exclusion, and promote the transport of some contaminants as a carrier; on the other hand, colloid-associated contaminants could be “immobilization” in the porous media if the porosity is small or the affinity between porous media and the colloids is strong.

### 3.3.2. Effect of Ion Strength

The effect of IS on  $\text{Ni}^{2+}$  transport in the sand column is shown in Figure 6. In the absence of soil colloids (Figure 6b), as compared to the breakthrough curve of the  $\text{Ni}^{2+}$  transport at the IS of 0 mM, the retention of  $\text{Ni}^{2+}$  in the sand column increased at the IS of 3 mM. Moreover, the migration rate of  $\text{Ni}^{2+}$  at the IS of 3 mM in the initial phase was faster than that of  $\text{Ni}^{2+}$  at the IS of 0 mM. However, in the presence of soil colloids (Figure 6a), although the migration rate of  $\text{Ni}^{2+}$  at the IS of 3 mM in the initial phase was also faster than that of  $\text{Ni}^{2+}$  at the IS of 0 mM, there was a small variation in the overall transport efficiency of  $\text{Ni}^{2+}$  in the sand column at IS of 0 mM (71.30%) and 3 mM (72.92%), which is shown in Table 3.



**Figure 6.** The effect of ion strength on  $\text{Ni}^{2+}$  transport in the sand column. (a) In the presence of soil colloids; (b) in the absence of soil colloids. The initial concentration of  $\text{Ni}^{2+}$  was  $0.6628 \text{ mg}\cdot\text{L}^{-1}$ , different ISs were adjusted with  $\text{NaNO}_3$ , the concentration of soil colloids was  $220 \text{ mg}\cdot\text{L}^{-1}$ .

**Table 3.** Results of the  $\text{Ni}^{2+}$  transport in the sand column with different conditions.

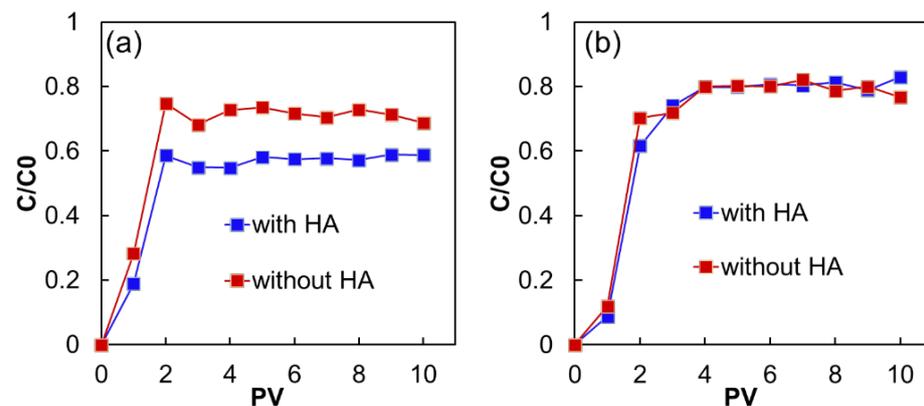
Column Experiment	Colloids	IS ( $\text{mmol}\cdot\text{L}^{-1}$ )	HA ( $\text{mg}\cdot\text{L}^{-1}$ )	Concentration of $\text{Ni}^{2+}$ Injection ( $\text{mg}\cdot\text{L}^{-1}$ )	Average Concentration of $\text{Ni}^{2+}$ at Plateau ( $\text{mg}\cdot\text{L}^{-1}$ )	Penetration Rate of $\text{Ni}^{2+}$ (%)
1	×	0	0	0.6628	0.54	81.39
2	×	3	0	0.6628	0.49	73.96
3	✓	0	0	0.6628	0.47	71.30
4	✓	3	0	0.6628	0.48	72.92
5	×	0	20	0.6628	0.54	80.88
6	✓	0	20	0.6628	0.38	58.01

It is obvious that the transport of  $\text{Ni}^{2+}$  at the IS of 3 mM in the initial phase was faster than the IS of 0 mM, whether the soil colloids existed or not. The possible reason is that the increasing  $\text{Na}^+$  presented competitive adsorption with the targeted  $\text{Ni}^{2+}$  for the active site on the surface of the quartz sand at the initial phase when the  $\text{Ni}^{2+}$  transported in the sand column. In the case of the presence of soil colloids (Figure 6a), the final transport efficiency of  $\text{Ni}^{2+}$  in the effluent slightly increased from 71.3% to 72.92% with the increase of ionic strength from 0 to  $3 \text{ mmol}\cdot\text{L}^{-1}$  (Table 3), indicating that less colloid-associated  $\text{Ni}^{2+}$  may accumulate in the sand column at higher IS conditions. It is reasonable to conclude that the ionic strength will affect the thickness of the double layer of the colloid surface [45,49,50]. Compared with monovalent cations, divalent cations in solutions were more favorable for the colloid deposition by increasing electrostatic attraction between the colloids and sand surfaces, causing the cation bridge [46,47,51]. Thus, the transport of reduced  $\text{Ni}^{2+}$  may be because it involved the interaction between soil colloids and sand.

### 3.3.3. Effect of Humic Acid

It was found that complexing with dissolved organic matter (DOM) has more significant effects on Cu and Pb than Cd, Zn, and Ni [52]. Figure 7 shows that there is little

difference in  $\text{Ni}^{2+}$  transport with or without HA in the absence of soil colloids (Figure 7b). In the presence of soil colloids (Figure 7a), although there is no significant difference in the migration rate of  $\text{Ni}^{2+}$  with or without HA at the initial phase, the final transport efficiency of  $\text{Ni}^{2+}$  without HA in the sand column was 71.30%, which is greater than the 58.01% of  $\text{Ni}^{2+}$  with HA (Table 3). This result is probably due to the co-effect of HA and soil colloids in the porous media [53]. HA can enhance the desorption of  $\text{Ni}^{2+}$  in the sand column in the presence of soil colloids. In fact, the decrease of metal ions in the solution is due to the adsorption of free metal ions by colloids, the chelation of metals with colloid-associated HA, and the chelation of metals with free HA [53]. The formation of insoluble metal complexes promotes the adsorption of more heavy metal ions. It was reported in the previous study that HA is easy to dissociate and it complexes with heavy metals, which has a certain binding ability with colloid [54]. In addition, HA can be adsorbed on the surface of colloids, forming stronger ion-exchange centers for metals. Thus, insoluble complexes are formed between heavy metal ions, HA, and colloids to further generate larger particles, resulting in the deposition of heavy metal ions in porous media.



**Figure 7.** The effect of HA on  $\text{Ni}^{2+}$  transport in the sand column. (a) In the presence of soil colloids; (b) in the absence of soil colloids. The initial concentration of  $\text{Ni}^{2+}$  was  $0.6628 \text{ mg}\cdot\text{L}^{-1}$ , the concentrations of soil colloids and HA were  $220$  and  $20 \text{ mg}\cdot\text{L}^{-1}$ , respectively;  $\text{IS} = 0 \text{ mmol}\cdot\text{L}^{-1}$ .

In the presence of soil colloids, HA plays an important role in the fate and transport of heavy metals in a subsurface environment. It was reported that organic matter usually affects the chemical properties of the colloidal surface, and even changes the surface characteristics of porous media [55,56]. Similarly, HA can increase the repulsive force between illite colloids and solid media and, thus, promote the transport of illite colloids [57]. However, in this study, HA inhibited the overall transport efficiency of  $\text{Ni}^{2+}$  with soil colloids, which may be related to the properties of soil colloids and the complex interaction between heavy metals, colloids, and sand, as discussed above.

#### 4. Conclusions

The effects of soil colloids on the adsorption and transport of  $\text{Ni}^{2+}$  in saturated porous media were explored in this study. The main conclusions are as follows:

- (1) Soil colloids have greater potential for  $\text{Ni}^{2+}$  adsorption than quartz sand, suggesting the important role of soil colloids in the subsurface environment. From this, we infer that most contaminants, such as heavy metals, could be immobilized by colloids in soil instead of transported from surface soil to groundwater.
- (2) Relatively higher pHs and smaller ISs were favorable for  $\text{Ni}^{2+}$  adsorption by soil colloids, indicating the hydrochemical conditions of groundwater greatly affected the fate of heavy metals in the subsurface environment. Human activities, such as artificial pumping, water injection experiment, or rapid infiltration of rainfall, may lead to the release of colloids and change the environmental conditions, which

should be considered to protect the groundwater safety and to take steps, carrying out contaminant remediation strategies.

- (3) A higher IS could slightly improve the initial transport rate of  $\text{Ni}^{2+}$ , but could not improve the final transport efficiency of  $\text{Ni}^{2+}$  in the absence (or presence) of soil colloids. HA has a negative effect on  $\text{Ni}^{2+}$  transport in the presence of soil colloids, while there is no obvious difference when  $\text{Ni}^{2+}$  transports with and without HA in the absence of soil colloids. This result indicates that HA is negligible when heavy metals transport without soil colloids.
- (4) All final transport efficiencies of  $\text{Ni}^{2+}$  were less than 100% when  $\text{Ni}^{2+}$  was transported in the sand column, which means that  $\text{Ni}^{2+}$  was retained in the sand column more or less. This result reveals that the soil or aquifer could act as a filter to remove heavy metals in the subsurface environment.

Therefore, soil colloids are important compositions in the subsurface environment, which affect the adsorption, transport, and fate of many contaminants. A future investigation should focus on the interaction mechanisms of different kinds of contaminants with natural colloids as well as solid media. At the same time, factors, such as colloids, types, hydrogeochemical conditions, and organic matter, should be considered when natural colloids are applied to study the heavy metal contamination of groundwater.

**Author Contributions:** Conceptualization, Z.W. and Y.W. (Yuanyuan Wang); methodology, Y.Z. and Y.W. (Yuanyuan Wang); validation, Z.S. and Y.W. (Yuanzhao Wu); formal analysis, W.M. and Y.H.; investigation, Z.W.; data curation, W.Z.; writing—original draft preparation, Z.W.; writing for review and editing, Y.Z. and Y.Y. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the Science and Technology Planning Project of Qinghai Province (grant no. 2019-ZJ-7063); Open-end Fund of Fujian Provincial Key Laboratory of Ecological-toxicological Effects & Control for Emerging Contaminants (PY19004).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Li, N.; Li, H.; Su, G.; Chen, J. Heavy metal distribution profiles in soil and groundwater near pig farms in China. *Chemosphere* **2022**, *294*, 133721. [[CrossRef](#)] [[PubMed](#)]
2. Jabbo, N.J.; Isa, N.M.; Aris, A.Z.; Ramli, M.F.; Abubakar, M.B. Geochemometric approach to groundwater quality and health risk assessment of heavy metals of Yankari Game Reserve and its environs, Northeast Nigeria. *J. Clean. Prod.* **2022**, *330*, 129916. [[CrossRef](#)]
3. Tan, M.; Liu, L.; Zhang, M.; Liu, Y.; Li, C. Effects of solution chemistry and humic acid on the transport of polystyrene microplastics in manganese oxides coated sand. *J. Hazard. Mater.* **2021**, *413*, 125410. [[CrossRef](#)] [[PubMed](#)]
4. Esfahani, A.R.; Batelaan, O.; Hutson, J.L.; Fallowfield, H.J. Effect of bacteria and virus on transport and retention of graphene oxide nanoparticles in natural limestone sediments. *Chemosphere* **2020**, *248*, 125929. [[CrossRef](#)]
5. Zhao, W.; Zhao, P.; Tian, Y.; Shen, C.; Li, Z.; Peng, P.; Jin, C. Investigation for Synergies of Ionic Strength and Flow Velocity on Colloidal-Sized Microplastic Transport and Deposition in Porous Media Using the Colloidal–AFM Probe. *Langmuir* **2020**, *36*, 6292–6303. [[CrossRef](#)]
6. Degueldre, C.; Triay, I.; Kim, J.-I.; Vilks, P.; Laaksoharju, M.; Miekeley, N. Groundwater colloid properties: A global approach. *Appl. Geochem.* **2000**, *15*, 1043–1051. [[CrossRef](#)]
7. Yang, X.; Zhang, Y.; Chen, F.; Yang, Y. Interplay of natural organic matter with flow rate and particle size on colloid transport: Experimentation, visualization, and modeling. *Environ. Sci. Technol.* **2015**, *49*, 13385–13393. [[CrossRef](#)]
8. Moradi, R.; Rokni, F.F. Synthesis, characterization and performance of nio/cnt nanocomposite for arsenic removal from aqueous media. *Curr. Nanosci.* **2017**, *13*, 579–585. [[CrossRef](#)]
9. Rao, G.P.; Lu, C.; Su, F. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. *Sep. Purif. Technol.* **2007**, *58*, 224–231. [[CrossRef](#)]

10. Hammes, J.; Gallego-Urrea, J.A.; Hassellöv, M. Geographically distributed classification of surface water chemical parameters influencing fate and behavior of nanoparticles and colloid facilitated contaminant transport. *Water Res.* **2013**, *47*, 5350–5361. [[CrossRef](#)]
11. Lu, X.; Lu, T.; Zhang, H.; Shang, Z.; Chen, J.; Wang, Y.; Li, D.; Zhou, Y.; Qi, Z. Effects of solution chemistry on the attachment of graphene oxide onto clay minerals. *Environ. Sci. Process. Impacts* **2019**, *21*, 506–513. [[CrossRef](#)]
12. Zhang, H.; Lu, T.; Zhang, R.; Wang, M.; Krishnan, S.; Liu, S.; Zhou, Y.; Li, D.; Qi, Z. Effects of clay colloids on ciprofloxacin transport in saturated quartz sand porous media under different solution chemistry conditions. *Ecotoxicol. Environ. Saf.* **2020**, *199*, 110754. [[CrossRef](#)]
13. Ryan, N.J.; Elimelech, M. Colloid mobilization and transport in groundwater. *Colloids Surf. Physicochem. Eng. Asp.* **1996**, *107*, 1–56. [[CrossRef](#)]
14. De Jonge, W.L.; Kjærgaard, C.; Moldrup, P. Colloids and colloid-facilitated transport of contaminants in soils: An introduction. *Vadose Zone J.* **2004**, *3*, 321–325. [[CrossRef](#)]
15. Sen, K.T.; Khilar, K.C. Review on subsurface colloids and colloid-associated contaminant transport in saturated porous media. *Adv. Colloid Interface Sci.* **2006**, *119*, 71–96.
16. Shen, C.; Jin, Y.; Zhuang, J.; Li, T.; Xing, B. Role and importance of surface heterogeneities in transport of particles in saturated porous media. *Crit. Rev. Environ. Sci. Technol.* **2020**, *50*, 244–329. [[CrossRef](#)]
17. Abollino, O.; Aceto, M.; Malandrino, M.; Sarzanini, C.; Mentasti, E. Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances. *Water Res.* **2003**, *37*, 1619–1627. [[CrossRef](#)]
18. Liu, T.; Yang, Y.; Wang, Z.-L.; Sun, Y. Remediation of arsenic (III) from aqueous solutions using improved nanoscale zero-valent iron on pumice. *Chem. Eng. J.* **2016**, *288*, 739–744. [[CrossRef](#)]
19. Grolimund, D.; Borkovec, M.; Barmettler, K.; Sticher, H. Colloid-facilitated transport of strongly sorbing contaminants in natural porous media: A laboratory column study. *Environ. Sci. Technol.* **1996**, *30*, 3118–3123. [[CrossRef](#)]
20. He, J.; Wang, D.; Fan, T.; Zhou, D. Cotransport of Cu with Graphene Oxide in Saturated Porous Media with Varying Degrees of Geochemical Heterogeneity. *Water* **2020**, *12*, 444. [[CrossRef](#)]
21. Hou, W.; Lei, Z.; Hu, E.; Wang, H.; Wang, Q.; Zhang, R.; Li, H. Cotransport of uranyl carbonate loaded on amorphous colloidal silica and strip-shaped humic acid in saturated porous media: Behavior and mechanism. *Environ. Pollut.* **2021**, *285*, 117230. [[CrossRef](#)] [[PubMed](#)]
22. Zhao, P.; Cui, L.; Zhao, W.; Tian, Y.; Li, M.; Wang, Y.; Chen, Z. Cotransport and deposition of colloidal polystyrene microplastic particles and tetracycline in porous media: The impact of ionic strength and cationic types. *Sci. Total Environ.* **2021**, *753*, 142064. [[CrossRef](#)] [[PubMed](#)]
23. Corapcioglu, Y.M.; Choi, H. Modeling colloid transport in unsaturated porous media and validation with laboratory column data. *Water Resour. Res.* **1996**, *32*, 3437–3449. [[CrossRef](#)]
24. Saito, T.; Suzuki, Y.; Mizuno, T. Size and elemental analyses of nano colloids in deep granitic groundwater: Implications for transport of trace elements. *Colloids Surf. Physicochem. Eng. Aspects* **2013**, *435*, 48–55. [[CrossRef](#)]
25. Fang, J.; Shan, X.-Q.; Wen, B.; Lin, J.-M.; Owens, G.; Zhou, S.-R. Transport of copper as affected by titania nanoparticles in soil columns. *Environ. Pollut.* **2011**, *159*, 1248–1256. [[CrossRef](#)]
26. Baumann, T.; Fruhstorfer, P.; Klein, T.; Niessner, R. Colloid and heavy metal transport at landfill sites in direct contact with groundwater. *Water Res.* **2006**, *40*, 2776–2786. [[CrossRef](#)]
27. Kjeller, C.; Postma, D.; Larsen, F. Groundwater acidification and the mobilization of trace metals in a sandy aquifer. *Environ. Sci. Technol.* **2004**, *38*, 2829–2835. [[CrossRef](#)]
28. Won, J.; Wirth, X.; Burns, S.E. An experimental study of cotransport of heavy metals with kaolinite colloids. *J. Hazard. Mater.* **2019**, *373*, 476–482. [[CrossRef](#)]
29. Tan, B.; Liu, C.; Tan, X.; You, X.; Dai, C.; Liu, S.; Li, J.; Li, N. Heavy metal transport driven by seawater-freshwater interface dynamics: The role of colloid mobilization and aquifer pore structure change. *Water Res.* **2022**, *217*, 118370. [[CrossRef](#)]
30. Shi, Y.; Zhou, W.; Wang, J.; Xian, D.; Tan, Z.; Du, L.; Li, X.; Pan, D.; Chen, Z.; Wu, W. Effect of pH on the formation of U (VI) colloidal particles in a natural groundwater. *J. Radioanal. Nucl. Chem.* **2021**, *328*, 785–794. [[CrossRef](#)]
31. Syngouna, I.V.; Chrysikopoulos, C.V. Experimental investigation of virus and clay particles cotransport in partially saturated columns packed with glass beads. *J. Colloid Interface Sci.* **2015**, *440*, 140–150. [[CrossRef](#)]
32. Shi, K.; Wang, X.; Chu, X.; Li, T.; Yin, Y.; Shen, C. Impact of heavy metal cations on deposition and release of clay colloids in saturated porous media. *Vadose Zone J.* **2022**, e20179. [[CrossRef](#)]
33. Yang, Y.; Yidan, Z.; Wenqing, Z.; Yuhui, W.; Dazhi, Z. Co-migration of nickel and natural colloids in groundwater system. *J. Jilin Univ. Earth Sci. Ed.* **2020**, *50*, 226–233.
34. Guo, H.; Wen, D.; Liu, Z.; Jia, Y.; Guo, Q. A review of high arsenic groundwater in Mainland and Taiwan, China: Distribution, characteristics and geochemical processes. *Appl. Geochem.* **2014**, *41*, 196–217. [[CrossRef](#)]
35. Chotpanarat, S.; Kiatvarangkul, N. Facilitated transport of cadmium with montmorillonite KSF colloids under different pH conditions in water-saturated sand columns: Experiment and transport modeling. *Water Res.* **2018**, *146*, 216–231. [[CrossRef](#)]
36. McBride, M.B. Cadmium uptake by crops estimated from soil total Cd and pH. *Soil Sci.* **2002**, *167*, 62–67. [[CrossRef](#)]
37. Nelson, S.; Yonge, D.; Barber, M. Effects of road salts on heavy metal mobility in two eastern Washington soils. *J. Environ. Eng.* **2009**, *135*, 505–510. [[CrossRef](#)]

38. Roy, B.S.; Dzombak, D.A. Chemical factors influencing colloid-facilitated transport of contaminants in porous media. *Environ. Sci. Technol.* **1997**, *31*, 656–664. [[CrossRef](#)]
39. Luo, X.; Yu, L.; Wang, C.; Yin, X.; Mosa, A.; Lv, J.; Sun, H. Sorption of vanadium (V) onto natural soil colloids under various solution pH and ionic strength conditions. *Chemosphere* **2017**, *169*, 609–617. [[CrossRef](#)]
40. McBride, M.B. A critique of diffuse double layer models applied to colloid and surface chemistry. *Clays Clay Miner.* **1997**, *45*, 598–608. [[CrossRef](#)]
41. Garcia-Garcia, S.; Wold, S.; Jonsson, M. Effects of temperature on the stability of colloidal montmorillonite particles at different pH and ionic strength. *Appl. Clay Sci.* **2009**, *43*, 21–26. [[CrossRef](#)]
42. Compère, F.; Porel, G.; Delay, F. Transport and retention of clay particles in saturated porous media. Influence of ionic strength and pore velocity. *J. Contam. Hydrol.* **2001**, *49*, 1–21. [[CrossRef](#)]
43. Bhattacharyya, G.K.; Gupta, S.S. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. *Adv. Colloid Interface Sci.* **2008**, *140*, 114–131. [[CrossRef](#)] [[PubMed](#)]
44. Montalvo, D.; Vanderschueren, R.; Fritzsche, A.; Meckenstock, R.U.; Smolders, E. Efficient removal of arsenate from oxic contaminated water by colloidal humic acid-coated goethite: Batch and column experiments. *J. Clean. Prod.* **2018**, *189*, 510–518. [[CrossRef](#)]
45. Bradford, A.S.; Torkzaban, S.; Walker, S.L. Coupling of physical and chemical mechanisms of colloid straining in saturated porous media. *Water Res.* **2007**, *41*, 3012–3024. [[CrossRef](#)]
46. Peng, S.; Wu, D.; Ge, Z.; Tong, M.; Kim, H. Influence of graphene oxide on the transport and deposition behaviors of colloids in saturated porous media. *Environ. Pollut.* **2017**, *225*, 141–149. [[CrossRef](#)]
47. Zhou, D.; Jiang, X.; Lu, Y.; Fan, W.; Huo, M.; Crittenden, J. Cotransport of graphene oxide and Cu (II) through saturated porous media. *Sci. Total Environ.* **2016**, *550*, 717–726. [[CrossRef](#)]
48. Baumann, T.; Müller, S.; Niessner, R. Migration of dissolved heavy metal compounds and PCP in the presence of colloids through a heterogeneous calcareous gravel and a homogeneous quartz sand—pilot scale experiments. *Water Res.* **2002**, *36*, 1213–1223. [[CrossRef](#)]
49. Espinasse, B.; Hotze, E.M.; Wiesner, M.R. Transport and retention of colloidal aggregates of C60 in porous media: Effects of organic macromolecules, ionic composition, and preparation method. *Environ. Sci. Technol.* **2007**, *41*, 7396–7402. [[CrossRef](#)]
50. Saleh, N.; Kim, H.-J.; Phenrat, T.; Matyjaszewski, K.; Tilton, R.D.; Lowry, G.V. Ionic strength and composition affect the mobility of surface-modified FeO nanoparticles in water-saturated sand columns. *Environ. Sci. Technol.* **2008**, *42*, 3349–3355. [[CrossRef](#)]
51. Zhang, M.; Bradford, S.A.; Šimůnek, J.; Vereecken, H.; Klumpp, E. Roles of cation valence and exchange on the retention and colloid-facilitated transport of functionalized multi-walled carbon nanotubes in a natural soil. *Water Res.* **2017**, *109*, 358–366. [[CrossRef](#)]
52. Weng, L.; Temminghoff, E.J.; Loftis, S.; Tipping, E.; van Riemsdijk, W.H. Complexation with dissolved organic matter and solubility control of heavy metals in a sandy soil. *Environ. Sci. Technol.* **2002**, *36*, 4804–4810. [[CrossRef](#)]
53. Chen, H.; Koopal, L.K.; Xiong, J.; Avena, M.; Tan, W. Mechanisms of soil humic acid adsorption onto montmorillonite and kaolinite. *J. Colloid Interface Sci.* **2017**, *504*, 457–467. [[CrossRef](#)]
54. Ma, J.; Guo, H.; Lei, M.; Li, Y.; Weng, L.; Chen, Y.; Ma, Y.; Deng, Y.; Feng, X.; Xiu, W. Enhanced transport of ferrihydrite colloid by chain-shaped humic acid colloid in saturated porous media. *Sci. Total Environ.* **2018**, *621*, 1581–1590. [[CrossRef](#)]
55. Wang, T.; Yen, Y.-J.; Hsieh, Y.-K.; Wang, J. Size effect of calcium-humic acid non-rigid complexes on the fouling behaviors in nanofiltration: An LA-ICP-MS study. *Colloids Surf. Physicochem. Eng. Aspects.* **2017**, *513*, 335–347. [[CrossRef](#)]
56. Aiken, R.G.; Hsu-Kim, H.; Ryan, J.N. Influence of Dissolved Organic Matter on the Environmental Fate of Metals, Nanoparticles, and Colloids. *Environ. Sci. Technol.* **2011**, *8*, 3196–3201. [[CrossRef](#)]
57. Wang, Q.; Cheng, T.; Wu, Y. Influence of mineral colloids and humic substances on uranium (VI) transport in water-saturated geologic porous media. *J. Contam. Hydrol.* **2014**, *170*, 76–85. [[CrossRef](#)]