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Original Research

Introduction of Resin Barrier to Improve the Efficiency of Electrokinetic Remediation for Pb-Contaminated Soil

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Abstract

Developing an effective strategy to solve the "focus effect" of the traditional electrokinetic remediation (EKR) method during treatment of Pb-contaminated soil is challenging, but meaningful. Here, a novel permeable reactive barrier was constructed by coupling H^+ modified D001 resins (H-type D001) with the electrokinetic remediation (EKR) method to achieve this goal. Owing to the existence of ion exchange between Pb^{2+} and H^+, after introduction of H-type D001 resin into the EKR systems, the "focusing effect" was significantly weakened. To be specific, Pb^{2+} ions were effectively adsorbed by the resin barrier (RB) before migrating to the precipitation zone, and the adsorption of Pb^{2+} ions enabled H^+ ions to be desorbed from the H-type D001 resins, thus improving the pH environment required for EKR. As a result, Pb^{2+} removal efficiency of the traditional EKR method was improved. Compared with the EKR method, the removal efficiency of Pb in soil by the RB-EKR method improved by 37.8%, relatively. Analysis on mass distribution proportion of Pb removed indicated that the majority (53.01%) of Pb was removed by RB adsorption process. This work provides a simple but effective method for modifying the traditional electrokinetic remediation system to improve remediation ability towards treating heavy metal-polluted soil.

Keywords: Pb-contaminated soil, electrokinetic remediation, resin barrier, H-type D001 resin, focusing effect

Introduction

Heavy metal pollution in soil has become a global issue [1-3]. It is reported that over 50% of the worldwide polluted soil is caused by heavy metals and metalloids [4]. As for China, the heavy metal pollution in soil is also increasingly prominent with the rapid development of the Chinese economy [5]. According to the National Soil Pollution Survey Bulletin of China, the contents of heavy metals such as Hg, Pb, Cr and Zn in soil exceeding the national standard limits accounted for 1.6%, 1.5%, 1.1%, and 0.9% of the survey sites. Owing

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to their high biological toxicity and extremely resistant to environmental degradation, once they enter the soil, heavy metals will be absorbed by plants, and may be eventually absorbed by the human body through the food chain. Meanwhile, they can also pollute groundwater through infiltration along with surface precipitation, and further threaten the health of human beings [6-11]. To resolve this dilemma, the "Action Plan for Soil Pollution Prevention and Control" was issued by the State Council of the People's Republic of China in May 2016. In it, developing efficient soil pollution prevention and control techniques as an important tool to achieve ecological civilization has been raised to a new height.

Nowadays, owing to the advantages of high efficiency, wide application, and capability of in-situ application, electrokinetic remediation (EKR), as a reliable method to remove heavy metals from contaminated soil, has attracted widespread attention [12-16]. During the process of EKR of heavy metal-polluted soil, an applied electric field between the anode and cathode is needed to induce the movement of ions, charged particles, and fluids through soil, and benefiting from the role of a series of electrochemical processes, such as electrolysis, electroosmosis, electrophoresis, heavy metals can be finally removed from contaminated soil [17-20]. Up till now, the successful application of EKR for decontaminating polluted soils containing heavy metals such as chromium, cadmium, mercury and arsenic has been widely reported [21-25]. The key to improve the efficiency of the EKR method for remediation of heavy metals contaminated soil has been ascribed to tackle well with the influence of electrolyte, potential gradient, and remediation time, etc. Gao et al. utilized the EKR method to remediate soil contaminated with cadmium and lead in a mining area using three common organic acids as electrolytes, and the results showed that the average removal efficiencies of cadmium and lead in soil treated with citric acid as the electrolyte were higher compared to those treated with tartaric acid and lactic acid as electrolytes [22]. Shao et al. investigated the impact of anolyte pH, catholyte pH, voltage gradient, and electrode shape on the EKR of chromium-contaminated soil, and the results demonstrated that the voltage gradient was the most influential factor in EKR [23].

However, with the deeper insight into this field, a lot of research results indicate that the "focusing effect" that occurs during the EKR process may cause adverse effects on the remediation efficiency [26-30]. In the process of EKR, the anodic electrolysis of water produces H^+ ions, which in turn leads to the production of an equal amount of OH^- ions at the cathode region. Due to the influence of the electric field force, OH^- ions tend to migrate towards the anode, where they encounter heavy metal ions migrating towards the cathode. This interaction inevitably results in the formation of hydroxide precipitation, which further hinders the migration of heavy metals towards the cathode for removal. This phenomenon is commonly referred to as the "focusing effect." To mitigate the "focusing effect" of EKR technique, various approaches have been explored by researchers, including the addition of chemical reagents, pH conditioning of the catholyte, the use of ion exchange membranes, and the implementation of an electrolyte circulation [31-34]. However, these methods primarily aim to control the pH changes. Liu et al. found that the "focusing effect" present in the EKR process was the key to impeding its application, and the earlier the precipitation of heavy metal ions such as lead, copper, nickel, and cadmium ions occurred, the lower their removal efficiencies [35]. Thus, removing heavy metal ions with adsorbent before they arrive at the precipitation zone may be an effective measure to alleviate the focusing effect, and improve the efficiency of the EKR process.

Ion exchange resin is a kind of synthetic polymer material with active functional groups on the insoluble cross-linked polymer as the skeleton. It has the advantages of stable adsorption performance, large specific surface area, high mechanical strength and easy regeneration [36, 37]. Among various resin materials, D001 is a cation exchange resin with sodium sulfonate groups on a macroporous styrene-divinylbenzene copolymer, and commonly used in wastewater treatment and heavy metal recovery for its excellent adsorption performance [38-41]. For example, Zeng et al. used D001 resin to adsorb Cu^{2+} in chemical wastewater, the adsorption efficiency can reach up to 99.8% [40]. Wang et al. prepared modified D001 resin by nano-sized goethite (nFeOOH@D001) to adsorb Cr^{6+} from water, and 80.2% of the Cr^{6+} removal was obtained [41].

In this study, a novel permeable reactive barrier was constructed by coupling H^+ modified D001 resins (H-type D001) with EKR method to treat Pb-contaminated soil. Benefiting from the role of D001 resin on preventing heavy metal precipitation, the "focus effect" that always existed in the traditional EKR process can be effectively alleviated. As a result, Pb^{2+} ions can be effectively adsorbed by the resin barrier (RB) before migrating to the precipitation zone, while the adsorbed Pb^{2+} ions enables H^+ ions to be desorbed from the H-type D001 resins, so that the pH environment becomes more suitable for EKR. The research results will provide a theoretical basis and technical support for the remediation of heavy metal contaminated soil.

Materials and Methods

Materials and Apparatus

Experimental soil was collected from Tashan park in Yanshan University. D001 cation exchange resin was obtained from Hangzhou Zhengguang Resin Co., Ltd. All the chemicals used were analytical grade.

A flame atomic absorption spectrophotometer (WFX-120, Beijing Rayleigh Analytical Instrument Company) was used for the determination of lead.

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Preparation of Pb-Contaminated Soil

The collected soil was air-dried and then sifted through a 10-mesh sieve to remove grass branches and large stones. 1 L of $Pb(NO_3)_2$ solution with a concentration of 4000 mg/L was added to the air-dried soil in a bucket (solid - liquid mass ratio = 4 : 1), then the mixture was stirred thoroughly and sealed with a lid for storage. The lid was opened and the mixture was stirred periodically during the storage period. After 30 days, the lid was opened and the bucket was put in a ventilated place to dry the Pb-contaminated soil thoroughly. The main properties of prepared Pb-contaminated soil are provided in Table 1.

Table 1. Main properties of contaminated soil.

Properties	Values
Organic matter content (g/kg)	19.62
pH	6.66
Total amount of Pb (mg/kg)	1149.10
Amount of weak acid extractable Pb (mg/kg)	573.56
Amount of oxidizable Pb (mg/kg)	80.47
Amount of reducible Pb (mg/kg)	203.80
Amount of residual Pb (mg/kg)	291.27

EKR Device

The schematic diagram of the experimental EKR device is shown in Fig. 1. The main device was a rectangular structure with an internal size of 45 cm × 8 cm × 13 cm, which was made of plexiglass with a thickness of 5 mm. The main device consisted of three tanks, one soil tank for holding Pb-contaminated soil with an internal size of 35 cm × 8 cm × 13 cm and two electrolytic tanks for holding electrolytes with an internal size of 4.5 cm × 8 cm × 13 cm. Separators composed of multiporous plexiglass plates and filter cloth were arranged between the electrolytic tanks and the soil tank which was equally divided into seven parts and named S1 - S7 from the anode to the cathode. Two graphite electrodes with a diameter of 10 mm were connected to the positive and negative electrodes of the DC regulated power supply, and were vertically fixed in the two electrolytic tanks respectively. Drainage holes were used to drain the overflowing solution in the electrolytic tanks.

H-Type Modification of D001 Resin and Preparation of RB

A certain amount of D001 resins were first acid washed with 3% hydrochloric acid solution, then alkali washed with 3% sodium hydroxide solution to remove the residual oil on the resin, and finally washed with deionized water to neutral. The washed D001 resins were mixed with 3% hydrochloric acid solution (V_{HCl} : V_{resin} = 2.5 : 1) and stirred for 10 h so that H^+ ions were fully loaded on the sulfonic acid groups of the resins. Then the resins were properly rinsed with deionized water and dried at about 50º.

The schematic diagram of the RB framework with an external size of 1 cm × 8 cm × 13 cm is shown in Fig. 2. Filter cloth was wrapped around and at the bottom of the framework, and 50 g of H-type D001 resins were evenly filled into the framework.

EKR and RB-EKR Experiments

In EKR experiments, 4 kg of Pb-contaminated soil was added to the soil tank and the remediation time was set to 5 d. The impacts of electrolytes (deionized water, 0.1 mol/L potassium nitrate solution, 0.1 mol/L acetic acid solution) and potential gradients (0.5 V/cm, 1.0 V/cm, 1.5 V/cm) on the EKR effect were determined. In addition, the impact of regular electrolyte replacement on the EKR effect was also considered. After the EKR, soils from units S1-S7 were sampled to determine pH, conductivity and the total Pb amount of the soil.

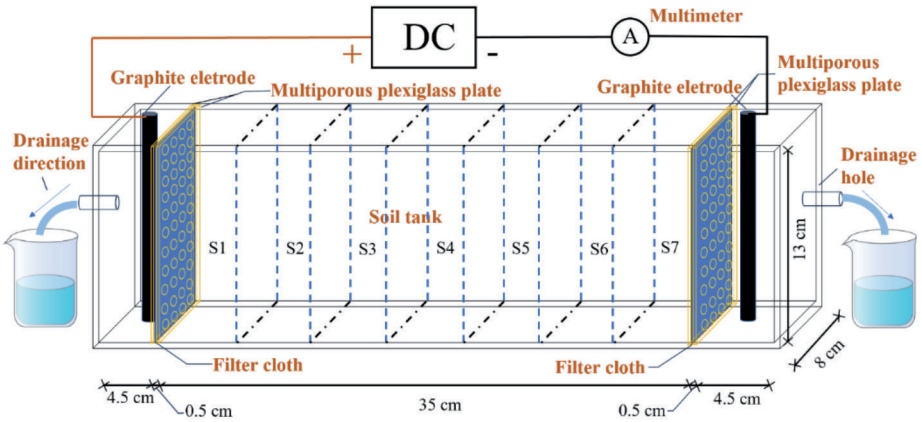

Fig. 1. Schematic diagram of the EKR device.

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In RB-EKR experiments, the RB was inserted between unit S3 and unit S4 in the soil tank. 0.1 mol/L acetic acid solution was applied as the electrolyte, the potential gradient was set to 1.0 V/cm, and the remediation time was set to 5 d. During the RB-EKR process, the electrolyte was replaced every 30 h. After RB-EKR, soils from units S1-S7 were sampled to determine pH and the total Pb amount of the soil. In addition, electrolytes in two electrolytic tanks and the resin eluent were sampled to determine the total Pb amount for tracking the trace of Pb removed from the soil. All experiments were carried out in quadruplicate.

Analytical Methods

Soil pH was measured at a 1 : 2.5 ratio of soil to water by a pH meter. Soil conductivity was measured at a 1 : 5 ratio of soil to water by a conductivity meter. The organic matter of the soil was measured by the method of external-heated potassium dichromate oxidation and ferrous sulfate titration [42]. The total Pb amount of the soil was measured by an air-acetylene flame atomic absorption spectrophotometer after the sequential digestion by hydrochloric acid, nitric acid, hydrofluoric acid and perchloric acid. Different chemical forms of lead were extracted by the modified BCR sequential extraction procedure.

The Pb removal efficiency of the soil was calculated as follows:

$$\eta = (C_0\text{-}C)/C_0 \quad (1)$$

Where C_0 is the initial Pb content in the soil, C is the Pb content in the soil after remediation.

Analysis of Variance (ANOVA) tests were used to evaluate the significance of differences.

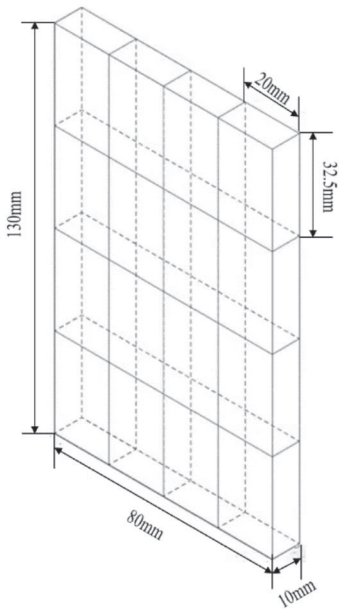

Fig. 2. Schematic diagram of the RB framework.

Results and Discussion

EKR Experiments

Effect of Electrolyte on EKR

To investigate the influence of electrolyte on heavy metal removal, deionized water, 0.1 mol/L potassium nitrate, and 0.1 mol/L acetic acid solution were employed as electrolyte, respectively, in EKR experiments (potential gradient 1 V/cm, remediation time 5 d). The Pb removal efficiencies in unit S1 - S7 of soil after 5 d of EKR treatment, and electric current variation during this period are shown in Fig. 3.

As shown in Fig. 3a), no matter which kind of electrolyte was used, the Pb removal efficiency in unit S1 of soil, which is closest to the anode, was the highest. While the Pb removal efficiencies in the soil units gradually decreased as the unit switches from anode side to cathode side, and even displayed negative effect on Pb removal (removal ratio less than 0%)

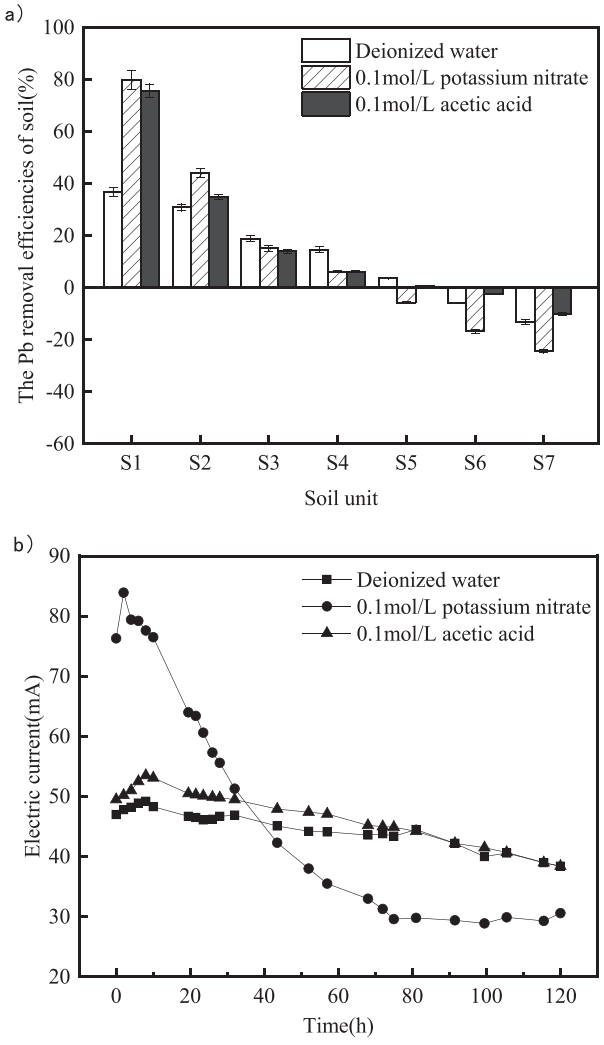

Fig. 3. Effect of electrolyte on EKR. a) The Pb removal efficiencies in unit S1-S7 of soil after EKR treatment; b) Electric current variation during EKR.

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in the soil units near the cathode (S6 and S7), indicating Pb was accumulated in these regions. This can be ascribed to the fact that Pb in the soil will transfer from anode side to cathode side under the assistance of electromigration and electroosmosis during the process of EKR. Noteworthy, from Fig. 3b), it can be seen that the currents in all the three electrolytes show similar trends of first increasing, then decreasing, and finally reaching to balance. The similar trend obtained between Pb removal and current variation can be explained by the following aspect, during the process of EKR, the applied electric field will drive the water electrolysis at both the anode and cathode:

$$\text{Anode: } 2H_2O - 4e^- \rightarrow 4H^+ + O_2(g) \quad (2)$$

$$\text{Cathode: } H_2O + 4e^- \rightarrow 4OH^- + 2H_2(g) \quad (3)$$

As a result, in the initial stage of remediation, the anode began to electrolyze H_2O to produce H^+, which will repulse salt ions in the soil away from the anode. Moreover, as more free conductive ions appeared in the system, the electric current rose in a short period of time. Subsequently, due to the gradual formation of the "focusing effect", that is, the generation of OH^- ions at the cathode led to the precipitation of salt ions including Pb^{2+} and the reduction of ion migration, the soil resistance increased and the electric current began to decrease.

Among the three electrolytes, the deionized water experimental group exhibited the worst remediation effect, the Pb removal efficiency was only 12.25%. Even in unit S1 of soil, the best Pb removal efficiency in this group was only 36.73%, which is much lower than that of potassium nitrate experimental group (79.80%) and acetic acid experimental group (75.69%). Although the experimental group with potassium nitrate as the electrolyte had the highest Pb removal efficiencies in soil units near the anode, the accumulation of Pb content in soil units near the cathode were also significantly higher than other groups ($P<0.05$). The Pb removal efficiency in unit S7 of soil under this condition even reached -24.45%. This is because the introduction of potassium nitrate enhanced the conductivity of the system, thus leading to a higher electrolytic water rate. Correspondingly, the anode will display a higher H^+ generation rate, further resulting in the removal efficiency of Pb in the soil near the anode higher than the other two groups. But meanwhile, the cathode also has a higher OH^- generation rate, OH^- has a larger flux repulsing from the cathode electrolytic tank to the soil under the action of electric field force and concentration difference, forming more hydroxide precipitate with Pb^{2+} and remaining in the region of soil near the cathode, which has adverse effects for the Pb removal. Based on this way, on the one hand, the overall Pb removal efficiency in the whole soil decreased; on the other hand, the soil resistance increased, and the current decreased, thus the electrolytic reaction rates of the two electrodes decreased. This result is consistent with the research results of Zhang Jing [43].

By contrast, although acetic acid is a weak electrolyte, and has limited effect in enhancing the conductivity of the system, as a monobasic organic acid, it can still assist in solubilizing Pb^{2+} in soil with H^+ generated by anode electrolysis. Besides, it can react with Pb^{2+} to form a water-soluble complex, which can be removed under the action of electroosmosis. Since the acetic acid solution buffered the rise of pH in the cathode electrolytic tank at the initial stage of the experiment, the increase efficiencies of Pb content in the soil units S6 and S7 near the cathode were significantly lower than those in the other two groups ($P<0.05$). Since the overall Pb removal efficiency of the acetic acid experimental group was the highest (16.99%). Therefore, 0.1 mol/L acetic acid solution was selected as the electrolyte in subsequent experiments.

Effect of Potential Gradient on EKR

Different potential gradients (0.5 V/cm, 1.0 V/cm, 1.5 V/cm) were applied in the EKR experiments to explore the effect of potential gradient on EKR, where 0.1 mol/L acetic acid solution was employed as electrolyte, and the remediation time was set as 5 d, and the corresponding results were shown in Fig. 4. From Fig. 4, the higher potential gradient generally resulted in higher Pb removal efficiency and electric current. With the increase of potential gradient, the H^+ electrolytic generation rate at anode increased, and the displacement rate of Pb^{2+} from the soil by H^+ also increased. Under the action of higher electric intensity, the electromigration rate of Pb^{2+} increased. However, when the potential gradient was 1.5 V/cm, some unfavorable phenomena occurred. A large amount of white sediment was formed on the surface of the cathode electrode and in the cathode tank. There was obvious skin detachment on the surface of the anode, indicating its poor stability under this condition, and it was no longer suitable for secondary use. Moreover, as the potential gradient increased to 1.5 V/cm, soil temperature increased obviously, resulting in soil moisture content decreased obviously. Based on the above experimental results, a potential gradient of 1.0 V/cm was applied in subsequent experiments.

Effect of Catholyte Replacement on EKR

When the concentration of OH^- in the catholyte is too high, the trend of OH^- flux into the soil will be more obvious, owing to the action of concentration gradient. As a result, both electrode reaction rate and electric current will decrease. Similarly, when a large number of Pb^{2+} are enriched in the catholyte, a large concentration difference of Pb^{2+} will occur between the catholyte and the soil that near the cathode, which will result in potential problems of Pb^{2+} diffusion and reflux. Therefore, the remediation experiment

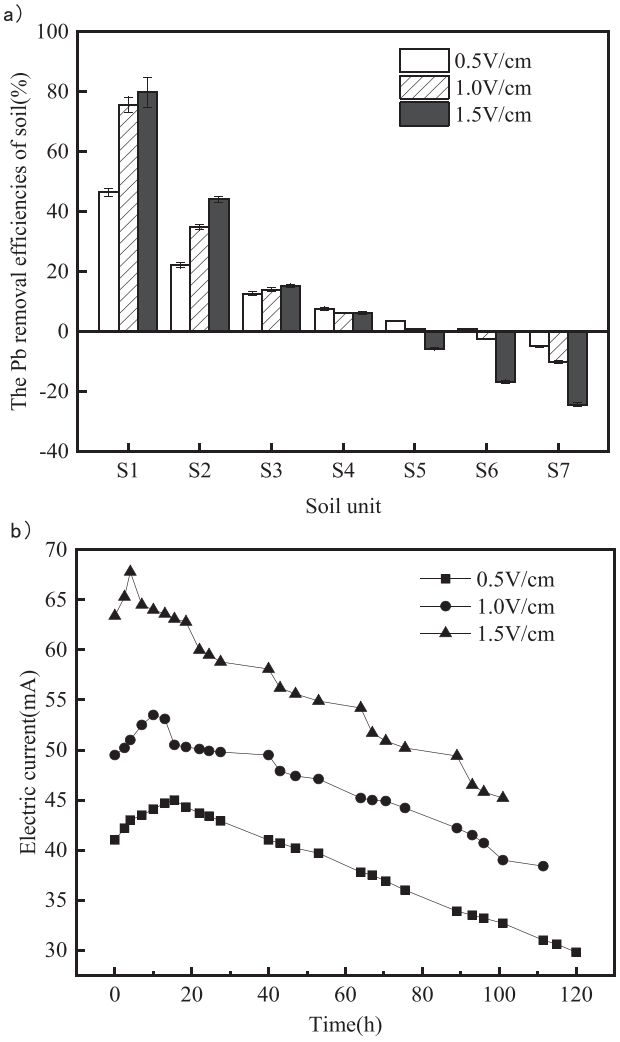

Fig. 4. Effect of potential gradient on EKR. a) The Pb removal efficiencies in unit S1-S7 of soil after EKR treatment; b) Electric current variation during EKR.

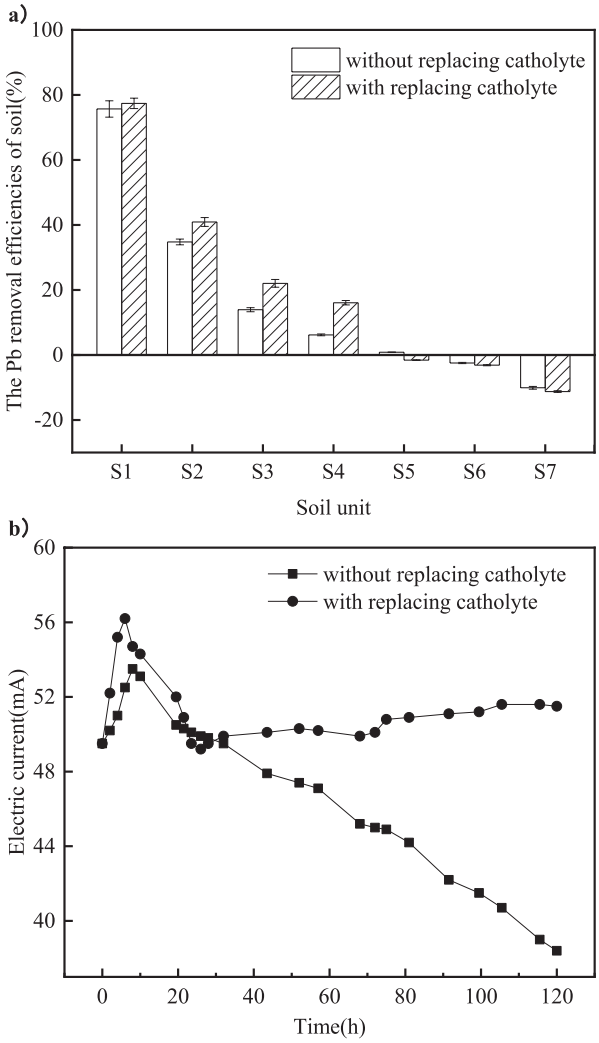

Fig. 5. Effect of catholyte replacement on EKR. a) The Pb removal efficiencies in unit S1-S7 of soil after EKR treatment; b) Electric current variation during EKR.

with replacing catholyte every 30 h was necessary, and the experimental results were shown in Fig. 5 and Table 2.

From Fig. 5a), it could be seen that the Pb removal efficiency from soil was obviously increased after regular replacement of catholyte. The Pb content in unit S7 of soil did not increase but decreased, because it was closest to the catholyte tank and soaked by the catholyte that remained acidic after replacement. Some of the precipitated Pb^{2+} dissolved again and migrated to the catholyte tank under the action of an electric field. This could also be demonstrated by the changes in soil pH before and after EKR (Table 2). In addition, after EKR treatment, the pH value in units S3 and S4 of soil decreased significantly compared with the experimental groups without catholyte replacement, and the Pb removal efficiencies in units S3 and S4 of soil also significantly improved ($P<0.05$), indicating that regularly replacing the catholyte was beneficial for enhancing the remediation effect of the intermediate area in soil tank.

From Fig. 5b), the electric current of the experimental group replacing the catholyte did not continue to decrease after 30 hours, but remained at a stable level, and even increased slightly. This is due to the control of OH^- flux by catholyte replacement, which leads to a near equilibrium state of H^+ production rate, salt ion dissolution rate, and "focusing effect" formation rate in the system in a short period of time.

RB-EKR Experiments

Location of RB

Based on the above EKR experimental results, the RB-EKR experiments were conducted with 0.1 mol/L acetic acid solution as the electrolyte. Meanwhile, 1.0 V/cm of potential gradient, 5 d of remediation time were applied, and the replacing period of catholyte was set as every 30 h. In order to determine the setting position of the resin barrier, the variation on soil conductivity before

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Table 2. Changes in soil pH before and after EKR.

	Without catholyte replacement							With catholyte replacement						
	S1	S2	S3	S4	S5	S6	S7	S1	S2	S3	S4	S5	S6	S7
Before EKR	6.69	6.72	6.71	6.69	6.69	6.70	6.69	6.88	6.87	6.89	6.88	6.89	6.89	6.88
After EKR	2.69	3.41	7.19	7.48	7.38	7.54	7.52	2.27	2.85	5.66	5.89	7.07	7.58	5.05

Table 3. Changes in soil conductivity before and after EKR. (μs/cm).

	S1	S2	S3	S4	S5	S6	S7
Before EKR	390	405	410	393	387	411	392
After EKR	708	608	637	283	221	183	268

and after EKR was measured, and the results were shown in Table 3.

As shown in Table 3, compared with the group unsubjected EKR treatment, the soil conductivity of units S1 to S3 increased, while that of units S4 to S7 decreased after EKR. This can be attributed to that the units S1-S3 of soil were close to the anode, correspondingly, a large number of H^+ with high ionic conductivity generated at the anode reached these units through electromigration, electroosmosis, and concentration diffusion, causing a large number of Pb^{2+}, Ca^{2+}, and Mg^{2+} in the soil to be displaced. Thus, the increase in the number of ions in the soil increased the soil conductivity of these three units. However, the numbers of free ions in the soil of units S4-S7 were greatly reduced due to the focusing effect, and then the soil resistance also increased by generated hydroxide precipitation, which finally reduced electrical conductivity. Based on these results, placing the resin barrier between S3 and S4 is most beneficial for the remediation of Pb-contaminated soil.

Effect of RB-EKR

The Pb removal efficiency in each soil unit after RB-EKR and the electric current variation during the process of RB-EKR are shown in Fig. 6. The changes on soil pH value before and after RB-EKR are shown in Table 4.

As shown in Fig. 6, compared with the EKR group, the Pb removal efficiencies in the soil units near the cathode in the RB-EKR group were improved significantly ($P<0.05$). In RB-EKR group, the Pb removal efficiencies in soil units S4, S5, S6, and S7 reached 30.14%, 16.90%, -1.51% and 29.10%, respectively, which were 14.06%, 18.48%, 1.62%, and 17.85% higher than those in single EKR treatment group. That is, the Pb removal efficiency in soil behind the RB (in the direction of the electric field) increased by 13.00% compared with the EKR group. The overall Pb removal efficiency in the soil of the RB-EKR group reached 32.10%, which was 8.82% higher than that of the EKR group. Obviously, the adsorption of H-type D001 reduced the precipitation of Pb^{2+} in the soil. Meanwhile, the adsorption reaction of H-type cation exchange resin with Pb^{2+} released H^+, which migrated

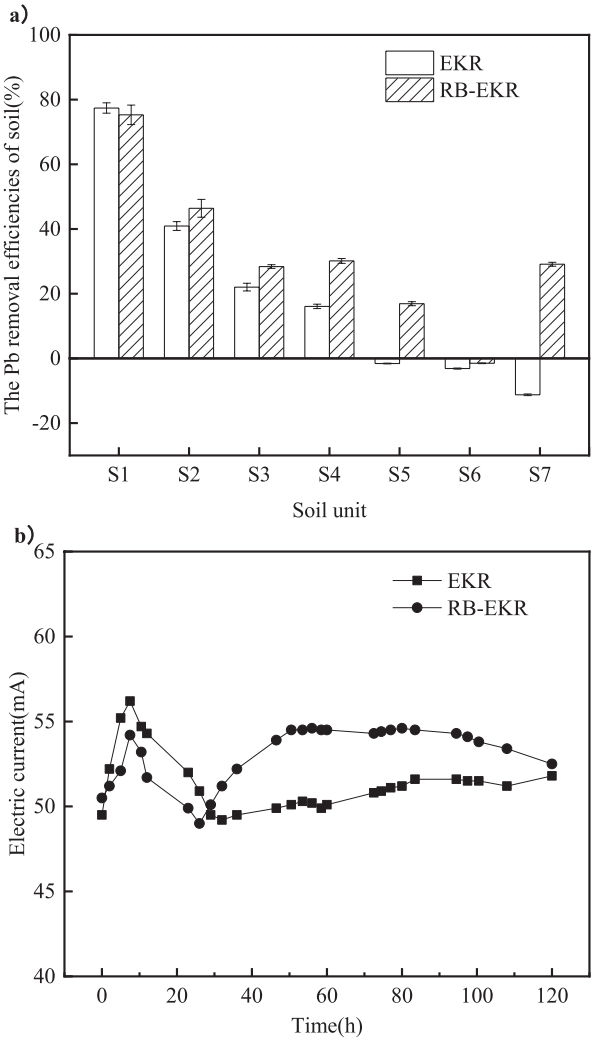

Fig. 6. Effect of RB-EKR. a) The Pb removal efficiencies in unit S1-S7 of soil after RB-EKR treatment; b) Electric current variation during RB-EKR.

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Table 4. Changes in soil pH before and after RB-EKR.

	S1	S2	S3	S4	S5	S6	S7
Before RB-EKR	6.62	6.61	6.62	6.62	6.63	6.62	6.62
After RB-EKR	2.41	3.84	6.24	3.91	5.35	7.50	5.21

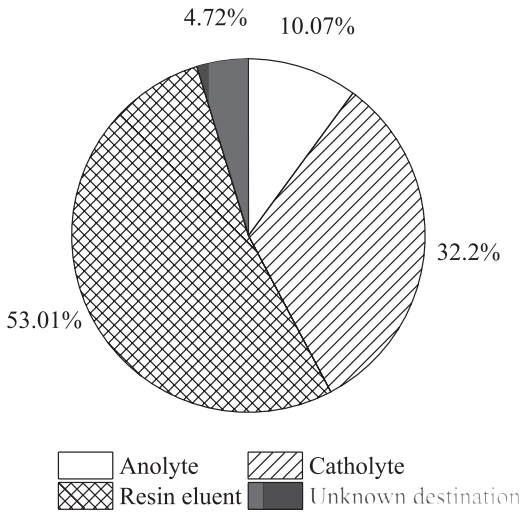

Fig. 7. The mass distribution proportion of the removed Pb in the RB-EKR experiment.

to the cathode under the action of electric field force. As a result, the concentration of H^+ in the soil pore solution behind the RB increased and the pH of soil decreased (Table 4), which not only promoted the replacement of Pb^{2+}, as well as the subsequent migration and removal in the soil units behind the RB, but also neutralized the OH^- migrating from the cathode, thus reducing the amount of Pb^{2+} precipitation caused by these OH^- ions. Thus, the focusing effect was weakened obviously.

According to the electric current variation curve during the process of RB-EKR, the electric current variation trends during the process of RB-EKR and EKR were essentially the same. After current fluctuations in the initial period, the electric current of RB-EKR was slightly higher than that of EKR in the subsequent remediation process. This is due to the early adsorption of Pb^{2+} migrating towards the cathode by the RB, which

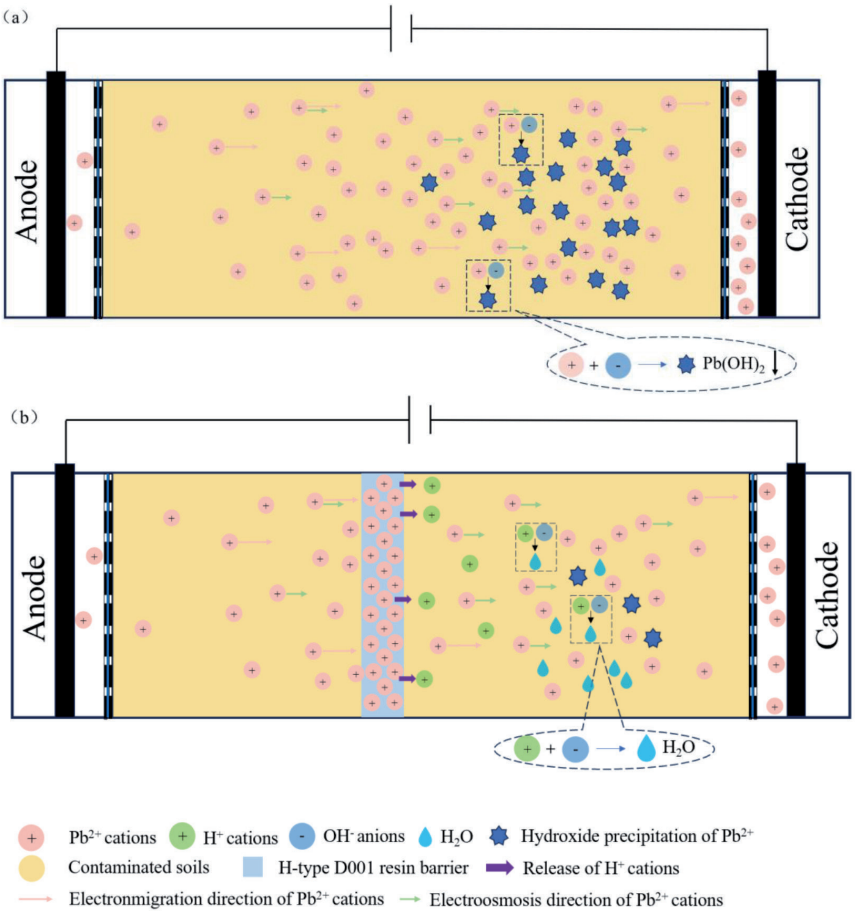

Fig. 8. Comparison of Pb^{2+} cations movement mechanism in the process of EKR a) and RB-EKR b).

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results in a decrease in the precipitation of Pb^{2+}, thereby reducing the resistance of the soil. At the same time, the H^+ ions released by the H-type D001 resins in the adsorption reaction made the soil acidified properly. Because H^+ has a faster movement rate than other ions and has higher ionic conductivity, the increase of its concentration also enhances the conductivity of the soil system. It is necessary to closely monitor the changes in pH, conductivity and lead removal efficiency of soil units adjacent to RB on the cathode side in practical applications to detect whether the inserted RB fails due to its ion exchange capacity.

Mass Distribution of the Removed Pb

The mass distribution proportion of the removed Pb in the RB-EKR experiment was determined by measuring the concentration of Pb in the resin eluent, anolyte and catholyte, and the result is shown in Fig. 7.

As shown in Fig. 7, the mass distribution of the removed Pb was the highest in the resin eluent, which accounted for 53.01%, indicating that the adsorption of RB toward Pb played a crucial role in remediation process. The lower Pb distribution was detected in the catholyte, accounting for 32.20%. After the introduction of RB, the removal efficiencies of Pb from soil units S4 to S7 behind the RB in the direction of the electric field were improved. Pb in these soil units was removed through electromigration and electroosmosis to the catholyte as shown in Fig. 8. The desorption of H^+ ions from the RB greatly reduced the focusing effect. In addition, some of the Pb leaking through the RB could also be removed in this way. In fact, this was also the main way to remove Pb in conventional EKR. However, the lowest Pb removal was in the anolyte, only accounting for 10.07%. Colloidal Pb particles with negative charges could migrate to the anolyte through electrophoresis, which was very limited compared with electromigration and electroosmosis. In addition, part of Pb in the soil unit S1 closest to the anolyte tank might enter into the anolyte through concentration diffusion.

Conclusions

An RB constructed by H-type D001 resins was introduced to couple with the EKR method to treat Pb-contaminated soil. The RB-EKR method exhibits great application potential in the field of heavy metals contaminated soil remediation.

For EKR, compared to deionized water and potassium nitrate solution, acetic acid solution was more suitable as the electrolyte, and the optimal potential gradient was determined to 1.0 V/cm. After 5d of remediation, the Pb removal efficiency in soil near the anode reached 75.69%, and the overall Pb removal efficiency reached 16.99% under the optimal experimental condition. When replacing catholyte every 30 h, a 6.29% increase in overall Pb removal efficiency and 21.34% increase in soil near the cathode can be further obtained due to improving the EKR effect.

However, no matter which operating conditions were adopted, the "focusing effect" always existed in the EKR process, which still displayed a significant impact on the Pb removal efficiency. By contrast, the introduction of RB greatly reduced the focusing effect in EKR, and the adsorption of RB toward heavy metal also played an important role in RB-EKR. As a result, Pb removal efficiencies in soil units behind the RB including units S4, S5, S6, and S7 increased by 14.06%, 18.48%, 1.62%, and 17.85% respectively. Subsequent analysis of the mass distribution proportion of Pb removed further confirmed that the majority (53.01%) of Pb was removed by the RB adsorption process.

The above results provide new references for the remediation of heavy metal contaminated soil, and further in situ remediation will be conducted in the future.

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Conflict of Interest

The authors declare no conflict of interest.

References

1. LADO L.R., HENGL T., REUTER H.I. Heavy metals in European soils: a geostatistical analysis of the FOREGS Geochemical database. Geoderma. **148**, 189, **2008**.
2. MARRUGO-NEGRETE J., PINEDO-HERNÁNDEZ J., DÍEZ S. Assessment of heavy metal pollution, spatial distribution and origin in agricultural soils along the Sinú River Basin, Colombia. Environmental Research. **154**, 380, **2017**.
3. KUMAR V., SHARMA A., KAUR P., SINGH SIDHU G.P., BALI A.S., BHARDWAJ R., THUKRAL A.K., CERDA A. Pollution assessment of heavy metals in soils of India and ecological risk assessment: A state-of-the-art. Chemosphere. **216**, 449, **2019**.
4. SÁNCHEZ-CASTRO I, MOLINA L, PRIETO-FERNÁNDEZ M Á, et al. Past, present and future trends in the remediation of heavy-metal contaminated soil-Remediation techniques applied in real soil-contamination events. Heliyon. **9**, **2023**.
5. CHEN Y.G., HE X.L.S., HUANG J.H., LUO R., GE H.Z. Impacts of heavy metals and medicinal crops on ecological systems, environmental pollution, cultivation, and production processes in China. Ecotoxicology and Environmental Safety. **219**, 112336, **2021**.
6. WANG L. Damage and remediation of soil heavy metal pollution. Modern Agriculture. **487**, 73, **2017**.

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7. HE X.W., WANG Y.X., FANG Z.Q., CUI X.Y., ZHANG S.Y. Pollution characteristics and pollution risk evaluation of heavy metals in soil of lead-zinc mining area. Journal of Environmental Engineering Technology. **6**, 476, **2016**.
8. CHEN Y., CHEN X., JIANG R., LI S., MA X., SUN Y., ZHANG T., FENG Z. Bioaccumulation characteristics of typical pollutants in seafood from coastal waters of Jiangsu, China. Continental Shelf Research. **263**, 105030, **2023**.
9. WIECZOREK J., BARAN A., BUBAK A. Mobility, bioaccumulation in plants, and risk assessment of metals in soils. Science of The Total Environment. **882**, 163574, **2023**.
10. ALI A., HUSSAIN M.Z., AZAM S.M., MUSTAFA G., AFZAL G., IDREES M., LQBAL K.J. Studies on bioaccumulation of lead and arsenic in different tissues of Rabbit (*Oryctolagus cuniculus*). Indian Journal of Animal Research. **57**, 254, **2023**.
11. LI X.Y.,YE F., ZhANG H., AHMAD MUNIR, ZENG Z.X., WANG S.J., WANG S.F., GAO D.W., ZHANG Q.R. Ternary rGO decorated $W_{18}O_{49}$@g-C_3N_4 composite as a full-spectrum-responded Z-scheme photocatalyst for efficient photocatalytic H_2O_2 production and water disinfection, Journal of Environmental Chemical Engineering. **11** (4), 110329, **2023**.
12. AYYANAR A., THATIKONDA S. Experimental and Numerical studies on remediation of mixed metal-contaminated sediments by electrokinetics focusing on fractionation changes. Environmental Monitoring and Assessment. **193**, 316, **2021**.
13. VILLEN-GUZMAN M., PAZ-GARCIA J.M., AMAYA-SANTOS G. Effects of the buffering capacity of the soil on the mobilization of heavy metals. Equilibrium and kinetics. Chemosphere. **131**, 78, **2015**.
14. MOHAMADI S., SAEEDI M., MOLLAHOSSEINI A. Enhanced electrokinetic remediation of mixed contaminants from a high buffering soil by focusing on mobility risk. Journal of Environmental Chemical Engineering. **7**, 103470, **2019**.
15. PHAM T.D., SILLANPÄÄ M. Electrokinetic remediation of organic contamination. Environmental Technology Reviews. **4**, 103, **2015**.
16. ZHANG S., ZHANG J., CHENG X., MEI Y., HU C., WANG M., LI G.F. Electrokinetic remediation of soil containing Cr(VI) by photovoltaic solar panels and a DC-DC converter. Journal of Chemical Technology & Biotechnology. **90**, 693, **2015**.
17. GIDUDU B., CHIRWA E.M.N. The Role of pH, Electrodes, Surfactants, and Electrolytes in Electrokinetic Remediation of Contaminated Soil. Molecules. **27**, 7381, **2022**.
18. LU P., FENG Q., MENG Q., YUAN T. Electrokinetic remediation of chromium- and cadmium- contaminated soil from abandoned industrial site. Separation & Purification Technology. **98**, 216, **2012**.
19. CAMESELLE C. Enhancement of electro-osmotic flow during the electrokinetic treatment of a contaminated soil. Electrochimica Acta. **181**, 31, **2015**.
20. ZHOU D.M., DENG C.F., CANG L., ALSHAWABKEH A.N. Electrokinetic remediation of a Cu–Zn contaminated red soil by controlling the voltage and conditioning catholyte pH. Chemosphere. **61**, 519, **2005**.
21. TANEJA S., KARACA O., HARITASH A.K. Combined effects of high voltage gradient and electrolyte conditioning on electrokinetic remediation for chromium (VI)-contaminated soils. Rendiconti Lincei. Scienze Fisiche e Naturali. **34** (13), 1, **2023**.
22. GAO J.M., CAI Z.P., SUN S.Y., LIAO X.J., HUANG X.R., CHEN H.S., LIU J.Y. Study on circulation-enhanced electrokinetic remediation of soils contaminated by heavy metals with different organic acids as electrolytes. Acta Scientiae Circumstantiae. **43**, 9, **2023**.
23. SHAO Y.Y., XIONG B. Process and influence factors of electro-kinetic remediation of chromium contaminated soil. Chinese Journal of Environmental Engineering. **10**, 10, **2016**.
24. CAI Z., SUN Y., DENG Y., ZHENG X., SUN S. Sinkkonen A., Romantschuk M. Enhanced Electrokinetic Remediation of Cadmium (Cd)-Contaminated Soil with Interval Power Breaking. International Journal of Environmental Research. **16**, 31, **2022**.
25. ROSESTOLATO D., BAGATIN R., FERRO S. Electrokinetic remediation of soils polluted by heavy metals (mercury in particular). Chemical Engineering Journal. **264**, 16, **2015**.
26. XU Y., LU Q., LI J., WAN L., CHEN S., LU Y. Effect of humus on the remediation of arsenic-contaminated soil by electrokinetic technology. Environmental Technology & Innovation. **21**, 101297, **2021**.
27. HU W., CHENG W.C., WANG Y., WEN S., XUE Z.F. Applying a nanocomposite hydrogel electrode to mitigate polarization and focusing effect in electrokinetic remediation of an Cu-and Pb-contaminated loess. Environmental Pollution. **333**, 122039, **2023**.
28. NG Y.S., SEN GUPTA B., HASHIM M.A. Remediation of Pb/Cr co-contaminated soil using electrokinetic process and approaching electrode technique. Environmental Science and Pollution Research. **23**, 546, **2016**.
29. TANG J., HE J., XIN X., HU H., LIU T. Biosurfactants enhanced heavy metals removal from sludge in the electrokinetic treatment. Chemical Engineering Journal. **334**, 2579, **2018**.
30. XU Y., XIA W., HOU H., ZHANG J., QIAN G. Remediation of chromium-contaminated soil by electrokinetics and electrokinetics coupled with CaAl-LDH permeable reaction barrier. Environmental Science and Pollution Research. **24**, 20479, **2017**.
31. CHEN J.L., YANG S.F., WU C.C., TON S.S. Effect of ammonia as a complexing agent on electrokinetic remediation of copper-contaminated soil. Separation and Purification Technology. **79**, 157, **2011**.
32. RYU B.G., PARK G.Y., YANG J.W., BAEK K. Electrolyte conditioning for electrokinetic remediation of As, Cu, and Pb-contaminated soil. Separation and Purification Technology. **79**, 170, **2011**.
33. KIM W.S., KIM S.O., KIM K.W. Enhanced electrokinetic extraction of heavy metals from soils assisted by ion exchange membranes. Journal of Hazardous Materials. **B118**, 93, **2005**.
34. MERDOUD O., AKRETCHE D.E. Electroremediation of an industrial area contaminated by chromium. Journal of Environmental Science and Health (Part A). **43**, 866, **2007**.
35. LIU F., FU R.B., XU Z. Optimization of electrode configuration in soil electrokinetic remediation. Environmental Science. **36**, 678, **2015**.
36. MARIN N.M., DOLETE G., MOTELICA L., TRUSCA R., OPREA O.C., FICAI A. Preparation of Eco-Friendly Chelating Resins and Their Applications for Water Treatment. Polymers. **15**, 2251, **2023**.
37. TANG Q., WU H., ZHOU M., YANG D. Preparation of a new gel-type lignin-based cationic adsorption resin for efficient removal of Ca^{2+} from aqueous solutions.

International Journal of Biological Macromolecules. **241**, 124505, **2023**.
38. FU L., ZU J., HE L., GU E., WANG H. An adsorption study of 99Tc using nanoscale zero-valent iron supported on D001 resin. Frontiers in Energy. **14**, 11, **2020**.
39. ZHENG Y., XIONG C., YAO C., YE F., JIANG J., ZHENG X., ZHENG Q. Adsorption performance and mechanism for removal of Cd (II) from aqueous solutions by D001 cation-exchange resin. Water Science and Technology. **69**, 833, **2014**.
40. ZENG Y.G., LI L. Study on treatment of heavy metal lons of chemical wastewater by ion exchange resin. Advanced Materials Research. **955**, 2230, **2014**.
41. WANG S., YIN W., BU H., ZENG W., LI P., ZHENG X.,CHANG P., WU J. A facile modification of cation exchange resin by nano-sized goethite for enhanced Cr (VI) removal from water. Environmental Technology. **43**, 1833, **2022**.
42. KUANG S.P., DONG Z.W., WANG B.C., WANG H.H., LI J.L., SHAO H.B. Changes of sensitive microbial community in oil polluted soil in the coastal area in Shandong, China for ecorestoration. Ecotoxicology and Environmental Safety. **207**, 111551, **2021**.
43. WU J.N., ZHANG J., XIAO C., Focus on factors affecting pH, flow of Cr and transformation between Cr(VI) and Cr(III) in the soil with different electrolytes. Electrochimica Acta, **211**, 652, **2016**.

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