Adsorption and reduction from modified polypyrrole enhance electrokinetic remediation of hexavalent chromium-contaminated soil

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Abstract
Toxic metal pollutant Cr(VI) in the environment will pose a severe threat to animal and human health. In this work, Fe3O4@PPy, Arg@PPy, and Arg/Fe3O4@PPy were prepared to enhance adsorption of Cr(VI) by doping Fe3O4 nanoparticles and amino radicals into the original PPy structure. Their characteristics were investigated by FTIR, SEM, EDS, BET analysis, and batch adsorption experiments. And they were used as permeable reaction barriers (PRB) to combine with electrokinetic remediation (EKR) to remediate Cr-contaminated soil. Adsorption experiment results showed that the maximum adsorption capacities of PPy, Fe3O4@PPy, Arg@PPy, and Arg/Fe3O4@PPy for Cr(VI) were 60.43 mg/g, 67.12 mg/g, 159.86 mg/g, and 141.50 mg/g, respectively. They all followed the kinetic pseudo-second-order model and the Langmuir isothermal model with a monolayer adsorption behavior. In the EKR/PRB system, the presence of Fe3O4@PPy, Arg@PPy, and Arg/Fe3O4@PPy obtained the higher Cr(VI) removal efficiency near the anode than that of the PPy, increasing by 74.60%, 26.04%, and 68.64%, respectively. A strong electrostatic attraction between anion contaminants and protonated modified PPy and a reduction from Cr(VI) to Cr(III) appeared in the EKR remediation process under acid conditions. This study opened up a prospect for applying modified PPy composites to treat toxic metal-contaminated soil.

Keywords Modified polypyrrole · Adsorption · Reutilization · Electrokinetic remediation · Permeable reaction barrier · Cr-contaminated soil

Introduction
Recent developments in industrialization have heightened the emphasis on soil contamination by toxic metals (Sarwar et al. 2017). The research to date about industrial chromium (Cr) pollution is considered to put an increasing burden on the environment and human health (Wang et al. 2019), that is attributed to its toxicity, persistence, and non-biodegradability gradually accumulating in the environment (Ayangbenro and Babalola 2017). Previously published studies have shown that Cr exists in nature mainly as two stable oxidation states, including hexavalent chromium and trivalent chromium (Sarin and Pant 2006). Cr(VI) usually occurs as anionic species such as CrO42−, HCrO4−, and Cr2O72−, which have high mobility in soil and groundwater, resulting in potential danger of toxicity and carcinogenicity (Eyvazi et al. 2019). Cr(III) species, like Cr3+, Cr3(OH)45+, and Cr(OH)3+, are less toxic and more stable than Cr(VI) (Sarin and Pant 2006). Therefore, there is an urgent need to find an effective way to address the soil contamination problems caused by Cr.
Numerous methods have been employed to treat Cr-contaminated soil, such as chemical leaching, bioremediation technology, solidification/stabilization, and electrokinetic remediation (EKR) (Alidokht et al. 2021; Chen et al. 2021a; Sarankumar et al. 2019; Zou et al. 2019). According to the previous literature, EKR, which possesses economic sustainability and satisfies the need to remove various contaminants covering organic pollutants and toxic metals, especially applicable to low permeability soils, is a promising in situ soil remediation technology (Al-Hamdan and Reddy 2008, Li et al. 2012). Electromigration, electroosmosis, electrophoresis, and electrolysis have been instrumental in our understanding of the mechanism of EKR for toxic metal-contaminated soils (Nasiri et al. 2020). However, some limitations of traditional EKR still need to be addressed. For instance, Cr(VI) as the oxygen anion tends to accumulate in near-anode soil layers and is challenging to remove due to adsorption and potential flattening (Tang et al. 2021; Wen et al. 2021b; Yu et al. 2020).

Combined EKR techniques to enhance the Cr(VI) remediation efficiency in near-anode soil layers have got more attention, such as the establishment of a main-auxiliary electrode system, approaching anode electrokinetic method, application of UV radiation and electrokinetic remediation, and permeable reactive barrier (PRB) coupled with the electrokinetic process (Liu et al. 2020; Suzuki et al. 2014; Tang et al. 2021; Wang et al. 2019; Zhang et al. 2012; Zheng et al. 2021). Considerable literature has shown that the EKR/PRB system has the advantage of avoiding secondary contamination of electrolytes (Nasiri et al. 2020; Suzuki et al. 2014; Yeung and Gu 2011). During the EKR/PRB system, the barrier padded with reactive materials bonds with pollutants by reduction, precipitation, and adsorption to remove the anticipated contaminants (Nasiri et al. 2020).

The selection of fillers is central to the entire EKR/PRB, depending on the contaminant category. Active carbon, zeolite, and zero-valent iron are the common reagent medium (Zhou et al. 2021). Previously, a good deal of novel materials with excellent efficiency has been examined. For example, the CaAl-layered double hydroxides were used as a PRB filler for reparation of Cr-contaminated soil in the EKR/PRB system, the union of graphene oxide and fly ash as reaction media could reach a 92.6% removal rate for lead(II) from contaminated soil by EKR/PRB technology (Xu et al. 2016; Zhou et al. 2021). Conductive polymers appear in more studies due to their outstanding electrochemical performance, electrical conductivity, high carrier mobility, and re-utilization (Yuan et al. 2019). Polypyrrole (PPy), which has remarkable environmental stability and non-toxicity as an environmentally friendly polymer material, has recently caught the attention of researchers (Ghorbani et al. 2010, Hasani and Eizazadeh 2013, Hosseini et al. 2015). Under acidic conditions, PPy can protonate and generate electrostatic attraction with anion pollutants (Ting et al. 2021). Moreover, PPy could adsorb anions by carrying nitrogen atoms with positive charge and restore Cr(VI) to Cr(III) (Wei et al. 1993). However, there is a π-π force between the PPy molecular chains, and individual spherical PPy particles are prone to aggregate (Wang et al. 2020). It leads to a small specific surface area limiting their ability to remove Cr(VI) because of low binding sites (Amalraj et al. 2016; Ballav et al. 2014a, b; Ballav et al. 2012; Bhaumik et al. 2011; Chigondo et al. 2019; Karthik and Meenakshi 2015). They all tend to use modified PPy as an adsorbent to remove pollutants from water, making it possible to remediate contaminated soil with modified PPy as PRB near the anode in the PRB/EKR system. This study intends to prepare three modified PPy materials, i.e., magnetic PPy (Fe₃O₄@PPy), arginine modified PPy (Arg@PPy), and arginine modified magnetic PPy (Arg/Fe₃O₄@PPy), which are based on PPy by polymerization of pyrrole monomer. Their microscopic morphology and physicochemical characteristics were studied using FTIR, BET, SEM, and EDS.

The parametric (pH, dosage, initial Cr⁶⁺ concentration, and temperature) effects on adsorption efficiency and absorption–desorption study were carried out to learn about the best reaction conditions and materials’ reusability. Kinetics and isotherm studies were performed to explore their adsorption mechanism. And then, these composites were used as the PRB fillers near the anode to remediate Cr-contaminated soil. During the EKR/PRB process, electric current, the characteristic of soil and electrolyte, and residual and leaching Cr(VI) concentration were measured to assess composites’ enhancement. The real aim of this study was to use modified PPy as PRB fillers to treat Cr-contaminated soil combined with EKR after understanding materials’ basic properties and then find out which modified material was most conducive to pollutant removal and analyze the reasons. And the original value of this study was that it was proposed to provide a little helpful insight for the design of the green PRB materials for toxic metal-contaminated soil and water treatment.
Materials and methods

Materials and pretreatment

Pyrrole (Py) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Other chemicals like L-arginine, ammonium persulphate (APS), Fe₃O₄ nanoparticles (50 nm), and potassium dichromate (K₂Cr₂O₇), of analytical grades, were procured from Chengdu Kelong Chemical Co., Ltd.

The contaminated soil samples in this study were from the 0–20 cm layer of a deserted chromate industrial site located in Chongqing, China. The soil samples were air-dried naturally, and then the apparent impurities and unnecessary debris were removed from them. Next, soil samples were homogenized for the sake of research by grinding in a ball grinder for 12 h and then passing through a 100-mesh sieve.

Synthesis of composite materials

Three composite materials were prepared as the following procedure by ameliorating other ways (Chigondo et al. 2019).

1. Put 0.3 g of Fe₃O₄ nanoparticles into 80 mL deionized water and then sonicate it for 30 min to get an excellent dispersion of Fe₃O₄.
2. Inject 1 mL PPy monomer rapidly into the above solution and stir the mixture sharply for about 30 min.
3. Put 3.9 g APS into 20 mL deionized water and add it to the 80 mL mixed solution dropwise.
4. Stir the 100 mL mixed solution consecutively for 20 min. Place the treated solution at room temperature for 12 h, and add 10 mL acetone to stop the polymerization process.
5. Wash it with deionized water, filter, and vacuum dry them at 60 °C for 12 h.
6. Grind the black solid using agate mortar to obtain Fe₃O₄@PPy.

In addition, the preparation of Arg@PPy and Arg/Fe₃O₄@PPy was similar to Fe₃O₄@PPy. The former replaced Fe₃O₄ in the first step with arginine 1.3 g and other steps followed above. The latter was to add 1.3 g of arginine at the start, and the rest of the process was the same as described above.

Characterization of composite materials and Cr-contaminated soils

Fourier transform infrared spectroscopy (FTIR, Thermo Scientific, USA) analyzed the surface functional groups of the composite materials. The microstructure of the composite materials was investigated using scanning electron microscopy (SEM, Thermo Scientific, USA). Using automated surface area and pore size analysis (MicrotracBEL, Japan) assessed the BET surface area of PPy and its modified materials. The specific analysis results are shown in the “Characterization of composite materials” section.

An X-ray fluorescence spectrometer (XRF, Thermo Scientific, USA) tested the types and contents of the elements in soil samples. The results are shown in Table 1. The other important physical and chemical properties of the soil sample used in the EKR/PRB system are listed in Table 2.

Batch adsorption studies

A series of adsorption studies were conducted in a conical flask of 250 mL and shaken at 200 rpm at room temperature for 24 h (except for the adsorption kinetics experiment). About 50 mg adsorbents were added to 50 mL Cr(VI) ion solution of 200 mg/L. And the formulas of the adsorption capacity and removal efficiency are given by Eq. (1) and (2):

\[ q = \frac{(C_0 - C_i)}{m} V \]  \hspace{1cm} (1)

\[ \eta = \frac{(C_0 - C_i)}{C_0} \times 100\% \]  \hspace{1cm} (2)
where \( q \) (mg/g), \( m \) (g), and \( V \) (L) represent the contaminant’s counterbalanced amount per unit mass of adsorbent, the adsorbent mass, and the sample volume, respectively; \( \eta \) means removal efficiency; \( C_0 \) is the initial Cr(VI) concentration; and \( C_t \) should be treated Cr(VI) concentration in \( t \) time.

Firstly, to understand the significance of new composites, seven different materials, including \( \text{Fe}_3\text{O}_4 \) nanoparticles, arginine alone, conventional powdered activated carbon (AC), pristine PPy, \( \text{Fe}_3\text{O}_4@\text{PPy} \), \( \text{Arg@PPy} \), and \( \text{Arg/Fe}_3\text{O}_4@\text{PPy} \), were used to compare their adsorption capacities by performing experiments. Secondly, to explore the effect of pH on adsorption properties, 0.1 mol/L HCl and NaOH solutions adjusted pH in the range of 2–12. And then, the subsequent experiments were conducted under optimal pH conditions. Studying the influence of the adsorbent dose was accomplished by changing adsorbents’ amounts from 0.01 to 0.09 g. Furthermore, the adsorption kinetics experiment was done by collecting the supernatants from the respective solutions at different times. And adsorption isotherm experiments were performed by varying the initial Cr(VI) concentration from 50 to 400 mg/L. The temperature study was conducted at 298, 308, 318, and 328 K under the same initial Cr(VI) concentration. Finally, in the regeneration experiment, 0.05 mol/L NaOH solution was used to desorb the materials after adsorption (Chigondo et al. 2019). The materials were washed three times with deionized water and dried at 60 °C. And then repeat the previous operation four times.

### Electrokinetic remediation experiments

The electric repair reactor was made of plexiglass, and it was separated into three areas: anode chamber, sample chamber, and cathode chamber. The soil of the sample room was averagely divided into three sections (S1, S2, S3) from anode to cathode, and a graphite plate and a stainless steel plate were used as the anode and cathode, respectively. An aluminum wire connected a DC power supply to two electrodes at a constant voltage (15 V). In the EKR/PRB, 200 g Cr-contaminated soils were placed in the sample reaction region after pretreatment. Four gram prepared composites were loaded into a 300-mesh filter bag and then put near the anode end. The diagram of the whole installation is shown in Fig. 1. Six groups of control experiments were set up. The initial experimental parameters are shown in Table 3. In the process of EKR, the system current and pH of anode and cathode electrolyte were measured every 12 h. After accomplishing EKR, the feasibility of several materials as PRB fillers was determined by the soil samples’ residual and leaching Cr(VI) concentration.

### Analysis method

The concentration of Cr(VI) in treated water was determined by the 1,5-diphenylcarbazide spectrophotometric method. The concentration of Cr(VI) in contaminated soil was measured based on Chinese standards HJ 1028–2019, using a flame atomic absorption spectrophotometer (AAS.

| Group | PRB               | Voltage gradients (V/cm) | Time (d) |
|-------|------------------|--------------------------|---------|
| EK_1  | /                | 1.5                      | 5       |
| EK_2  | AC               | 1.5                      | 5       |
| EK_3  | PPy              | 1.5                      | 5       |
| EK_4  | \( \text{Fe}_3\text{O}_4@\text{PPy} \) | 1.5 | 5 |
| EK_5  | \( \text{Arg@PPy} \) | 1.5 | 5 |
| EK_6  | \( \text{Arg/Fe}_3\text{O}_4@\text{PPy} \) | 1.5 | 5 |

Fig. 1 The installation diagram of EKR/PRB
AA6300C, Japan). The leaching toxicity of Cr-contaminated soils was determined, adopting sulfuric acid and nitric acid methods according to Chinese standard HJ/T 299–2007. Moreover, the pH and electrical conductivity of soils were also determined based on potentiometry and

Fig. 2  a FTIR. b N₂ adsorption–desorption isotherm. c SEM. d EDS photograph of four composites
Results and discussion

Characterization of composite materials

The FTIR spectroscopy of four composites is shown in Fig. 2a. From the chemical structure of pristine PPy, the characteristic peak at 1553 cm\(^{-1}\) was assigned to the C=C stretching vibration of the pyrrole ring, which confirmed the successful formation of PPy (Chithra et al. 2018; Sarojini et al. 2021). The other characteristic absorption bands at 1473 cm\(^{-1}\), 1314 cm\(^{-1}\), 1049 cm\(^{-1}\), 902 cm\(^{-1}\), and 682 cm\(^{-1}\) corresponded to the C-N stretching of pyrrole ring, C-N in-plane deformation, the plane deformation of C-H bond, C-H out-of-plane deformation, and C-H out-of-plane ring deformation, respectively (Abdi et al. 2017; Chithra et al. 2018; Sarojini et al. 2021; Wang et al. 2019). On the other hand, the typical characteristics of PPy could also be identified in Fe\(_3\)O\(_4\)@PPy, Arg@PPy, and Arg/Fe\(_3\)O\(_4\)@PPy. For Fe\(_3\)O\(_4\)@PPy, Arg@PPy, and Arg/Fe\(_3\)O\(_4\)@PPy, their bands were shifted to 1557, 1473, 1316, 1050, 922, and 685; 1556, 1473, 1315, 1051, 929, and 685; and 1560, 1476, 1299, 1052, 931, and 685, respectively. It indicated that adding dopants caused a subtle displacement compared to the pure PPy bands. That was caused by both Fe\(_3\)O\(_4\) and Arg penetrating the polymer structures to the binding energy of composites affecting each other. This conclusion was based on previous research, which attributed the shift caused by dopants in the FTIR spectra of pure polypyrrole to the infiltration of these substances into the polymer structures and their interaction with the bond energy of the synthetic polymer (Abdi et al. 2017).

Figure 2b exhibits the \(N_2\) adsorption–desorption isotherms of four composites. From Fig. 2b, the graphs of original PPy and modified PPy materials show IV-type isotherms with an evident \(H_2\) hysteresis loop in the range of \(P/P_0\) 0.8–1.0, indicating the presence of mesopores in all materials (Zhou et al. 2018). The porosity data were estimated to be listed in Table 4. Fe\(_3\)O\(_4\)@PPy, Arg@PPy, and Arg/Fe\(_3\)O\(_4\)@PPy revealed a larger surface area and pore volume than pristine PPy. It suggested the success of modified materials with a better adsorption capacity.

Scanning electron microscope analysis was done to investigate the morphology of the composites. SEM images of these polymers were obtained at a magnification of 40,000. It can be ascertained from Fig. 2c that pure PPy was composed of stacked and dense spherical particles. And Fe\(_3\)O\(_4\)@PPy reduced a part of the agglomeration phenomenon compared to PPy. Moreover, the Arg@PPy particles were distinctly smaller than pure PPy particles. Some large particles with smooth surfaces were exposed between those smaller particles, and it is supposed that these smooth and large particles were due to the presence of arginine. However, Arg/Fe\(_3\)O\(_4\)@PPy particles had a better dispersion because of the adulteration of Fe\(_3\)O\(_4\) nanoparticles. As can be seen, the type of dopants impacted the shape and size of polymer particles (Abdi et al. 2017).

EDS spectra are shown in Fig. 2d, revealing the elemental constituents of four materials. It displayed the obvious peak for Fe, confirming the incorporation of Fe\(_3\)O\(_4\) into PPy and Arg@PPy successfully. Furthermore, the semi-quantitative analysis of elements, including C, N, O, Fe, and Cr, was carried out through EDS spectra of four materials after EKR. It was found that the weight of Cr was 0.21%, 0.26%, 0.36%, and 0.22%, respectively. The results suggested that PPy, Fe\(_3\)O\(_4\)@PPy, Arg@PPy, and Arg/Fe\(_3\)O\(_4\)@PPy could remove Cr effectively from the contaminated soil.

Adsorption experiments

Comparison of adsorption properties of different materials

Figure 3 shows the adsorption capacities of seven different materials under the same reaction condition to justify the necessity of the composite materials. From it, the single arginine had little adsorption effect on Cr(VI) in the solution. And both AC and Fe\(_3\)O\(_4\) nanoparticles had a little adsorption capacity. However, the adsorption capacity of polymers was much higher than the above three materials, proving the necessity of materials’ recombination instead of a simple superposition. Protonation of PPy occurs in the acidic condition, producing electrostatic attraction with Cr(VI) to remove Cr(VI) and reducing high-toxicity Cr(VI) to low-toxicity Cr(III) probably (Shao et al. 2021). The addition of dopant, which causes chain alteration, can reduce the aggregation phenomenon during polymerization, further improving adsorption capacity (Kera et al. 2016).

Effect of pH

The pH of the aqueous solution plays a significant role during the attachment process, which affects adsorbent
adsorption on the adsorbate by altering the adsorbent’s ionization degree and superficial charge. Cr(VI) can mainly exist in five species, namely $\text{H}_2\text{CrO}_4$, $\text{HCrO}_4^{-}$, $\text{CrO}_4^{2-}$, $\text{HCr}_2\text{O}_7^{-}$, and $\text{Cr}_2\text{O}_7^{2-}$ (Wang et al. 2012). And the concrete species of Cr(VI) are strongly associated with the pH and concentration of the solutions. Under this working concentration, at pH 2 to 6.5, HCrO$_4^{-}$ is predominant, while CrO$_4^{2-}$ is predominant at pH $> 6.5$ (Zhao et al. 2010).

The effect of pH (2–12) is shown in Fig. 4a. It offers a downtrend in adsorption property with the increase of pH on the whole. A maximum adsorption capacity was recorded at pH 2 for all the composite materials, consistent with the previous study (Chigondo et al. 2019; Sun et al. 2014).
The adsorption capacities of several adsorbents decreased sharply from pH 2 to 3 and then fell further to below 10 mg/g at pH 12. This result at low pH (2–6.5) was mainly attributed to two factors. One was electrostatic adsorption between toxic metal ions and adsorbents due to the protonation of nitrogen atoms included in the adsorbent. So, there was high adsorption to HCrO$_4^-$ by the positively charged surface of composite materials (Avila et al. 2014; Kera et al. 2017; Sun et al. 2014). The other was a possible reduction process, and it was effortless for Cr(VI) to convert to Cr(III) through reduction because of the abundance of electrons in the polymer matrix (Qiu et al. 2014). On the contrary, deprotonation occurred on the positively charged nitrogen atoms of composite materials at relatively high pH, and between CrO$_4^{2-}$ species and material surface existed electrostatic repulsion. More HO$^-$ in strongly alkaline conditions may compete for binding sites with CrO$_4^{2-}$ (Avila et al. 2014; Qiu et al. 2014). In addition, the adsorption capacity of Arg@PPy was significantly higher than that of the other three materials at any pH because per arginine molecule containing four amino groups in Arg@PPy would generate more protonated nitrogen atoms.

**Effect of adsorbent dosage**

Adsorbent dosage is also a crucial parameter that decides the removal efficiency of Cr(VI). The effect of adsorbent dosage is observed from Fig. 4b, showing the removal efficiency of four composite materials increased with the increase in adsorbent amount. From 0.01 to 0.07 g, the extent of their growth was huge because of an increase in binding sites. However, the removal efficiency of Cr(VI) increased slightly from 0.07 to 0.09 g. There was a similar trend in research about the effect of dosage on adsorption capacity previously (Abdi et al. 2017; Chigondo et al. 2019). The reason was that the solution’s Cr(VI) ions were limited despite the number of available adsorption sites increasing. Attentionally, the removal efficiency of Cr(VI) by modified PPy was much higher than that of pristine PPy. Considering the removal...
efficiency and cost comprehensively, 0.05 g was used to the optimal adsorbent amount for the subsequent experiments.

**Effect of the initial Cr(VI) concentration and temperature**

The adsorption of Cr(VI) by four composite materials was investigated in the initial Cr(VI) concentration of 50–400 mg/L at four temperatures of 298, 308, 318, and 328 K, shown in Fig. 5. Obviously, the initial Cr(VI) concentration substantially affected the adsorption capacities of all varieties of composite materials. As a whole, the removal efficiency decreased with an increase in initial Cr(VI) concentration during this process, because the adsorbent will gradually reach a saturated state over time. The adsorbent available adsorption sites were relatively more than toxic metal ions at a low initial concentration of Cr(VI) at a constant dosage. In contrast, at a higher initial Cr(VI) concentration, the usability of these composites’ sites was lower than toxic metal ions. Hence, there was a descent of Cr(VI) removal efficiency.

Figure 5a depicts the effect of temperature on Cr(VI) adsorption by the pristine PPy, demonstrating a faint impact on Cr(VI) removal efficiency. Figure 5b, c, and d depict the influence of temperature on the adsorption of Cr(VI) by Fe₃O₄@PPy, Arg@PPy, and Arg/Fe₃O₄@PPy, respectively. In contrast to Fig. 5a, the Cr(VI) removal efficiency increased visibly with rising temperature under a constant initial Cr(VI) concentration, which represented the adsorption of Cr(VI) on the modified PPy materials was an endothermic process (Amalraj et al. 2016; Chigondo et al. 2019). Especially, it also found that the adsorption property of Arg@PPy was the smallest affected by temperature among the three.

**Adsorption isotherm study**

Adsorption isotherm is a basic design to investigate the partition of metal ions between the adsorbent and the liquid phase at equilibrium (Chithra et al. 2018). Freundlich adsorption isotherm is appropriate for asymmetrical
interface and multimolecular layer adsorption. Langmuir adsorption isotherm abides by the hypothesis of rhythm and uniformity of the adsorbent and combines with unilaminar adsorption onto an interface of numerous blank spots (Sarojini et al. 2021). The linear and nonlinear forms of them, $R_L$ (represents the applicability of the Langmuir isotherm), are shown in Eq. S1–S5. This study shows adsorption isotherms model data fit in Fig. 6.

The result, which included the correlate constants ($k_f$, $n$, and $q_m$) and coefficient ($R^2$) of adsorption isotherms after fitting, is shown in Table S1. The obtained result showed the highest $R^2$ value of the linear Langmuir model for the four materials. It suggested that the Langmuir isotherm had a great anastomose with the experimental results compared to other isotherms. On the other hand, based on the obtained experimental data, the $R_L$ at different initial concentrations is illustrated in Table S2. It is evident from the table that the values of $R_L$ were all between 0 and 1. Therefore, the linear Langmuir isotherm was thought to be favorable for the four materials. Consequently, the conclusion can be drawn that the adsorption mechanisms tended to agree with the Langmuir model.

**Adsorption kinetic study**

In this study, an adsorption kinetic study was conducted to estimate the adsorption rate of Cr(VI) with those composites. The obtained experimental results were fitted using pseudo-first-order and pseudo-second-order kinetic models. Those two models assume, respectively, that diffusion and chemisorption are the rate-limiting steps of the adsorption process. The equations of them are shown in Eq. S6–S9.

The graphs associated with the above equation are presented in Fig. 7. The related constants ($k_1$, $k_2$, and $q$) and correlation coefficient ($R^2$) obtained from Fig. 7 are revealed in Table S3. From Fig. 7, the $R^2$ obtained through the linear pseudo-second-order kinetic model was the highest among the models. Meanwhile, the adsorption capacities at equilibrium calculated by the pseudo-second-order kinetic model were closer to the values of the experiment. As a result, their

![Adsorption kinetics for Cr(VI) ion removal by four composites and fit data to linear a pseudo-first-order, b pseudo-second-order, nonlinear c pseudo-first-order, and d pseudo-second-order kinetic models' data fit](image_url)
Adsorption process can be explained by the linear pseudo-second-order kinetic model very well.

**Adsorption–desorption study**

It is essential to take the adsorbents’ cost into account, especially in large-scale applications. So, the reusability of adsorbents is vital. Figure 8 describes the change in the amount of the materials adsorbed after each desorption. It was noted that the adsorption capacity decreased by degrees as the number of cycles increased for all the adsorbents. For pristine PPy and Fe₃O₄@PPy, the variation range of adsorption capacity was small. That might be caused by the loss of adsorbents’ mass during operation. And the loading capacity of Arg@PPy and Arg/Fe₃O₄@PPy reduced relatively larger with the increase in desorption times. But the last adsorption capacity of both was more than 50% of the initial capacity, and they account for 52.94% and 55.48% of the initial adsorption capacity, respectively. One reason for this phenomenon was likely to be the imperfect desorption of Cr(VI) ions (Sarojini et al. 2021). Of course, the loss of mass was another factor. During the adsorption–desorption experiment, the materials after an adsorption test needed to be filtered and dried for the next adsorption test. There were inevitable residues in the filter paper when the materials were transferred from filter paper to conical flask, so it is difficult to ensure that the final amount of adsorbent remaining was equal to the 0.05 g used initially. Experimental data indicated that the lost mass of Arg@PPy and Arg/Fe₃O₄@PPy was 8.60% and 10.20%, respectively, after five cycles of adsorption–desorption experiments.

**Electrokinetic remediation experiment**

**Variation of electric current**

The trend of electric current change in all experiments over time is depicted in Fig. 9a. In EK₁–EK₆, traditional EKR and EKR/PRB systems filled with five different materials were applied.

It is worth mentioning that the initial current of EK₁–EK₆ had a difference. The initial current of EK₄ (3.6 mA), EK₅ (3.0 mA), and EK₆ (4.0 mA) was all higher than that of EK₁ (2.6 mA). However, the initial current of EK₂ (1.7 mA) and EK₃ (1.2 mA) was lower than that of EK₁. The plausible reason for this phenomenon was that modified PPy materials could release more charges at the beginning of the test (Wang et al. 2019). Overall, the electric current increased dramatically to reach a peak in the first 12 h and then a gradual decline to keep a relative stabilization, the same as that of most EKR processes (Nasiri et al. 2020; Tang et al. 2021; Wang et al. 2019). The possible reason for this tendency is presented below. The leading cause of the ascending pattern in early times could be the metal ion desorption in the soil.
Electrolyte permeated into the contaminated soil, resulting in the movement of Cr(III) diversified forms in the effect of electroosmosis and electromigration (Prakash et al. 2018). It also suggested the migration of toxic and hazardous metals and a positive remediation process. The decrease in electric current afterward could be deemed for reducing mobile free ions in the soil and the formation of hydroxide deposits.

In EK2, not only did the rate of current increase slowly, but the current was lower than EK1 from beginning to end. It proved that the presence of AC impeded probably the charge transport to a certain extent. However, the current of EK3–EK6 was higher than that of EK2. The improvement of electrolysis reaction speed made the ion concentration in the sample reactor increase (Wang et al. 2019). The reason may be the excellent electroconductibility of pristine PPy and modified PPy materials, which favored the charge transportation by the ions in the soil. Thus, the materials of EK3–EK6 were more suitable as PRB fillers compared to AC. That further illustrated that fabricated composites as PRB were beneficial to the EKR/PRB system.

Variation of pH in electrolyte

As shown in Fig. 9b and c, from beginning to end, the pH of EK3–EK6 in the anode compartment was lower than that of EK1, and it in the cathode compartment was higher than that of EK1. And it suggested that more H\(^+\) and HO\(^-\) were generated because of the current intensity with the presence of PPy or modified PPy materials in the EKR/PRB system. In general, the anolyte pH decreased sharply in EK1–EK6 in the early stage of the reaction and then held a strong acid condition until the termination of EKR. Oppositely, the catholyte pH increased at the start of the EK1–EK6 tests, and it kept a strong alkali environment until the experiment finished.

Remarkably, as shown in Fig. 9b, the pH value of EK6 was the lowest at the start. In the first 12 h, the pH value decreased to 2.89 drastically. The strength of the current at the beginning could explain this. And then, it dropped to 2.09 at 72 h, stabilizing around this value until the end of the test subsequently. The low pH of the electrolyte would cause the PRB near the anode chamber to be in an acidic environment, which was beneficial to the adsorbent’s adsorption of Cr. Similarly, as shown in Fig. 9c, the cathode chamber pH increased to 11.58 with the first 12 h of the process in EK6 quickly, and then it kept fluctuating up and down at this value. The presence of Arg/Fe\(_3\)O\(_4\)@PPy should be responsible for the noticeable phenomenon.

The soil pH and electrical conductivity after EKR

The pH value of contaminated soil in different areas (S1, S2, S3) after EKR is shown in Fig. 10a. The pH value of soil increased gradually from S1 to S3 after EKR in all experiments. The reason was that the electrolysis of water in the anode and cathode produced H\(^+\) and HO\(^-\), and then H\(^+\) and HO\(^-\) migrated towards the opposite electrode through the soil, respectively. At the same time, the pH of S1 in EK3–EK6 was lower than that of EK1. As explained in the “Variation of pH in electrolyte” section, PPy and modified PPy materials were possibly beneficial to the generation of H\(^+\). The more acidic the soil near the anode was, the better the PRB could remove Cr.
The electrical conductivity of contaminated soil in different areas before and after EKR is shown in Fig. 10b. The electrical conductivity of S1 was generally higher than that of S3 after EKR. It could be attributed to more enrichment of free anions near the anode than free cations near the cathode because the cathode cations combined with HO\(^-\) to form hydroxide precipitation. Moreover, the electrical conductivity of S1 in EK3–EK6 was much higher than that of the initial. Maybe because PPy has good charge storage capacity and good electrochemical performance, it could release charge to maintain high electrical conductivity nearby (Wang et al. 2019). The high conductivity indicated more free ions in the pore fluid and the relatively small resistance, which was conducive to the movement of Cr(VI). As for the electrical conductivity difference among EK3–EK6, the type of the dopant was the primary reason. They affected the electrical conductivity of the polymers by altering their arrangement and aggregation of molecular chains. From Fig. 10b, Fe\(_3\)O\(_4\) nanoparticles were the most conducive to the improvement of electrical conductivity.

**Residual and leaching concentration of Cr(VI)**

The residual Cr(VI) concentration was an essential criterion for measuring the effect of EKR. Cr(VI) concentration in soil was 212.69 mg/kg before EKR. As shown in Fig. 10c, it demonstrated two different patterns of change. The first one was a stepped distribution from S3 to S1 in EK1–EK3 and EK5. That resulted from the directional migration of Cr(VI) in the form of anions from the cathode to the anode.
in the EKR system. And the contaminants near the anode accumulated continually during the migration process, leading to the phenomenon of aggregation. The other was in EK₄ and EK₆, which resembled a normal distribution high in the middle and low on the two sides. The concentration of S₁ was lower than that of the former, which was significantly different from the previous model. The existence of Fe₃O₄@PPy and Arg/Fe₃O₄@PPy could be reasonable for explaining this phenomenon. The electrostatic attraction between the positively charged nitrogen atoms and the negatively charged Cr(VI) ions led to the PPy adsorption to Cr(VI) species. Then perhaps the Cr(VI) on the PPy interface occurred reduction reaction on account of electron-rich polymeric moieties of PPy to become Cr(III) (Wang et al. 2019). Additionally, the biggest otherness of Fe₃O₄@PPy and Arg/Fe₃O₄@PPy with other materials was that they contained Fe₃O₄ nanoparticles.

As shown in Fig. 11, the concentration of Fe in the anolyte reached a peak at 24 h and then declined until the EKR process was over. It could be speculated that Fe₃O₄ under a complex background would be released from the composite materials by Eq. (3). And Fe³⁺ near the anode would reduce Cr(VI) to Cr(III), further improving the Cr(VI) removal efficiency in S₁. The lowest Cr(VI) concentration was found in the section S₁ of EK₄. It illustrated the importance of Fe₃O₄@PPy for the removal of Cr(VI) in the EKR system. Unlike the consequence in the “Comparison of adsorption properties of different materials” section, the effect of Fe₃O₄@PPy was better than that of Arg/Fe₃O₄@PPy in the soil, possibly because it was in a more complex environment without pH 2. But the Cr(VI) removal efficiency in S₁ of EK₄ still increased by 26.04% compared to EK₃, illustrating that the profound of Arg@PPy for EKR was superior to pure PPy.

Unreasonable disposal of Cr-contaminated soil will cause substantial environmental hazards, and leaching toxicity was an essential indicator for identifying hazardous waste. Therefore, it was necessary to reduce the leaching concentration of Cr(VI) in Cr-contaminated soil. Cr(VI) initial leaching concentration was 8.41 mg/L. The pattern of the Cr(VI) leaching concentration after EKR was similar to the corresponding Cr(VI) residual concentration in soil. As shown in Fig. 10d, the lower the leaching concentration was meant to the higher the removal efficiency. That was the reason why its tendency was consistent with Fig. 10c.

Environmental implications and viability analysis of EKR/PRB for in situ application

The EKR combined PRB technology, an emerging technique for the polluted soil in situ remediation, makes the transmission of contaminants an initiative process under the function of electroosmotic flow and electromigration (Wen et al. 2021a). And it could remediate all kinds of pollutants, including persistent organic and metal/metalloid pollutants (Chen et al. 2021b; Raffa et al. 2021). Therefore, EKR/PRB technology exploration with high remediation efficiency and green PRB fillers had significant environmental impacts. This combinative technique has been studied and discussed deeply by many scholars in the lab (Kim and Han 2020, Ruiz et al. 2014; Wang et al. 2021; Wen et al. 2021a). Moreover, studying the issue of using EKR/PRB technology to remediate actual contaminated soil is of great significance for in situ application. Regrettably, some researchers tended to use artificially contaminated soil to study the characteristics of this technology (Alyani et al. 2021; Lee et al. 2021; Ribeiro et al. 2019). In this study, three kinds of modified polypyrrole green materials as PRB fillers were prepared to treat natural Cr-contaminated soil combined with EKR. The highest Cr(VI) removal efficiency increased by 74.16% compared with a single EKR in this work. It offered a further theoretical foundation for in situ application in the future.

Since the 1960s, due to the complexity and challenge of surface and underground pollution and the high cost of remediation technology, less than one-tenth of potentially contaminated sites worldwide have been repaired, and contaminated site remediation remains a major challenge (Naidu 2013). In the recent 20 years, the EKR/PRB technology was one of the few techniques developed for in situ treated contaminated soil, which is now expanding from basic laboratory research to remediate in the field.

The EKR/PRB technology mentioned in this work was filled with modified PPy possessing high contaminants’ adsorption capacity and renewability, which could satisfy good contaminants’ removal efficiency and economy.

\[ \text{Fe}_3\text{O}_4 + 8\text{H}^+ \rightarrow \text{Fe}^{2+} + 2\text{Fe}^{3+} + 4\text{H}_2\text{O} \] (3)
The adsorption property of Arg@PPy and Arg/Fe₃O₄@PPy was much higher than pristine PPy in Cr-polluted water at pH 2. PPy, Fe₃O₄@PPy, Arg@PPy, and Arg/Fe₃O₄@PPy accorded well with the kinetic pseudo-second-order and Langmuir isothermal models. In the EKR/PRB system, the three composites (Fe₃O₄@PPy, Arg@PPy, and Arg/Fe₃O₄@PPy) would influence system current, soil characteristic, and electrolyte pH, which was beneficial to improve the removal efficiency of Cr(VI), especially near the anode. The removal process of Cr(VI) by them included electrostatic attraction between Cr(VI) and protonated PPy and a possible reduction process from high-toxicity Cr(VI) to low-toxicity Cr(III). In all, this study offered a few ideas to deal with Cr-contaminated soil and water using green adsorbents.

**Conclusion**

The adsorption property of Arg@PPy and Arg/Fe₃O₄@PPy was much higher than pristine PPy in Cr-polluted water at pH 2. PPy, Fe₃O₄@PPy, Arg@PPy, and Arg/Fe₃O₄@PPy accorded well with the kinetic pseudo-second-order and Langmuir isothermal models. In the EKR/PRB system, the three composites (Fe₃O₄@PPy, Arg@PPy, and Arg/Fe₃O₄@PPy) would influence system current, soil characteristic, and electrolyte pH, which was beneficial to improve the removal efficiency of Cr(VI), especially near the anode. The removal process of Cr(VI) by them included electrostatic attraction between Cr(VI) and protonated PPy and a possible reduction process from high-toxicity Cr(VI) to low-toxicity Cr(III). In all, this study offered a few ideas to deal with Cr-contaminated soil and water using green adsorbents.
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