

Applying electrokinetic technology coupled with enzyme-induced carbonate precipitation treatment to Cu- and Pb-contaminated loess remediation

Application de la technologie électrocinétique associée à un traitement par précipitation de carbonate induit par des enzymes à l'assainissement du loess contaminé par le Cu et le Pb

W.C. Cheng*

School of Civil Engineering/Xi'an University of Architecture and Technology, Xi'an, China

L. Wang, Z.F. Xue

School of Civil Engineering/Xi'an University of Architecture and Technology, Xi'an, China

M.M. Rahman

UniSA STEM, ScaRCE, University of South Australia, Mawson Lakes, Australia

*w-c.cheng@xauat.edu.cn

ABSTRACT: Excessive copper (Cu) or lead (Pb) in soils can cause serious threats to surrounding environments and human health. In the present work, a modified EK (electrokinetic) reactor was proposed where the single and multiple EICP (enzyme-induced carbonate precipitation) treatments were incorporated into a permeable reactive barrier (PRB) for the first time to remove Cu and Pb metals. Results showed that the EK-PRB technology outperformed the EK technology. The PRB worked with the cathode electrolyte well to reduce the remaining Pb^{2+} by about 35%. The effect of multiple EICP treatments increased the potential of combining Cu^{2+}/Pb^{2+} with CO_3^{2-} , which caused difficulty in performing the electromigration and electroosmosis during the EK remediation. It, however, depressed the focusing effect. The higher cathode pH, induced by the effect of a single EICP treatment, was accompanied by the copper-ammonia complex formation, improving the fraction of Cu^{2+} removed by the cathode electrolyte well. The Pb removal behaved similarly to the Cu removal.

RÉSUMÉ: Un excès de cuivre (Cu) ou de plomb (Pb) dans les sols peut constituer de graves menaces pour l'environnement et la santé humaine. Dans le présent travail, un réacteur EK (électrocinétique) modifié a été proposé dans lequel les traitements EICP (précipitation de carbonate induite par des enzymes) simples et multiples ont été incorporés pour la première fois dans une barrière réactive perméable (PRB) afin d'éliminer les métaux Cu et Pb. Les résultats ont montré que la technologie EK-PRB surpassait la technologie EK. Le PRB a bien fonctionné avec l'électrolyte cathodique pour réduire le Pb^{2+} restant d'environ 35 %. L'effet de plusieurs traitements EICP a augmenté le potentiel de combinaison de Cu^{2+}/Pb^{2+} avec CO_3^{2-} , ce qui a rendu difficile la réalisation de l'électromigration et de l'électroosmose pendant l'assainissement EK. Cependant, cela a diminué l'effet de focalisation. Le pH cathodique plus élevé, induit par l'effet d'un seul traitement EICP, s'est accompagné de la formation d'un complexe cuivre-ammoniac, améliorant la fraction de Cu^{2+} éliminée par le puits d'électrolyte cathodique. L'élimination du Pb s'est comportée de manière similaire à l'élimination du Cu.

Keywords: Electrokinetic remediation; permeable reactive barrier; enzyme-induced carbonate precipitation; loess.

1 INTRODUCTION

The electrokinetic (EK) technology is applied to a variety of contaminated sites due to its good maneuverability (Han et al., 2021). Despite that, the electromigration and electroosmosis require a period of time and their energy consumption may be extremely high to achieve a satisfactory remediation efficiency (Song et al., 2022). Thus, a combination of the EK technology and other technologies may provide

a pathway to address the mentioned problems. The enzyme-induced carbonate precipitate (EICP) has drawn great attention as bacterial cultivation is not required prior to catalyzing urea hydrolysis (Sun et al., 2021). Permeable reactive barriers (PRB) are often applied to adsorb heavy metals in water bodies (Ma et al., 2022). The EICP technology may be incorporated into PRB to not only eliminate the discharge of NH_4^+ into surrounding environments but also improve the removal of heavy metals. Despite that, its interplay

with EK process is still unclear. In addition, OH⁻ can combine with Cu²⁺ or Pb²⁺ to develop the hydroxide precipitation surrounding the cathode, clogging the electroosmosis and electromigration during the EK remediation (Li et al., 2012). The main objectives of this study are to: (1) propose an EK reactor where the multiple EICP treatments are incorporated into PRB, (2) mitigate the focusing effect, and (3) explore the inherent mechanism affecting the removal efficiency.

2 METHODOLOGY

2.1 Electrokinetic reactor

The EK reactor was proposed and applied to the removal of Cu and Pb in the loess soil, as shown in Figure 1. The soil compartment containing five soil sections, namely A1 to A5, was separated from the anode and cathode electrolyte wells using a graphene plate. The Cu- or Pb- contaminated loess was loaded into A1, A2, A4, and A5, respectively, while a PRB was deployed into A3.

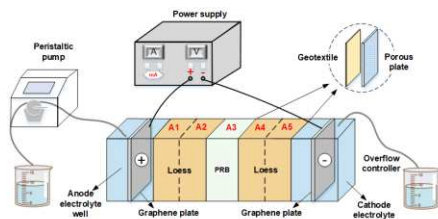


Figure 1. Schematic illustration of electrokinetic reactor.

2.2 Materials

The loess was taken from Jingyang County, Shaanxi Province, China, which is classified as low plasticity clay (CL). Copper nitrate (Cu(NO₃)₂) and lead nitrate (Pb(NO₃)₂) of analytical pure as a contaminant were applied to prepare Cu- or Pb-contaminated loess. Their concentration was manipulated to 500 mg/kg. In addition, PRB mainly consisted of urea, urease, and chitosan addition. The use of chitosan isolated the urease from Cu²⁺ or Pb²⁺, preventing its inactivation.

2.3 Experimental design

The experimental design mainly consisted of the control group (CG) and test group-2 (TG-2). CG neglected PRB. TG-2 took PRB into account where the multiple EICP treatments intervened in the EK remediation. The concentration of Cu or Pb was measured in accordance with the Tessier's sequential extraction procedure (Tessier et al., 1979). Five fractions (EXC: Exchangeable state, CAR: Carbonate combination state, OX: Fe-Mn oxides state, ORG:

Organic state, RES: Residue state) denoted different species of Cu or Pb.

3 RESULTS

3.1 EK remediation

Figure 2a shows the temporal relationships of electric conductivity applied to Cu removal using the EK technology. In CG test, the changes in electric conductivity fall within a 300 to 2000 μs/cm range. The electric conductivity in A5 goes into a decline at 4 h after the commencement of CG test, which is earlier than A4. Similar phenomena can also be seen in the temporal relationships of electric conductivity applied to Pb removal (see Figure 2b). Figures 2c and 2d show the temporal relationships of pH applied to Cu and Pb removals. As CG test progresses, the difference in pH between the anode and cathode becomes much more significant.

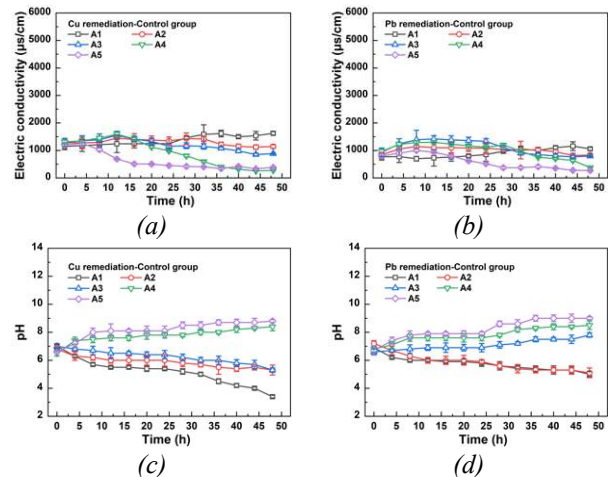


Figure 2. Temporal relationships of: (a) EC applied to Cu removal, (b) EC applied to Pb removal, (c) pH applied to Cu removal, and (d) pH applied to Pb removal.

Figures 3a and 3b show the temporal relationships of cumulative EOF (electroosmotic flow) and electric current applied to Cu and Pb removals. EOF increases very quickly to above 900 mL/h at 15 h for Cu removal and then remains a small change until the end of CG test. The electric current for Cu removal behaves similarly to Pb removal.

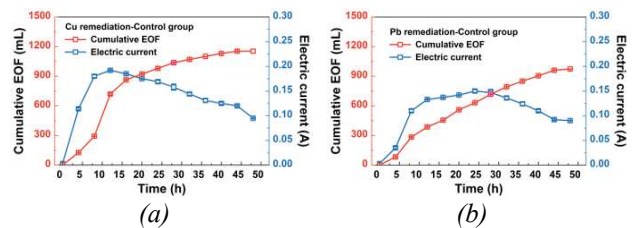


Figure 3. Temporal relationships of cumulative EOF and electric current applied to: (a) Cu removal and (b) Pb removal.

The relationships of removal efficiency versus soil section (A1 to A5) are shown in Figure 4. The removal efficiency decreases in a gentle manner from A1 to A5. The highest removal efficiency of 16% is attained in A1, while the lowest removal efficiency of 2% is attained in A5, most likely because of the hydroxide precipitation in the vicinity of the cathode.

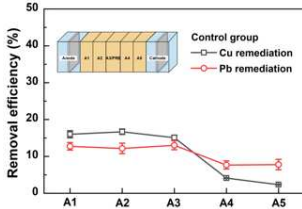


Figure 4. Variations of removal efficiency against soil section.

3.2 EK-PRB remediation considering the effect of multiple EICP treatments

Figure 5 shows the temporal relationships of electric conductivity applied to Cu and Pb removals respectively considering the effect of multiple EICP treatments. The multiple EICP treatments applied to TG-2 test encourage the sequential discharge of NH_4^+ and OH^- . Some of the EC curves lie above those in CG test (see Figures 5a and 5b). In CG test, the difference in pH between the anode and cathode enlarges with time (see Figures 2c and 2d). Here this phenomenon is not as pronounced as that in CG test (see Figures 5c and 5d).

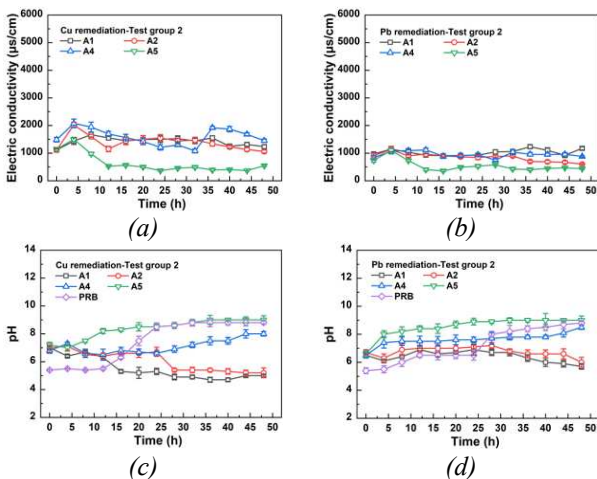


Figure 5. EK remediation (multiple EICP treatments) - Temporal relationships of EC applied to: (a) Cu removal and (b) Pb removal, - Temporal relationships of pH applied to: (c) Cu removal and (d) Pb removal.

Unlike CG test, EOF in TG-2 test starts increasing after a period of time (see Figure 6). The maximum EOF for Cu removal is higher in CG test than in TG-2 test. The maximum EOF for Pb removal is also higher

in CG test than in TG-2 test. Although the effect of multiple EICP treatments depresses the focusing phenomenon, it causes a side effect to prevent EOF from going higher. More details would be presented later in this paper.

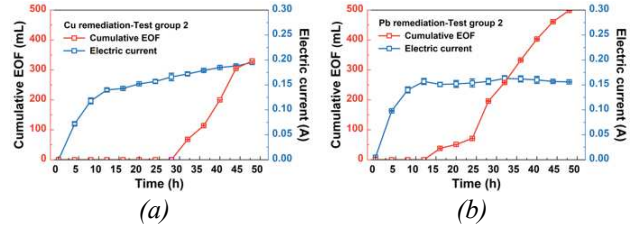


Figure 6. EK remediation (multiple EICP treatments) - Temporal relationships of cumulative EOF and electric current applied to: (a) Cu removal and (b) Pb removal.

The relationships of removal efficiency versus soil section (A1 to A5) are shown in Figure 7. In TG-2 test, the closer the soil section to the cathode, the higher the removal efficiency, meaning that Cu^{2+} or Pb^{2+} can migrate toward the cathode with no difficulty due to the absence of hydroxide precipitation. Despite that, the aforesaid side effect raises up the possibility of combining Cu^{2+} or Pb^{2+} with CO_3^{2-} that is heading toward the anode.

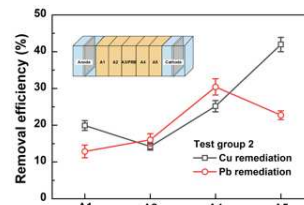


Figure 7. Variations of removal efficiency against soil section.

4 DISCUSSION

Compared to the initial CAR-Cu, CAR-Cu in A1 and A2 in CG test presents a small decrease (see Figure 8), indicating that a part of CAR-Cu desorbs due to exposure to acidic environments in the vicinity of the anode and migrates toward the cathode electrolyte well to achieve their removal (see Figure 9a). CAR-Cu in A4 and A5 in CG test shows a small change compared to the initial CAR-Cu. Alkaline environments around the cathode impede their desorption, causing CAR-Cu in A4 and A5 in CG test to remain nearly the same. In TG-2 test, CAR-Cu in A1 and A2 does not present a further decrease but an increase compared to CAR-Cu in A1 and A2 in TG-1 test (see Figure 8). TG-1 has been omitted herein due to limited space and takes the effect of a single EICP treatment intervenes into account. The effect of multiple EICP treatments increases the possibility of combining Cu^{2+} with CO_3^{2-}

and causes malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$) and azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) to precipitate, reducing the fraction of Cu^{2+} removed by PRB (referred to also as the ‘side effect’). CAR-Cu in A4 in TG-2 test also presents an increase rather than a further decrease. Since the effect of multiple EICP treatments narrows pH ranges in CG-2 test (see Figure 5), the lower pH of about 8 prevents copper-ammonia complex from developing (Xie et al., 2023), reducing the fraction of Cu^{2+} removed by the cathode electrolyte well. It is worth noting that the fraction of Cu^{2+} removed by the cathode electrolyte well is higher than that removed by PRB (see Figure 9a). In spite that the effect of multiple EICP treatments results in the side effect, it, however, mitigates the focusing effect, improving the fraction of Cu^{2+} removed by the cathode electrolyte well. Pb removal behaves similarly to Cu removal (see Figures 9b and 10).

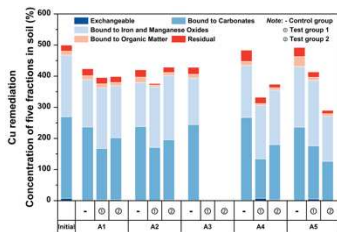


Figure 8. Distributions of five species applied to Cu removal.

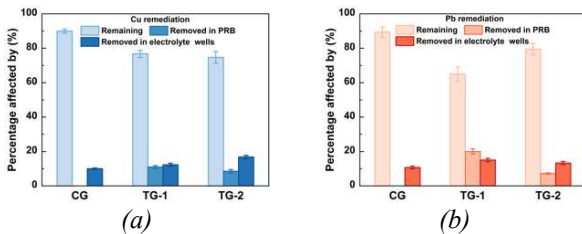


Figure 9. Mass balance calculation: (a) Cu removal and (b) Pb removal.

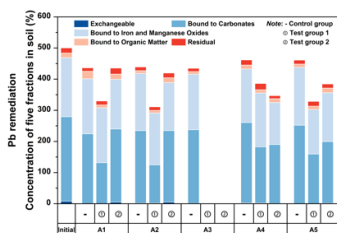


Figure 10. Distributions of five species applied to Pb removal.

5 CONCLUSIONS

Based on the results and discussion, some main conclusions can be drawn as follows:

(a) In this study, the bio-PRB that incorporates the EICP treatment applies to the EK technology as an

adsorbent. The EK-PRB technology outperforms the EK technology regarding the Cu and Pb removals.

(b) PRB reduces the remaining Cu^{2+} and Pb^{2+} by 10% and 20% respectively. PRB works with the cathode electrolyte well to reduce the remaining Pb^{2+} by 35%. The above highlights the role of PRB in the EK-PRB technology.

(c) The effect of multiple EICP treatments reduces the fraction of Cu^{2+} or Pb^{2+} removed by PRB. This, in turn, encourages the formation of azurite and malachite precipitation. Due to this reason, only a small number of Cu^{2+} or Pb^{2+} can migrate toward the cathode, reducing the focusing effect. Pb removal behaves similarly to Cu removal, although Pb^{2+} is more willing to combine with CO_3^{2-} .

REFERENCES

- Han, D., Wu, X., Li, R., Tang, X., Xiao, S., and Scholz, M. (2021). Critical review of electro-kinetic remediation of contaminated soils and sediments: Mechanisms, performances and technologies, *Water Air and Soil Pollution*, 232, 335. <http://doi.org/10.1007/s11270-021-05182-4>.
- Li, G., Guo, S.H., Li, S.C., Zhang, L.Y., and Wang, S.S. (2012). Comparison of approaching and fixed anodes for avoiding the 'focusing' effect during electrokinetic remediation of chromium-contaminated soil. *Chemical Engineering Journal*, 203, 231–238. <http://doi.org/10.1016/j.cej.2012.07.008>.
- Ma, L., Zhang, C., Liu, S., Luo, Q., Zhang, R., and Qian, J. (2022). Sensitivity analysis of factors influencing pollutant removal from shallow groundwater by the PRB method based on numerical simulation, *Environmental Science and Pollution Research*, 29, 82156-82168. <http://doi.org/10.1007/s11356-022-21406-4>.
- Song, P., Xu, D., Yue, J., Ma, Y., Dong, S., and Feng, J. (2022). Recent advances in soil remediation technology for heavy metal contaminated sites: A critical review, *Science of the Total Environment*, 838, 156417. <http://doi.org/10.1016/j.scitotenv.2022.156417>.
- Sun, X., Miao, L., Wang, H., Yuan, J., and Fan, G. (2021). Enhanced rainfall erosion durability of enzymatically induced carbonate precipitation for dust control, *Science of the Total Environment*, 791, 148369. <http://doi.org/10.1016/j.scitotenv.2021.148369>.
- Tessier, A., Campbell, P.G.C., and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals, *Analytical Chemistry*, 51(7), 844-851. <http://doi.org/10.1021/ac50043a017>.
- Xie, Y.X., Cheng, W.C., Wang, L., Xue, Z.F., Rahman, M.M., and Hu, W. (2023). Immobilizing copper in loess soil using microbial-induced carbonate precipitation: Insights from test tube experiments and one-dimensional soil columns, *Journal of Hazardous Materials*, 444, 130417. <http://doi.org/10.1016/j.jhazmat.2022.130417>.

INTERNATIONAL SOCIETY FOR SOIL MECHANICS AND GEOTECHNICAL ENGINEERING



This paper was downloaded from the Online Library of the International Society for Soil Mechanics and Geotechnical Engineering (ISSMGE). The library is available here:

<https://www.issmge.org/publications/online-library>

This is an open-access database that archives thousands of papers published under the Auspices of the ISSMGE and maintained by the Innovation and Development Committee of ISSMGE.

The paper was published in the proceedings of the 18th European Conference on Soil Mechanics and Geotechnical Engineering and was edited by Nuno Guerra. The conference was held from August 26th to August 30th 2024 in Lisbon, Portugal.