Influence of aquifer heterogeneity on Cr(VI) diffusion and removal from groundwater

Weidong Zhao¹ · Xinxiang Huang¹ · Jianshi Gong² · Lei Ma¹ · Jiazhong Qian¹

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Abstract
Previous studies have indicated aquifer heterogeneity has an important influence on the removal of Cr(VI) in groundwater, but little attention is paid to the effects of aquifer heterogeneity during the process especially under conditions like actual groundwater temperature and hydraulic gradient in the field. Thus, in this study, in situ remediation of Cr(VI)-contaminated shallow groundwater in a sandbox was conducted, and the influences of the heterogeneous aquifer composed of coarse, medium, and fine sand on Cr(VI) diffusion and removal before and after emulsified vegetable oil (EVO) injection were investigated, under the conditions of 19±0.5 °C and hydraulic gradient 3‰. The results show that Cr(VI) diffused consistently with groundwater from top left to bottom right; Cr(VI) spread faster in the horizontal direction than in vertical direction, and the horizontal diffusion of Cr(VI) in coarse, medium, and fine sand was 0.054 m/day, 0.036 m/day, and 0.018 m/day, respectively; a high performance of EVO toward Cr(VI) removal by over 95% was mainly because different concentrations of microorganisms migrated among heterogeneous aquifers vertically and horizontally; compared with coarse and medium sand, fine sand, with a better adsorption capacity and a lower permeability, retained relatively more microorganisms, providing favorable conditions during the remediation; a stable and unified effective removal zone, similar to the shape of (approximately 1357.87 cm²), was ultimately formed downstream of the injection well.

Keywords Groundwater · Heterogeneity · Emulsified vegetable oil · Cr(VI) removal · Permeable reactive barrier · Biodegradation

Introduction
Groundwater contamination with chromium may occur due to leakage from chromite mines, inappropriate disposal of mining tools and supplies, industrial wastewater of steel production, wood and paper processing, and leather tanning (Liang et al. 2021; Prasad et al. 2021; Ukhurebor et al. 2021), especially, in the shallow groundwater. The oxidation states of chromium vary ranging from −2 to +6 and the most stably and commonly occurs in trivalent/Cr(III) and hexavalent/Cr(VI) states, both of which have different physicochemical and biochemical properties (Dhal et al. 2013). But Cr(VI) is a more stable and predominant state in the natural environment (Elzinga and Cirmo 2010). Further, Cr(VI) can be transformed into Cr(III) under acidic conditions, and this reduction process is benefited in acidic soils with a high proportion of organic matter (Sinha et al. 2018). Cr(III) is an essential trace element for human health, and it helps to transport glucose, while Cr(VI) is harmful to microorganisms, plants, animals, and humans as it exerts carcinogenic, mutagenic, and teratogenic effects and causes tissue damage (Coetzee et al. 2018; Mitra et al. 2017).

Cr(VI) is more water-soluble and thus more mobile in aquifers than Cr(III) (Coyte et al. 2020). Cr(VI) retention in groundwater is mostly controlled by adsorption and desorption processes (Bradly 2004; Cao et al. 2021; Chen et al. 2019). The Suzhou coal mine area (Huaibei coal mine area, northern Anhui Province, China) has substantially subsided and thus shallow aquifers have formed relatively uniform drop funnels due to long-term and large-scale coal mining. Shallow groundwater in the Huaibei coal mine area has been contaminated by conventional components like ammonia nitrogen
and heavy metals like Cr(VI) (Peng and Sun 2014). The concentration of Cr(VI) in the Baiyangdian Basin has reached 86 μg/L in the groundwater (Guo et al. 2020). WHO set the provisional guideline value for Cr total in drinking water at 0.05 mg/L (WHO 2020). Therefore, it is necessary to develop methods for the long-term remediation of Cr(VI) contaminated groundwater.

Most of the conventional, physico-chemical remediation methods include chemical precipitation (Stylianou et al. 2018), electrochemistry (Breslin et al. 2018; Onyancha et al. 2021), ion exchange (Shao et al. 2019), reverse osmosis (Mnif et al. 2017), and adsorption (Yang et al. 2021), which either are expensive or generate toxic sludges, and thus lead to an increase in secondary contamination (Long et al. 2018). These remediation methods also destroy the biological community and put great pressure on the ecosystem (Ukhurebor et al. 2021). In the interest of great accessibility, low cost, and sustainability, an in situ reactive zone (IRZ) is widely applied in groundwater remediation (Liu et al. 2021; Liu et al. 2015). An IRZ is created by injecting chemical or microbial reagents into contaminated groundwater environment through an injection well and thus contaminants can be intercepted and permanently fixed or degraded to harmless products. The common in situ remediation technologies for heavy metals and organic compounds in the field include permeable reactive barrier (PRB) remediation and in situ well treatment.

PRBs have become an innovative and effective technology for continuous in situ remediation of Cr(VI)-contaminated shallow groundwater in the field due to its efficiency, low cost, and convenient construction (Wang et al. 2021). The concept of the technology involves the emplacement of permeable barriers containing reactive materials (added or replaced in time if needed) across the flow path of the contaminated groundwater to intercept and treat the contaminants as the plume flows through it under the influence of the natural hydraulic gradient (Obiri-Nyarko et al. 2014). With the polluted groundwater flowing through the reactive media and microbial reaction zones comprehensively formed inside and around the barriers, the concentration of contaminants can be reduced through mechanisms such as adsorption, precipitation, oxidation-reduction, and biodegradation (Xia et al. 2021). The key part of PRB is the reactive media filled and the reaction zone formed. The most applied reactive media are zero-valent iron (Qiu et al. 2020), nanoscale zero-valent iron (Eljamal et al. 2020; Maamoun et al. 2018), activated carbons (Su et al. 2019), zeolites (Buenano et al. 2017), bentonite (Wang et al. 2020), and emulsified vegetable oil (EVO) (Harkness and Fisher 2013), etc. Batch and column experiments employed in PRB technology for Cr(VI) removal from groundwater have confirmed that 1g/L dosage of the synthesized nFeO/Cu could remove around 85% of 20 mg/L initial Cr(VI) concentration over 3-h reaction time (Maamoun et al. 2021).

EVO, a slowly soluble emulsion of vegetable oil and surfactants, can long-term provide electron donor sources to enhance the biological reductive and stimulate indigenous microbial communities effectively without needing to inject an inoculant or environmentally harmful chemical constituents (Brodie et al. 2011; Chi et al. 2018; Dong et al. 2018). Numerous laboratory column, sandbox, and field studies have proved EVO is cost-effective, effective, and durable in the treatment of various contaminants, such as chlorinated solvents (Dong et al. 2019), nitrate (Ding et al. 2021), and heavy metals (Wen et al. 2017), and EVO can be transported considerable distances through fine silty or clayey sand and fractured rock (Borden 2007; Linjie et al. 2021; Tang et al. 2013; Watson et al. 2013). A reasonably uniform distribution of emulsified oil can be found in the top, middle, and bottom layers of sandy sediments under homogeneous and heterogeneous conditions (Jung et al. 2006). EVO-added columns (EVO, EVO + acetate, EVO + Mg(OH)2) retained and removed Cr(VI) contamination in simulated groundwater for 177, 191, and more than 240 days, respectively (Wen et al. 2017).

Compost technology can be used for bioremediation of soil contaminated with organic pollutants and heavy metals through the active microorganisms present in the matrix of contaminants (Chen et al. 2015; Taiwo et al. 2016). Compost provides nutrients to indigenous microorganisms. Cr(VI) could be adsorbed by the positive charge on the compost biomass surface and partly reduced to Cr(III) by biomass groups such as hydroxyl, carboxyl, and amino groups (Chen et al. 2017; Zhou et al. 2016).

Reactive solutes flow, transport, and transform in natural subsurface that is ubiquitously heterogeneous (Wang et al. 2018). Heterogeneous aquifers could lead to fluid bypassing, meaning that preferential flow channels in the high-permeability zones often make the low permeability zones bypassed during remedial amendment injection (Bekele et al. 2019). Grain sizes and clay mineral contents are key factors controlling the adsorption capacity and rate, especially higher adsorption capacity and lower adsorption rate were observed in the sediments with smaller grain size and higher clay mineral content (Cao et al. 2021). The difference in permeability played an important role in residence time and phosphorus removal efficiency, and a combination of 70% marble dust and 30% volcanic ash (as porous packed layers in one column) made a reasonable compromise between high steady phosphorus removal efficiency (~80%) and longevity (over 180 days) (Eljamal et al. 2017).

Previous studies have mostly focused on the effective diffusion distance of emulsified vegetable oil, reactive media in PRB, service life and removal effect, etc. Additionally, laboratory experiments were generally carried out at room temperature and conditions like actual water temperature and hydraulic gradient of groundwater in the field were not fully
considered. However, the formation and evolution of the in situ reaction zone after the injection of EVO into Cr(VI)-contaminated heterogeneous aquifers at water temperature in the field must be further understood.

Therefore, the objectives of this study are to (i) illustrate the diffusion of Cr(VI) in heterogeneous aquifers composed of coarse sand, medium sand, and fine sand, and (ii) investigate the process of the removal of Cr(VI) after a one-time EVO injection into compost and quartz sand within PRB during in situ remediation, and especially the roles of aquifer heterogeneity in the EVO reactive zone. The whole study was conducted under field simulation conditions of 19±0.5 °C and hydraulic gradient 3‰, according to the Suzhou coal mining area (Anhui, China).

Materials and methods

Materials

EVO (5 g/L) was prepared by the volume ratio of soybean oil, Tween 85, and water of 60:13:27 using a booster mixer constant stirring at 3000 rpm for 10 min, then was put in a 55 °C water bath for 10 min, taken out, cooled down naturally to room temperature, sealed, and stored in a cool place for later use. The prepared EVO was stable at room temperature and no stratifications occurred in the liquid phases. The compost (purchased in a flower market) was stored in a cool, ventilated, and dry place. The sand was purchased from a building materials market, carefully sieved in a standard wire sieve, dried, and made into coarse, medium, and fine sand according to the ratio shown in Table 1, respectively. Table 1 describes the characteristics of packed sand in the diffusion and removal study. The simulated Cr(VI) contaminated groundwater sample with a 20 mg/L concentration (Li et al. 2019; Lv et al. 2019), which was prepared with potassium dichromate (excellent grade pure) and deionized water.

| Material       | Particle size mm | Weight content |
|----------------|------------------|----------------|
| Coarse sand    | 0.5–1.0          | 60%            |
|                | 0.25–0.5         | 20%            |
|                | 0.075–0.25       | 20%            |
| Medium sand    | 0.5–1.0          | 20%            |
|                | 0.25–0.5         | 60%            |
|                | 0.075–0.25       | 20%            |
| Fine sand      | 0.25–0.5         | 20%            |
|                | 0.075–0.25       | 80%            |

Batch experiments

Experiments were conducted in conical flasks, in which medium sand (200 g), compost mass, and 200 mL uniformly mixed Cr(VI) and EVO solution were placed to simulate the contaminated aquifer and remediation agent, and pH was adjusting to neutral. Conical flasks were wrapped in dark brown paper and incubated in an intelligent biochemical incubator at room temperature during the experiments.

Three experimental groups were implemented to examine the Cr(VI) removal performance of compost/EVO ratios (1:100, 1:50, and 1:10), and the theoretical mass of compost was 0.01, 0.02, and 0.1 g, respectively. The concentration of EVO was 5 g/L. One compost-free system control group, named the contaminated control group, was conducted at the same time. Each group contained ten sample conical flasks. Cr(VI) concentration was determined by the 1,5 diphenylcarbohydrazide spectrophotometric method. Cr(IV) absorbance was determined using a spectrophotometer at a wavelength of 540 nm, and Cr(IV) concentration in solution was quantified following a standard curve method (Li et al. 2019).

Experiment equipment

A three-dimensional sandbox composed of plexiglass was used in this study. The plexiglass sandbox (90 cm in length, 25 cm in width, and 48 cm in height) was composed of an inlet tank (10 cm in width), stratified aquifers (coarse, medium, and fine sand), PRB, an injection well (a plexiglass column), an outlet tank (10 cm in width), and other auxiliary equipment in order from left to right as shown in Fig. 1. Figure 1 shows the detailed experimental design. There were 18 sampling ports from the front glass of the box, one water inlet and one water outlet from each side of the box. The sampling ports were both laid every 10 cm horizontally from left to right (6 columns), and every 10 cm vertically from bottom to top (3 rows). Each sampling port was a plexiglass column (5 mm in inner diameter) inserted into the sandbox 12 cm. One port of plexiglass columns was wrapped with gauze inside the sandbox and the other port was connected with a rubber tube, of which clamps stopped the rubber tube from water. There was 15 cm of fine sand, 15 cm of medium sand, and 13 cm of coarse sand which were compacted and packed sequentially from bottom to top into the sandbox. The sand finally reached a level of 43 cm and 2 cm of wet clay was used to cover its surface tightly for reducing water evaporation. PRB (25 cm in length, 20 cm in width, 43 cm in height) was laid 15.5 cm away from the inlet tank on the left, and the filled reactive media was a mixture of quartz sand and compost, according to the best compost/EVO ratio in the batch experiments which was 1:10, then the compost was 4 g. After each 5-cm lift, filled reactive media was repeatedly compacted using a wooden stick to ensure the homogeneity of each filling. In this way, both sides of the PRB in the sandbox...
were packed with sand as the heterogeneous aquifer media. The injection well was set in the bottom center of the PRB, 48 cm in total height, and 3 cm in inner diameter, of which small holes were distributed uniformly between 5 and 43 cm from the top. After the filling was completed, tap water was flooded into the sandbox from left to right using a peristaltic pump, and the whole aquifer was saturated with water by standing for 2 days. Then, the rate of the peristaltic pump and outlet height was set to maintain the inlet water level at 40 cm from the bottom of the inlet tank, the pore water flow rate was 10 cm/day, and the hydraulic gradient was 3‰. Thermometers are embedded in the aquifers to monitor the temperature of groundwater in the simulated tank. The experiment was conducted from November 22, 2019, to January 10, 2020, under conditions of hydraulic gradient constant of 3‰ and water temperature of 19±0.5 °C adjusted by indoor air conditioning.

Experimental method

The experiment comprised of two stages. The diffusion stage (stage 1) lasted for 25 days from November 22 to December 18, 2019. When the water level stabilized, contaminated groundwater containing 20 mg/L of Cr(VI) instead of tap water continuously flowed into the whole inlet tank rapidly agitated by a glass rod, making it a relatively uniform and typical source of lateral runoff pollution. The concentration of Cr(VI) of 18 sampling ports increased, reached a maximum value (close to or equal to 20 mg/L), and remained stable for 5 days, indicating a stable Cr(VI)-contaminated groundwater chemical field was formed in the whole heterogeneous aquifer. Then, a one-time injection of 8 L of EVO (5 g/L) was into the PRB at 1500 mL/h by a peristaltic pump through the injection well. When the Cr(VI) concentration of all water samples decreased, it reached a minimum value (equal to or close to 0 mg/L) and maintained constant for 5 days until the end of the removal stage (stage 2), which lasted for 23 days from December 19, 2019 to January 10, 2020.

Render maps of the distribution of Cr(VI) concentration and removal efficiency corresponding to the I-I’ section (Fig. 1) were generated using the Kriging interpolation method in ArcGIS 10.1 software to analyze characteristics of Cr(VI) diffusion and removal with time in the heterogeneous aquifer. In render maps, the aquifers are coarse, medium, and fine sand from top to bottom, respectively. The direction of water flow is from left to right, and the PRB is X-axis coordinate range from 7.5 to 27.5 cm. The different gradient colors from off-white to red indicate the concentration of Cr(VI) from the low to the high, and the different gradient colors from dark blue to red indicate Cr(VI) removal efficiency from high to low.

Results and discussion

Effect of aquifer heterogeneity on Cr(VI) diffusion in groundwater

Figure 2 shows the diffusion characteristics of Cr(VI) in heterogeneous aquifers with time during stage 1. Cr(VI)
contaminants continuously diffused in heterogeneous aquifers, and horizontal diffusion was significantly faster than vertical diffusion. Specifically, we studied the diffusion characteristics of Cr(VI) contaminants in heterogeneous stratified aquifers by taking the orange zone (OZ) (Fig. 2) as an example, where Cr(VI) concentration was equal to or over 12 mg/L and less than 16 mg/L. Generally, the OZ mainly migrated horizontally and rapidly, but expanded vertically and slowly in the whole downstream, indicating that Cr(VI) generally diffused with groundwater flow from top left to bottom right. Also, Fig. 2 depicts that the diffusion characteristics of the OZ changed gradually over time in each homogeneous aqueous media. On days 1 to 2, the OZ migrated into the PRB within coarse sand and medium sand layers along the flow direction. Maybe due to the unevenness of the coarse sand, Cr(VI) diffused horizontally in the coarse sand slightly slower than in the upper part of medium sand, but its horizontal diffusion rate in coarse and medium sand was still much faster than that in fine sand. Simultaneously, diffusion rates of Cr(VI) varied with the migration of OZ toward the outlet over time. In three heterogeneous aquifers, the OZ first reached the top of each in 3, 5, and 14 days, respectively, and first migrated to the bottom of each in 5, 14, and 15 days, respectively. This indicates that the diffusion rates of Cr(VI) were different in permeable aqueous media, and the fastest one in coarse sand, followed by medium sand and the slowest one in fine sand, which was related to particle size and permeability. Specifically, in coarse, medium, and fine sand, the horizontal diffusion rate of Cr(VI) calculated based on the time of reaching a stable maximum concentration of potassium dichromate at the outlet was 0.054 m/day, 0.036 m/day, and 0.018 m/day, respectively, and Cr(VI) concentration of the whole heterogeneous aquifer almost reached 20 mg/L at the end of stage 1.

**Effect of aquifer heterogeneity on Cr(VI) removal effect**

The distribution of Cr(VI) removal efficiency after EVO injection in the heterogeneous aquifer with time during stage 2 is shown in Fig. 3. Before injecting EVO (after stage 1 and before stage 2), the Cr(VI) removal efficiency of the entire heterogeneous aquifer was nearly zero. At 7 pm on day 27, a one-time injection of 8 L of EVO (5 g/L) accompanied with carbon source facilitated microorganisms’ performance in the PRB and heterogeneous aquifers on Cr(VI) removal. In order to describe Cr(VI) removal effect of the whole heterogeneous aquifer more conveniently, the zone of Cr(VI) removal efficiency above 95% was defined as the ERZ (effective removal zone) in this paper. The ERZ is the light blue and dark blue areas in Fig. 3. The maximum (Lmax) and minimum (Lmin) distances between the ERZ and the injection well in three sand layers are shown in Fig. 4. And Fig. 5 depicts the area changes of the ERZ in sand layers.

As shown in Fig. 3, the groundwater flow field played a significant role in the spatial distribution of the ERZ. Generally, the ERZ migrated consistently with groundwater flow, similar to Cr(VI) diffusion, whether it is seen from the whole heterogeneous aquifer or the inside of each sand layer. Also, the spatial distribution and migration characteristics of the ERZ were quite different within the heterogeneous aquifer. On days 28 to 29 (stage 2), the left border of the ERZ migrated toward the injection well, while in coarse sand, the right border of the ERZ reached the edge of the sandbox, and then diffused into the central section in the medium sand, which was relevant to the changes of the distance shown in Fig. 4. The ERZ diffused throughout coarse sand except for a small area in its bottom right but did not diffuse into fine sand because of the inhomogeneity of the reaction zone. This indicates that the microorganisms in the PRB and heterogeneous aquifers could effectively remove Cr(VI) in a certain range downstream of the injection well after EVO injection. The ERZ generally diffused upward and toward right horizontally in coarse and medium sand, but tended to migrate to the upper left in coarse sand. This tendency was most obvious on day 30 when the ERZ first diffused toward upstream of the injection well and almost filled in the PRB of coarse sand level. The ERZ in coarse sand shrunk downstream of the injection well on day 31 and then there was no expansion toward upstream in the whole heterogeneous aquifer until the end of stage 2. The ERZ first appeared in fine sand on day 30, and became unified (the ERZ below refers to the unified ERZ, unless otherwise specified) in the heterogeneous aquifer on day 32. Its shape resembled a pistol with the muzzle pointing to the right. On days 33 to 34, the area of the ERZ varied slightly without big changes in the morphology. The ERZ covered a local maximum area of 901.97 cm² on day 34 mainly because the area of the EZR in coarse sand rapidly increased (Fig. 5). The area of the ERZ in the whole heterogeneous aquifer decreased drastically on days 35 to 38, with a minimum area of 59.87 cm² on day 38. This indicates that as contaminated groundwater flowed continuously, the reactive zone in coarse sand decreased sharply and migrated to the outlet of the tank. Also, consumption of EVO and quick diffusion of Cr(VI) contaminants resulted in the decrease of Cr(VI) removal efficiencies of the three aqueous media. However, in the whole heterogeneous aquifer, maybe different concentrations of microorganisms and EVO in the vertical and the horizontal flow direction, and the different abilities of adsorption capacity of the heterogeneous aquifers, led to interactive migrations of microorganisms and EVO. The ERZ in coarse, medium, and fine sand increased and decreased in fluctuation and reached a maximum area simultaneously (Fig. 5). The whole EZR achieved a maximum area of 1357.87 cm² on day 47 and remained stable until the end of stage 2. Finally, a stable and unified ERZ (approximately 38 cm in length, 40 cm in height) with a removal efficiency of 97%, similar to the shape of \( \text{, was} \)
Fig. 2  Diffusion of Cr(VI) in the sandbox on different days during stage 1
Fig. 3  Distribution of Cr(VI) removal efficiency in the sandbox on different days during stage 2
established toward downstream of the injection well, which filled the whole region except for a small part in fine sand. The maximum distance between the ERZ and the injection well of coarse sand, medium sand, and fine sand was close to the distance between the injection well and the outlet, which was approximately 42.5 cm (Fig. 4). This indicates that aquifer heterogeneity had the least impact on the ERZ at the end of stage 2.

Figure 6, Fig. 7, and Fig. 8 show the variation of Cr(VI) removal efficiency over time in the sampling ports of coarse sand, medium sand, and fine sand, respectively. Cr(VI) removal efficiency was calculated for each aquifer media using Eq. (1) (Maamoun et al. 2020)

$$\text{Removal efficiency} = \left(1 - \frac{C_d}{C_0}\right) \times 100\%$$  (1)

Fig. 4 The maximum and minimum distances between the ERZ and the injection well in three sand layers during stage 2

Fig. 5 Area change of the ERZ in sand layers
where $C_0$ and $C_d$ are initial concentration and concentration at time day of Cr(VI), respectively. The removal efficiency of Cr(VI) from the left to right 6 sampling ports in the coarse sand were represented as $C_1$–$C_6$, and the representatives of other sampling ports could be deduced by analogy.

As shown in Fig. 6, Fig. 7, and Fig. 8, Cr(VI) removal efficiency of coarse sand, medium sand, and fine sand was positively correlated with the migration of reactive zone during stage 2. After EVO injection, microorganisms, EVO, and Cr(VI) contaminants diffused downstream along the flow direction. The time to reach the high and steady removal state was different. On day 32, Cr(VI) removal efficiency of sampling ports M2 to M5 exceeded 97.66% in medium sand, while that of sampling ports M6 and M1 approached 25.20 to 32.17% due to being far away from the PRB or in the upstream of the injection well. On day 34, Cr(VI) removal efficiency of coarse sand was stable at 97.86% except that sampling port C1 approached 38.02% because of its proximity.
to the pollution source. On day 35, Cr(VI) removal efficiencies of sampling ports F1, F5, and F6 in fine sand were below 10% while those of sampling ports F3 and F4 were over 90%. However, Cr(VI) removal efficiencies of coarse sand showed a sharp decline on day 35, especially that of sampling port C2 dropped to 39.36%, and sampling port M2 in medium sand decreased to 20.95%, and sampling port F2 in fine sand reduced to 67.20%. This could be due to that the reactive zone in the coarse sand decreased sharply and migrated to the outlet of the tank as contaminated groundwater flowed continuously, low adsorption ability of coarse sand, and quick diffusion ability of Cr(VI) contaminants. In the next 6 days, Cr(VI) removal efficiency of 18 sampling ports continuously wave-like rose due to vertical and horizontal interaction of microorganisms and EVO in the heterogeneous aquifer caused by the difference between their concentrations in different aquifers. Finally, Cr(VI) removal efficiency of almost the whole aquifer recovered equilibrium with 90 to 97% approximately, except for sampling ports C1, M1, and F1 of 12.54% due to being upstream of the injection well.

**Conclusion**

In this study, we investigated significant influences of heterogeneous aquifers (coarse sand, medium sand, and fine sand) on Cr(VI) diffusion and removal during in situ remediation of Cr(VI) contaminated shallow groundwater, under the conditions of 19±0.5 °C and hydraulic gradient 3‰, according to Suzhou coal mining area (Anhui, China). The groundwater flow played a significant role in Cr(VI) diffusion and removal reactive zone. Generally, Cr(VI) migrated consistently with groundwater flow from top left to bottom right, causing the whole heterogeneous aquifer to be contaminated. Cr(VI) migrated faster in the horizontal direction than in the vertical direction whether seen from the whole heterogeneous aquifer or inside of each relatively homogeneous aqueous media. The horizontal diffusion of Cr(VI) in coarse sand, medium sand, and fine sand was 0.054 m/day, 0.036 m/day, and 0.018 m/day, respectively. After a one-time EVO injection into the PRB containing compost, indigenous microorganisms immediately propagated and bioreactions and biogeochemical reactions occurred in EVO reactive zone. Simultaneously, aquifer heterogeneity generated differences in the concentration of microorganisms and EVO in the vertical and horizontal flow fields among heterogeneous aquifers. Due to the low permeability of fine sand, microorganisms migrated slowly with a low Cr(VI) removal efficiency in fine sand while it had the opposite feature in coarse sand in the early remediation, but a high Cr(VI) removal efficiency in fine sand compared with coarse sand in the middle period owing to high adsorption capacity retaining relatively more microorganisms in fine sand. Then, following interactive transference of microorganisms, almost the whole heterogeneous aquifer achieved a high Cr(VI) removal efficiency of 97%, a stable and unified ERZ similar to the shape of (approximately 1357.87 cm²) was formed downstream of the injection well. Our results shed light on the role of heterogeneous aquifers during in situ remediation of Cr(VI)-contaminated groundwater at simulated conditions in the field and provide novel insights into Cr(VI) treatment in mining areas. Further research should focus on microbial species identification to better understand the

![Fig. 8 The variation of Cr(VI) removal efficiency in the sampling ports of fine sand during stage 2 (Cr(VI) = 20 mg/L, 19 ±0.5 °C, hydraulic gradient = 3‰)](image-url)
distribution of microorganisms in heterogeneous aquifers, and comprehensive simulations of Cr(VI) removal by EVO and compost within mixed pollution with other metal and organic compounds in heterogeneous aquifers.

Author contribution Conceptualization: Weidong Zhao; methodology: Weidong Zhao, Lei Ma; formal analysis and investigation: Weidong Zhao, Xinxiang Huang, Jianshi Gong; writing—original draft preparation: Xinxiang Huang; writing—review and editing: Weidong Zhao, Lei Ma; funding acquisition: Jiazhong Qian, Lei Ma, Weidong Zhao; Resources: Xinxiang Huang; supervision: Weidong Zhao, Lei Ma.

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Availability of data and materials The datasets generated during and/or analyzed during the current study are not publicly available due to data confidentiality but are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable

Consent for publication Not applicable

Competing interests The authors declare no competing interests.

References

Bekele DN, Du J, de Freitas LG, Mallavarapu M, Chadalavada S, Naidu R (2019) Actively facilitated permeable reactive barrier for remediation of TCE from a low permeability aquifer: Field application. Journal of Hydrology 572:592–602

Borden RC (2007) Effective distribution of emulsified edible oil for enhanced anaerobic bioremediation. J Contam Hydrol 94:1–12

Bradl HB (2004) Adsorption of heavy metal ions on soils and soils constituents. J Colloid Interface Sci 277:1–18

Breslin CB, Branagan D, Garry LM (2018) Electrochemical detection of Cr(VI) with carbon nanotubes decorated with gold nanoparticles. Journal of Applied Electrochemistry 49:195–205

Brodie EL, Joyner DC, Faybishenko B, Conrad ME, Rios-Velazquez C, Malave J, Martinez R, Mork B, Willett A, Koenigsberg S, Herman DJ, Firestone MK, Hazen TC (2011) Microbial community response to addition of polylactate compounds to stimulate hexavalent chromium reduction in groundwater. Chemosphere 85:660–665

Buenano X, Canoira L, Martin Sanchez D, Costafreda J (2017) Zeolitic tufts for acid mine drainage (AMD) treatment in Ecuador: breakthrough curves for Mn(2+), Cd(2+), Cr(3+), Zn(2+), and Al(3+). Environ Sci Pollut Res Int 24:6794–6806

Cao Y, Dong S, Dai Z, Zhu L, Xiao T, Zhang X, Yin S, Soltanian MR (2021) Adsorption model identification for chromium (VI) transport in unconsolidated sediments. Journal of Hydrology 598:126228

Chen H, Dou J, Xu H (2017) Removal of Cr(VI) ions by sewage sludge compost biomass from aqueous solutions: reduction to Cr(III) and biosorption. Applied Surface Science 425:728–735

Chen L, Wang C, Liu S, Zhu L (2019) Investigation of adsorption/desorption behavior of Cr(VI) at the presence of inorganic and organic substance in membrane capacitive deionization (MCDI). J Environ Sci (China) 78:303–314

Chen M, Xu P, Zeng G, Yang C, Huang D, Zhang J (2015) Bioremediation of soils contaminated with polycyclic aromatic hydrocarbons, petroleum, pesticides, chlorophenols and heavy metals by composting: applications, microbes and future research needs. Biotechnol Adv 33:745–755

Choi Z, Lei J, Ding L, Dong J (2018) Mechanism on emulsified vegetable oil stimulating nitrobenzene degradation coupled with dissimilatory iron reduction in aquifer media. Biosensour Technol 260:38–43

Coetzee JJ, Bansal N, Chirwa EMN (2016) Chromium in environment, its toxic effect from chromite-mining and ferrochrome industries, and its possible bioremediation. Exposure and Health 12:51–62

Coyte RM, McKinley KL, Jiang S, Kerr J, Dwyer GS, Keyworth AJ, Davis CC, Kondash AJ, Vengosh A (2020) Occurrence and distribution of hexavalent chromium in groundwater from North Carolina, USA. Sci Total Environ 711:135135

Dhah B, Thatoi HN, Das NN, Pandey BD (2013) Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: A review. J Hazard Mater 250–251:272–291

Ding L, Song J, Huang D, Lei J, Li X, Sun J (2021) Simultaneous removal of nitrate and hexavalent chromium in groundwater using indigenous microorganisms enhanced by emulsified vegetable oil: interactions and remediation threshold values. J Hazard Mater 406:124708

Dong J, Jingu Y, Qiburi B (2018) Simulated reactive zone with emulsified vegetable oil for the long-term remediation of Cr(VI)-contaminated aquifer: dynamic evolution of geological parameters and groundwater microbial community. Environ Sci Pollut Res Int 25:34392–34402

Dong J, Yu D, Li Y, Li B, Bao Q (2019) Transport and release of electron donors and alkalinity during reductive dechlorination by combined emulsified vegetable oil and colloidal Mg(OH)2: Laboratory sand column and microcosm tests. J Contam Hydrol 225:103501

Eljamal O, Khalil AME, Matsunaga N (2017) Experimental and modeling column study of phosphorus removal by permeable reactive materials. International Journal of Environmental & Agriculture Research 3:62–70

Eljamal O, Thompson IP, Maamoun I, Shubair T, Eljamal K, Laneangwattanapong K, Sugihara Y (2020) Investigating the design parameters for a permeable reactive barrier consisting of nanoscale zero-valent iron and bimetallic iron/copper for phosphate removal. Journal of Molecular Liquids 299:112144

Elzinga EJ, Cirmo A (2010) Application of sequential extractions and X-ray absorption spectroscopy to determine the speciation of chromium in Northern New Jersey marsh soils developed in chromite ore processing residue (COPR). J Hazard Mater 183:145–154

Guo H, Chen Y, Hu H, Zhao K, Li H, Yan S, Xiu W, Coyte RM, Vengosh A (2020) High hexavalent chromium concentration in groundwater from a deep aquifer in the Baiyangdian Basin of the North China Plain. Environ Sci Technol 54:10068–10077

Harkness M, Fisher A (2013) Use of emulsified vegetable oil to support bioremediation of TCE DNAPL in soil columns. J Contam Hydrol 151:16–33

Jung Y, Coulibaly KM, Borden RC (2006) Transport of edible oil emulsions in claysey sands: 3D sandbox results and model validation. Journal of Hydrologic Engineering 11:238–244

Li Z, Xu S, Xiao G, Qian L, Song Y (2019) Removal of hexavalent chromium from groundwater using sodium alginate dispersed nano-zero-valent iron. J Environ Manage 244:33–39

Liang J, Huang X, Yan J, Li Y, Zhao Z, Liu Y, Ye J, Wei Y (2021) A review of the formation of Cr(VI) via Cr(III) oxidation in soils and groundwater. Science of The Total Environment 774:145762
Liu Y, Mou H, Chen L, Mirza ZA, Liu L (2015) Cr(VI)-contaminated groundwater remediation with simulated permeable reactive barrier (PRB) filled with natural pyrite as reactive material: environmental factors and effectiveness. J Hazard Mater 298:83–90

Long B, Ye B, Liu Q, Zhang S, Ye J, Zou L, Shi J (2018) Characterization of Penicillium oxalicum SL2 isolated from indoor air and its application to the removal of hexavalent chromium. PLoS One 13: e0191484

Lv D, Zhou J, Cao Z, Xu J, Liu Y, Li Y, Yang K, Lou Z, Lou L, Xu X (2019) Mechanism and influence factors of chromium(VI) removal by sulfide-modified nanoscale zerovalent iron. Chemosphere 224: 306–315

Maamoun I, Eljamal O, Khalil AME, Sugihara Y, Matsunaga N (2018) Phosphate removal through nano-zero-valent iron permeable reactive barrier; column experiment and reactive solute transport modeling. Transport in Porous Media 125:395–412

Maamoun I, Eljamal O, Falyouna O, Eljamal R, Sugihara Y (2020) Multi-objective optimization of permeable reactive barrier design for Cr(VI) removal from groundwater. Ecotoxicol Environ Saf 200: 110773

Maamoun I, Falyouna O, Eljamal R, Bensaida K, Eljamal O (2021) Optimization modeling of nFe0/Cu-PRB Design for Cr(VI) removal from groundwater. International Journal of Environmental Science and Development 12:131–138

Mitra S, Sarkar A, Sen S (2017) Removal of chromium from industrial effluents using nanotechnology: a review. Nanotechnology for Environmental Engineering 2:11

Mnif A, Bejaoui I, Mouelhi M, Hamrouni B (2017) Hexavalent chromium removal from model water and car shock absorber factory effluent by nanofiltration and reverse osmosis membrane. Int J Anal Chem 2017:7415708

Obiri-Nyarko F, Grajales-Mesa SJ, Malina G (2014) An overview of permeable reactive barriers for in situ sustainable groundwater remediation. Chemosphere 111:243–259

Onyancha RB, Aigbe UO, Ukherubor KE, Nwankwo W, Osibote OA, Paumo HK, Ama OM, Adetunji CO, Siloko IU (2021) Effect of hexavalent chromium on the environment and removal techniques: a review. J Environ Manage 280:111809

Wang F, Xu W, Xu Z, Liu H (2020): CTMAB-modified bentonite–based PRB in remediating Cr(VI) contaminated groundwater. Water, Air, & Soil Pollution 231:20

Wang J, Hou LA, Yao ZK, Jiang YH, Xi BD, Ni SY, Zhang L (2021) Aminated electrospray nanofiber membrane as permeable reactive barrier material for effective in-situ Cr(VI) contaminated soil remediation. Chemical Engineering Journal 406:126822

Wang L, Wen H, Li L (2018) Scale dependence of surface complexation capacity and rates in heterogeneous media. Sci Total Environ 635: 1547–1555

Watson DB, Wu WM, Mehlhorn T, Tang G, Earles J, Lowe K, Ghihring TM, Zhang G, Phillips J, Boyanov MI, Spalding BP, Schadt C, Kemner KM, Criddle CS, Jardine PM, Brook SC (2013) In situ bioremediation of uranium with emulsified vegetable oil as the electron donor–microcosm tests and model development. Environ Sci Technol 47:3209–3217

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