



Exploring electrode capture potential in different Cr-contaminated soils with enhanced electrolytes based on chemical fractionation



Junnian Wu*, Chaozheng Xiao, Honglin Wu

Gansu Key Laboratory for Environmental Pollution Prediction and Control, College of Earth and Environmental Sciences, Lanzhou University, Lanzhou 730000, China

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ABSTRACT

This paper investigated the electrode capture potential (ECP) of Cr in artificially and real contaminated soils during the electrokinetic remediation (EKR) with different electrolytes from a view of chemical fractionation to better understand the migration and transformation of Cr for a more efficient and environmentally friendly remediation process. The results indicated that the ECP includes the transformation potential (TP) among Cr fractions, the exchange potential (EP) and the migration potential (MP) of Cr. The ECP during Exp. 1, Exp. 2, Exp. 3 and Exp. 4 are 386.2, 0, 1412.76 and 347.73 g m^{-1} , respectively. The ECP for the real contaminated soil is limited by the transformation process among Cr fractions in the solid phase. For the artificially contaminated soil, the ECP mainly depended on the migration process of exchangeable Cr in the liquid phase. The MP of Cr in the liquid phase in real contaminated soil is higher than that in artificially contaminated soil. Citric acid as an electrolyte was a better choice for the real contaminated soil compared with KCl due to the higher TP of residual Cr and the low ecotoxicity risk. The ecotoxicity risk index (ERI) shown that the ecotoxicity risks of Cr in soils after experiments followed the sequence Exp. 4 > Exp. 2 > Exp. 1 > Exp. 3. The ecotoxicity risk of remaining Cr in Exp. 1, Exp. 3 and Exp. 4 after the EKR reduced, while that in Exp. 2 increased due to the high TP to the bound to Fe–Mn oxides (FM) and bound to organic matter (OC) fractions and the very low ECP. High ECP may potentially increase the ecotoxicity risk unless the MP is greater than the TP.

1. Introduction

Heavy metal pollution of soil has become a global environmental problem. It is particularly dangerous due to its ubiquity, toxicity and persistence [1]. Many previous studies have shown the feasibility of removing heavy metal from soil by electrokinetic remediation (EKR) [2–4]. The principal mechanisms of heavy metal contaminant transport under an electric field during EKR are electromigration, electroosmosis and electrophoresis [2,4,5]. And the most important electromigration, for which the heavy metal transport is one to two orders greater than that for the other mechanisms, is significantly dependent on the chemical species present in the soil [6–8], heavy metals easily moving in the cases of soluble and exchangeable forms, cannot easily mobilizing with organic ligands [9]. EKR applies a low current or low potential gradient to electrodes inserted into the contaminated areas. The level of current across the soil can determine the electroosmotic and electromigration, the greater the current the better the removal of the heavy metal [2,10]. And the redistribution of the chemical fractionation of the heavy metal in soil can be promoted by the current effect [11]. Therefore, the removal efficiency of EKR is directly related to the

chemical fractionation of heavy metal and the soil conductivity which vary with the soils. However, it is unclear that what role the chemical fractionation of metal plays during the EKR.

To increase the removal of heavy metal with the EKR technique, some researchers have proposed the use of enhanced electrolyte [12–14]. Some acid is added to the cathode chamber to adjust the soil pH and avoid the precipitation of heavy metals [15,16]. KNO_3 , NaNO_3 , Na_2SO_4 , etc. additives are used as baseline electrolytes [3,17–19]. Further, a complexing agent, chlorine or organic acid salt, was used as an electrolyte to increase the desorption of contaminants in the soil [20,21]. An enhanced electrolyte is not universally applicable, and different soils require different enhanced electrolytes [11,20] because the enhancement effect of different electrolytes on EKR is different. The understanding of the specific enhancement of enhanced electrolyte will help its expanded application and effective remediation of contaminated soil.

The removal efficiency is an indicator that we usually focus on during the EKR. It is only a final obtained simple result, and does not reflect the process in which heavy metal ions are removed. In order to improve the removal efficiency, it is necessary to understand the

* Corresponding author.

E-mail address: wu_jn@lzu.edu.cn (J. Wu).

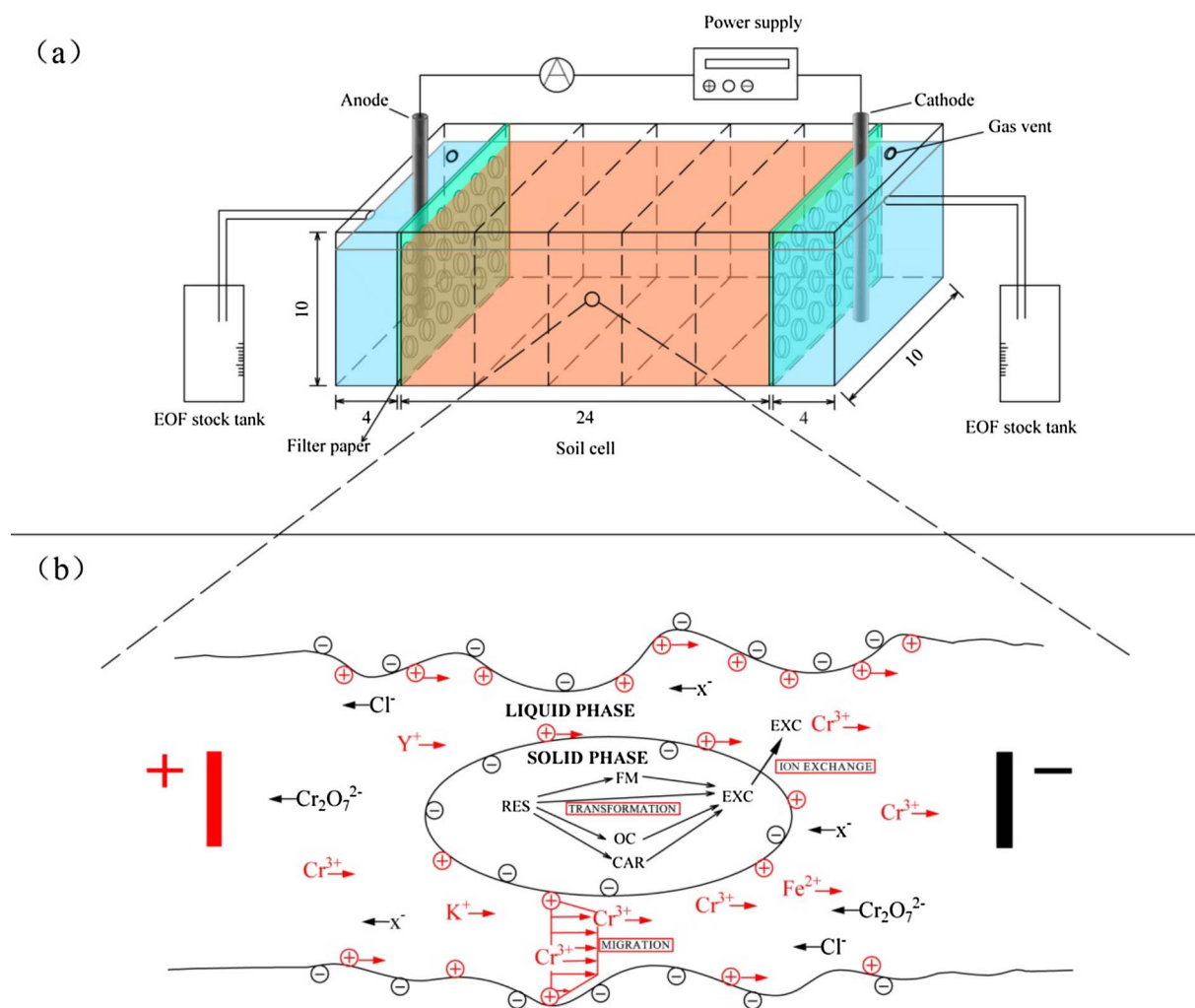


Fig. 1. (a) Schematic of the electrokinetic cell for setup A. (b) detail of the main mechanisms occurring during an EKR, X⁻: anions in the liquid phase, Y⁺: cations in the liquid phase, ⊕: Positive surface charge of soil, ⊖: Negative surface charge of soil.

migration and transformation of heavy metal in soil - water system. So, electrode capture potential (ECP) is proposed, which represents how easily heavy metals bound to soil particles are trapped by the electrode during EKR. It considers the chemical fractionation of heavy metal in solid phase and the migration of heavy metal ions in the liquid phase in soil - water system during EKR. There is no paper to systematically study it.

Although EKR has great potential for soil remediation, a large number of remaining heavy metals are sometimes still maintained in the soil after EKR [16,17]. Evaluating the ecotoxicity risk of remaining metal in soil after the EKR is of great importance for soil environmental safety. The total concentration of heavy metals does not represent their potential environmental impact, because their toxicity is not only related to their concentration, but also to their fractionations [22,23]. And chromium (Cr) is special heavy metal pollutant. Two common oxidation states of Cr in soil are Cr(III) and Cr(VI), which have drastically different charges and bioavailability. Cr(III) is stable and nontoxic but Cr(VI) is active and harmful. Wang et al. evaluate the environmental risks of Cu contaminated soil before and after EKR by using a series of bioassays [24] and suggest that the ecotoxicological effects of soil heavy metals on the soil biota and their bioavailability can be better understood in terms of their chemical fractionation [25]. Using animal experiments to quantify the bioavailable heavy metal concentrations as a base for assessing the ecotoxicological is usually expensive and may get into touch with ethical concerns [26,27]. Heavy metal chemical species may be a good choice for assessing the ecotoxicity risk of heavy

metals in soils, especially for real contaminated soils.

In this study, EKR experiments of real and artificially contaminated soils were conducted. Ultra-pure water, KCl and citric acid were selected as electrolytes. The main object of this paper is to research the ECP under different electrokinetic treatments to better understand the specific enhancement of KCl and citric acid on the EKR process, the role of Cr chemical fractionation and the differences of EKR for different Cr-contaminated soils. Finally, the ecotoxicity risk of remaining Cr in the soil after EKR was evaluated using the ecotoxicity risk index (ERI), which is of great importance for soil environmental safety. And the effects of the ECP on the ecotoxicity risk of Cr were studied for a more efficient (high ECP) and environmentally friendly (low ecotoxicity risk) remediation process.

2. Materials and methods

2.1. Soil samples for EKR

The real soil was collected in the vicinity of a chromate production plant, which is located in Zhangye, Gansu Province, China. The air-dried real soil was sieved with mesh 10 (2 mm). The real contaminated soil was pretreated by mixing real soil (< 2 mm particle size) with ultra-pure water for approximately 25% moisture content. The artificially contaminated soil was prepared to an initial Cr concentration of 485.6 mg kg⁻¹ by incubating the kaolin (Tianjin Hengxing Chemical Reagent Co., Ltd, China, pure chemical) with K₂Cr₂O₇ solution, and

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