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PII: S1385-8947(17)32122-8
DOI: https://doi.org/10.1016/j.cej.2017.12.010
Reference: CEJ 18171

To appear in: *Chemical Engineering Journal*

Received Date: 28 September 2017
Revised Date: 2 December 2017
Accepted Date: 2 December 2017

Please cite this article as: J. Tang, J. He, X. Xin, H. Hu, T. Liu, Biosurfactants enhanced heavy metals removal from sludge in the electrokinetic treatment, *Chemical Engineering Journal* (2017), doi: https://doi.org/10.1016/j.cej.2017.12.010

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Biosurfactants enhanced heavy metals removal from sludge in the electrokinetic treatment

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Abstract

High content of heavy metals in the sludge was the obstacle of sludge land application and resource recycling. In this work, rhamnolipid, saponin and sophorolipid were used to enhance heavy metals removal from the sludge in the electrokinetic tests. Also, the 0.1 mol L^{-1} HNO_3 was used to control catholyte pH in the electrokinetic tests. The electric current with the duration time variation, sections pH and heavy metals residual concentrations with space and time variations were investigated in the electrokinetic tests. Results indicated that these three biosurfactants and catholyte conditioning (0.1 mol L^{-1} HNO_3) could enhance heavy metals removal from sludge in the electrokinetic experiments. After EK experiments, Cu, Zn, Cr, Pb, Ni, Mn, Fe and Hg removal efficiencies in the enhanced EK experiment were higher than unenhanced EK experiment. Cu, Zn, Cr, Pb, Ni, Mn, Fe and Hg obtained an effective removal efficiency in the EK3 test, which were 55.8±5.46%, 73.8±6.23%, 64.0±5.11%, 51.6±5.32%, 60.8±2.12%, 56.0±3.21%, 41.0±2.12%, 35.0±2.12%, respectively. Heavy metals transferring toward the cathode were greater than anode, due to the free heavy metal ions and positively charged complexed heavy metal moved to the cathode chamber by electromigration. Rhamnolipid, saponin and sophorolipid can effectively enhance heavy metals removal from the sludge in the electrokinetic tests.

Keywords: Heavy metals, Electrokinetic tests, Rhamnolipid, Saponin, Sophorlipid

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1. Introduction

The biological treatment methods were commonly adopted by wastewater treatment plants (WWTPs) in the worldwide, which led to a large amount of sludge production [1, 2]. The latest statistics indicated that 6.25 million tons dry solids (DS) were generated in 2013 [3], and the amount of dewatered sludge (at a water content of 80%) has been increased from 30 million tons in 2012 to 34 million tons in 2015 in China [1, 3]. Nowadays, sludge disposal would be confronted with great challenges in China. Many sludge disposal methods have been used, such as utilization in building, land application, landfill and incineration [1, 3, 4]. As a matter of fact, land application is considered as the best way, because the sludge contains nutrient substances, such as nitrogen, phosphorus, potassium and organic matter [3]. However, wastewater treatment plants (WWTPs) treated the combining municipal and industrial wastewater, which lead to heavy metals concentrations increased in the sludge [5]. It is well known that several types of heavy metals, such as copper, zinc, chromium, lead, nickle, mercury and manganese, these heavy metals can be harmful to ecological environments and human beings, due to it can retain in soil limitlessly and accumulate in the environment, causing various disorders and diseases [5]. Therefore, heavy metal is restricted significantly in the utilization of sludge [1, 5].

Many techniques have been used to remove heavy metals from sludge, such as bioleaching, chemical extraction, electrokinetic treatment, ultrasound-assisted citric acid and super critical fluid extraction [2, 6, 7]. In these methods, the chemical

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extraction has been used more than other methods, because it obtained a high removal efficiency in the short time. However, it can produce high cost and low pH in the treatment process. Also, the chemical reagents may pose secondary pollution through the soil and groundwater. Therefore, it is necessary to find a proper method for removing heavy metal from sludge. In particular, electrokinetic (EK) technology can remove inorganic and organic compounds from soils [8], and demonstrate low cost and high effective method for removing heavy metal from sludge, contaminated soil and sediment [8, 9]. EK technology involves the application a low direct current (0-1 A) or direct electric voltage gradient (0-2 V cm^{-1}) across electrodes inserted into the contaminated soil, sludge, sediment, which can produce direct current electric field and cause heavy metal ions migration through the contaminated sites towards the anode or cathode [1, 8, 10], because three main migration mechanisms in the EK process: (1) electroosmosis, (2) electromigration, and (3) electrophoresis. For instance, toxic heavy metal ions are mainly transported by electromigration, which is the migration of ions towards an oppositely charged electrode [1, 8, 11]. In the EK process, water reduction occurs at the cathode, hydroxyl ions (OH^-) generated, which indicated high pH at the cathode. On the other hand, water oxidization occurs at the anode chamber, and produced H^+ ions, which demonstrated low pH at the anode. In this process, the electrolyte pH variation led to heavy metal desorption, charge, fractions, and residual concentration variation [12, 13]. The high pH value at near the cathode is a predominant obstacle, which impeded heavy metal solubilization and

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migration. Dissolved metal ions adsorbed onto the soil or sludge particles, precipitated as hydroxides, carbonates and other compounds in the high pH zone at near the cathode [8, 12, 14]. However, using the improving program or regulating conditions can break the obstacle in the EK process. In order to obtain a high removal efficiency, it is necessary to maintain heavy metal in the dissolved state. The chelant-enhanced EK experiment can improve heavy metal removal from contaminated matrices [12]. However, these chelants and organic acids are non-biodegradable, which can pose secondary pollution in the environment. Therefore, replacement of these chelants, which have these following characteristics: environmental-friendly, biodegradable, less expensive and high removal efficiency, they would be highly desirable.

The non-toxic and biodegradable agents can be utilized to enhance heavy metal removal from soil, sediment and sludge. These agents mainly contain humic acids [13], cyclodextrins [15], and biosurfactants [16]. In particular, these biosurfactants mainly extracted from microbes, such as bacteria, fungi and yeast, which indicated the bioavailable surface-active ability [17-19]. Compare with synthetic surfactants, biosurfactants have larger molecular structures and more functional groups, have a strong surfactivity, can decrease surface and interfacial tension, and form micelles, these characteristics can enhance heavy metal and hydrophobic organic compound removal from contaminated sites [7, 20, 21]. Moreover, the biosurfactant have higher biodegradablility, ecological safety, and low toxicity [7]. Rhamnolipid, an anionic

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biosurfactant, it has low toxicity, biodegradability, and renewable production sources, it produced by *Pseudomonas aeruginosa,* which is a class of biosurfactant known to complex heavy metals, the rhamnolipid have conditional stability constants for heavy metals cations [7, 18]. Therefore, rhamnolipid was used as a collector in the flotation of chromium from the aqueous solution, and obtained a high removal efficiency [16]. Rhamnolipid can effectively remove cadmium and chromium from the soil, significantly and simultaneously promote heavy metal and arsenic removal from mine tailings, and effectively enhance EK technique removal metals from dredged marine sediments [22-24]. Saponin as non-ionic biosurfactant with excellent performance and wide presence in nature, are mainly secondary compounds in many plants resulting in mass production with low cost [17, 25]. It can enhance removal heavy metals (Cu, Cd and Zn) from contaminated soils, the highest removal efficiency was 82-90% [25]. Therefore, the performance is comparable with inorganic acids (HCl and H_2SO_4) and even higher than for chelating agents. Also, the saponin has ability to complex heavy metals. The environmental compatability, low toxicity and biodegradability of saponin make it a useful agent [17]. Sophorolipid produced the yeast *Torulopsis bombicola*, it can reduce the surface tension to 33 mN m^{-1}, increase heavy metal solubility, and form micelles above the CMC (critical micelle concentration). Sophorolipid can enhance heavy metal removal from contaminated sediments and soils [26]. According to previous studies, these biosurfactants have both carboxyl and hydroxyl, which are able to form mobile and stable complexes with heavy metal ions [21, 27], these

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complexes promote heavy metals mobilization and migration from contaminated sites. Therefore, rhamnolipid, saponin and sophorolipid were used to enhance heavy metal removal from sludge in the EK technique, which have not explored. As far as we know, few scientific studies have reported about these biosurfactants (rhamnolipid, saponin and sophorolipid) as enhancing agents in the EK technique.

In view of above-mentioned studies about interaction of biosurfactant with heavy metal, these biosurfactants would be able to promote removal heavy metal from the sludge in the EK technique, and obtain high removal efficiency. Therefore, the aim of this study were to examine (1) rhamnolipid, saponin and sophorolipid were used as enhancing agents, and 0.1 mol L^{-1} HNO_3 was used as catholyte in EK experiments, electric current and sludge pH variations were investigated. (2) these different biosurfactants enhance heavy metals removal with time and space variations were compared in the EK tests.

2. Materials and methods

2.1. Sludge sample

The sludge sample was collected from Qun Li Urban Wastewater Treatment Plant, which located in Harbin. It treats municipal wastewaters with industrial wastewater accounting for 40% of total wastewater [17]. The sludge sample was air-dried, and then followed by grinding and sieving to a #100 (0.149 mm) before analysis, then the sieved sample was stored in the desiccator. Sludge sample main properties are summarized in Table 1.

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Heavy metal concentrations were presented Table 1, Cu and Zn concentrations were higher than the control standards for pollutants in sludge from agricultural use (500 and 250 mg kg^{-1} for acid soil where pH$<$6.5, 1000 and 500 mg kg^{-1} for alkaline soil where pH$\geqslant$6.5 for Zn and Cu, respectively) and the environmental quality standard for soils (500 and 400 mg kg^{-1} for Zn and Cu, respectively). High concentrations of heavy metals can destroy ecosystem and human health without treatment. Take into account these heavy metals (Cu, Zn, Cr, Pb, Ni, Mn, Fe and Hg) accumulation in the environment. The above mentioned heavy metals were studied in this work.

2.2. Biosurfactants characteristics

The rhamnolipid (purity over 85%) was purchased from Daqing Victex chemical Co., Ltd. It was composed of $RhaRhaC_{10}C_{10}$ ($C_{32}H_{58}O_{13}$, m/z=649) and $RhaC_{10}C_{10}$ ($C_{26}H_{48}O_9$, m/z=503). The rhamnolipid critical micelle concentration (CMC) was determinated to be 13.25$\pm$2.58 mg L^{-1} with minimal surface tension of 33.45$\pm$4.52 mN m^{-1}.

Saponin is brown power, it was purchased from Shanghai Ryon Biological Technology CO., Ltd. It consists of triterpene glycosides mixture, which obtained from the tree *Qullajasaponaria* [17]. The maximum sapogenin concentration was 25%, and hydrophilic portion is functional group, which consist of sugar chains. The ring method was used to measure the minimal surface tension and critical micelle concentration (CMC) of saponin, which values were 37.12±5.78 mN m^{-1} and

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57.21±8.35 mg L^{-1}, respectively [17].

Sophorolipid is yellow liquid and purity is 52.00%. It was purchased from Shandong Jin Mei Biotechnology Co., Ltd. The ring method was used to measure the minimal surface tension and critical micelle concentration (CMC) of sophorolipid, which values were 34.23±3.23 mN m^{-1} and 56.21±5.35 mg L^{-1}, respectively.

2.3. EK system and experimental conditions

Fig. S1 shows a schematic diagram of electrokinetic reactor, which used in this study. The electrokinetic reactor was made of Plexiglass. It was composed of sludge chamber (L×W×H=20 cm×10 cm×10 cm), two graphite electrodes (L×W×H=12 cm×9 cm×1 cm) and two electrode compartments (L×W×H=5 cm×10 cm×10 cm), which were used as anode and cathode chamber, respectively. One DC power supply, two peristaltic pumps, one multimeter, and two working solution reservoirs. To avoid sludge leakage into electrode chambers, two pieces of cellulose filter paper were placed between electrode compartment and sludge cell. Two electrodes were connected to the DC power supply, which supplied the constant voltage. The multimeter monitored the electric current during the electrokinetic process. Two peristaltic pumps were used to circulate the electrolyte from the electrolyte chamber into the corresponding electrolyte compartment to maintain a constant level in electrode compartments during the electrokinetic process.

2.4. Electrokinetic tests

Electrokinetic tests were carried out under the different electrokinetic conditions

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(Table 2). In the EK tests, the deionized water was used as the anolyte, while the deionized water and 0.1 mol L^{-1} HNO_3 were used as catholyte in the unenhanced EK test (EK1) and enhanced EK tests (EK2, EK3, EK4, and EK5), respectively. During all the EK tests processes, to maintain the electrolyte solutions properties constant, the electrolyte solution was refreshed every 24 h to maintain the continuous operation of experiments and ensure the regularity of electrolyte addition. EK tests were performed in the eletrokinetic reactor using 2000 g of dry sludge, mixed with 1000 mL of deionized water for EK1 and EK2 tests, and with 1000 mL rhamnolipid solution (2.0 g L^{-1}), saponin solution (2.0 g L^{-1}) and sophorolipid solution (2.0 g L^{-1}) for EK3, EK4 and EK5 tests, respectively. To make uniformity, the sludge and saturation were mixed and stirred several minutes. All of the EK tests were carried out under the constant voltage gradient (1 V cm^{-1}) for 192 h. Table 2 presented all the EK tests conditions. The inserting pH electrode into the sludge, which measured sludge pH every 10 h. The sludge sample was equally divided into 5 sections from anode to cathode (from S1 to S5). Sludge sample were taken at these sections with a plastic tube, after EK treatments for 48, 96, 144 and 192 h, respectively. All the sludge samples were oven dried at 105℃ for 24 h and analyzed for heavy metals concentrations (C). Heavy metals removal efficiencies (R) was then calculated as following Eq. (1):

$$R = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where C_0 is the initial heavy metal concentration (mg kg^{-1}).

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2.5. Chemical and analytical methods

First, an appropriate amount of sludge sample was used to analyze water content, which was measured by weight loss after heating the sample to 105 ℃ for 24 h, the sludge water content is 79.35±3.32%, and other sludge sample was air dried, then ground and sieved using a #100 (0.149 mm) mesh. Heavy metals concentrations were measured by acid digestion in before and after electrokinetic treatments. The digestion instrument (SH230N, Jinan) was use to digest sludge samples with the strong acid digestion (HCl-$HClO_4$-HNO_3) at 180-200 ℃ [17]. Heavy metals concentrations were analysed by an Optima5300DV ICP-MS (PerkinElmer, USA). All the experiments were carried out in triplicate to evaluate the reproducibility of the results, and the average result was reported.

2.6. Calculations of electric energy consumption

The accumulated energy consumption (W) in the electrokinetic experiment was calculated as:

$$W = \int_0^t UI dt \tag{2}$$

where U is the voltage between the anode and cathode (V), I is the electric current (A), and t is the electrokinetic treatment time (h).

2.7. Reproducibility assurance and laboratory quality control

Test procedures were used to ensure the reproducibility of EK tests [28] : (1) graphite electrodes and filter papers were new in this study; (2) the plexiglass reactor was washed by HNO_3 (5% w/w) solution, and then with tap water and deionized

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water to avoid contamination; (3) three parallel samples in each and twice chemical analyses with one sample were performed; (4) all digestion tests had a blank sample; (5) all the data were shown as the mean values and relative standard deviation.

3. Results and discussion

3.1. Electric current variation during EK treatment

Electric current with the duration time was indicated in Fig. 1. It is closely bound up with mobile metals ions, which indicated mobile heavy metals ions contents in the EK treatments [28]. As can be observed Fig. 1, the deionized water was used as catholyte in the EK1 treatment, which pH value was not adjusted. The electric current was lower than other EK experiments, due to heavy metal ions formed precipitates and high resistance at near the cathode [13, 29]. As seen in Fig. 1, the 0.1 mol L^{-1} HNO_3 was used as the catholyte in the EK2, EK3, EK4 and EK5 tests. The electric current immediately increased from initial value to maxmium value, and then dropping slowly towards the minimum value. In the first stage (0-10 h), EK1 obtained the maxmium value (82.37 mA) after 8 h, EK2 and EK4 obtained the maximum value 88.84 mA and 95.23 mA after 5 h, respectively. EK3 and EK5 obtained the maximum value 93.53 mA and 101.12 mA after 4 h, respectively. After reaching the maximum value, the electric current decreased in the EK tests, and then maintained the constant, because of the depletion of electrolyte, non-conductive solids, heavy metal hydroxide precipitation [8, 10], and electrode polarization [13, 30, 31]. During enhanced EK experiments (EK2, EK3, EK4 and EK5) process, 0.1 mol L^{-1} HNO_3 was used to

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control catholyte pH value, impeded the high pH region and reduced the precipitate at the cathode zone. Moreover, a large amount of mobile heavy metals ions migrated into cathode chamber, which could lead to a raised electric current [32]. Results demonstrated that rhamnolipid, saponin and sophorolipid solutions were used to pretreat the sludge, which led to electric conductivity increasing rapidly. These biosurfactants promoted heavy metals removal from sludge, bound with heavy metals, and then form complexes [17, 18].

3.2. Sludge pH variations during EK process

Fig. 2 indicated sludge profile pH variations with duration time during the electrokinetic process. As can be observed Fig. 2, the sludge pH value continuously raised at near the cathode (S5) during the EK1 process. However, the sludge pH dropped to 2.0 or slightly below at near the anode (S1), due to the electrolysis of water in the anode chamber produced H^+ ions with the liberation of O_2. For this reason, the pH near the anode (S1) was lower than other four sections in the EK experiments. After the electrokinetic test, the sludge pH was 11.25 at near the cathode (S5), whereas, it obtained 5.50 at near the anode (S1) in the EK1 experiment, in which catholyte refreshment with 0.1 mol L^{-1} HNO_3 was not implemented. The sludge pH varied from 7.01 to 5.50 at the anode, while it varied from 8.67 to 11.25 at the cathode. In the unenhanced EK experiment (EK1), the pH variation caused by the electromigration of OH^-/HCO_3^- and H^+ from the cathode and anode chambers, respectively [13, 32]. As can be observed Table 2, EK2, EK3, EK4 and EK5 were

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performed under the different EK enhanced types, the acidic solution (0.1 mol L^{-1} HNO_3) was used to maintain the lower pH at near the cathode. It can be observed in Fig. 2, the sludge pH variation at near to cathode (S5) in the enhanced EK experiments (EK2, EK3, EK4 and EK5) were significantly different from in the unenhanced experiment (EK1). For enhanced EK experiments, Fig. 2 demonstrated that sludge pH values were lower than 8.0 in the enhanced EK tests, H^+ produced at the anode and transferred toward the cathode in the electric field, which lead to sludge pH values decreasing at near the cathode. Sludge pH values about 8.0 at near the cathode, because the catholyte was adjusted by the 0.1 mol L^{-1} HNO_3 in the enhanced EK experiments, also the H^+ migration is 1.75 times higher than OH^- [13].

3.3. Effect of different time and sapce on heavy metals distribution during the electrokinetic process

3.3.1. Unenhanced EK experiment

Heavy metals residual concentrations with time and space variations in the different five sections were demonstrated in Fig. 3. Heavy metals migrated toward the cathode from anode chamber, due to the electromigration and electroosmosis in the electric field [12, 33]. Fig. 3 indicated that heavy metals removal efficiencies increased with treatment time raising, and can migrate close to the cathode. In the EK1 experiment, the catholyte solution was not implemented by the nitric acid during the electrokinetic process, and heavy metal removal efficiency was 25.00-40.00% at near the anode, whereas, the removal efficiency was lower at near the cathode,

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because heavy metal ions formed $M(OH)_n$ precipitate in the high pH region at near the cathode [8]. Also, heavy metals bind with sulfide and organic matters (oxidizable fraction), and non-silicate, silicate and mineral matter (residual fraction), these fractions are hardly to remove without destroying the compound [7, 10, 29]. Therefore, the different enhanced EK techniques were investigated in this wrok. By the end of EK1 experiment, Cu, Zn, Cr, Pb, Ni, Mn, Fe and Hg removal efficiencies were 25.20%, 42.4%, 39.80%, 30.80%, 33.20%, 27.60%, 30.00% and 30.00% respectively. In order to obtain a high removal efficiency, enhanced EK tests were investigated in this work.

3.3.2. Acid-enhanced EK experiment

Fig. 4 demonstrated that heavy metals residual concentrations with time and space variations in the different five sections during the EK2 process. Generally speaking, heavy metal obtained a higher removal efficiency at S1 section than S5 section during the EK2 process, due to the positive charged heavy metals migrated the opposite anode chamber by electromigration and electroosmosis in direct current electric field [8, 29]. Furthermore, heavy metals removal efficiencies were higher than EK1 experiment, because the nitric acid was used as the catholyte conditioning, which led to heavy metals desorption from the sludge particles [5, 17, 23], the low pH value at near the anode, heavy metals mainly existed as ions and transferred toward the cathode [34]. At the end of this experiment, Cu, Zn, Cr, Pb, Ni, Mn, Fe and Hg removal efficiencies were 32.00%, 39.60%, 47.00%, 37.20%, 47.80%, 41.20%,

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39.00% and 32.00%, respectively. Ni obtained a high removal efficiency in the EK2 tests, due to Ni mainly formed unstable fractions (exchangeable and reducible fractions) in the sludge, which were easy to remove from the sludge in an acidic condition [17].

3.3.3. Rhamnolipid-enhanced EK experiment

Heavy metals residual concentrations in the different five sludge sections with time and space variations during the EK3 process was shown in Fig. 5. In the EK3 experiment, the sludge was pretreated by rhamnolipid solution, and the nitric acid was used to control catholyte pH. Therefore, heavy metal obtained a higher removal efficiency. After the EK3 test, Cu, Zn, Cr, Pb, Ni, Mn, Fe and Hg removal efficiencies were 55.80%, 73.80%, 64.00%, 51.60%, 60.80%, 56.00%, 41.00% and 35.00%, respectively. Heavy metal obtained removal efficiencies in the EK3 test were higher than EK1 and EK2 tests, due to fuctional groups of rhamnolipid, such as carboxyl and hydroxyl, these groups has ability to form mobile heavy metal complexes. Also, rhamnolipid can reduce the surface tension and increase heavy metals solubility [18].

3.3.4. Saponin-enhanced EK experiment

Fig. 6 demonstrated that heavy metals residual concentrations distribution with time and space variations in the different five sections during the EK4 process. Heavy metal ions moved toward the oppositely charged electrodes in the direct electric field. In the EK4 experiment, the saponin solution was used to pretreated sludge, and the nitric acid was used to control catholyte pH, which can avoid the high pH at near the

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cathode. As can be observed Fig. 6, heavy metals can migrate from anode to cathode in the constant electric field. At the end of EK4 experiment, heavy metal obtained an effective removal efficiency. Cu, Zn, Cr, Pb, Ni, Mn, Fe and Hg removal efficiencies were 59.00%, 66.40%, 60.60%, 57.40%, 58.40%, 56.20%, 38.00% and 40.00%, respectively. As can be observed in Fig. 6, from the analysis of heavy metals removal efficiencies in the different treatment times (48, 96, 144 and 192 h), it can be indicated that higher treatment times would promote heavy metals removal from the sludge section at near the anode.

3.3.5. Sophorolipid-enhanced EK experiment

Fig. 7 demonstrated that heavy metals residual concentrations in the different five sections with time and sapce variation during the EK5 process. In the EK5 experiment, the sophorolipid was used to pretreat the sludge, and the nitric acid was used to control catholyte pH. Fig. 7 indicated that heavy metals migrated from anode to cathode, and residual concentrations decreased at near the anode. As well as, with the increase of processing time, heavy metals residual concentrations decreased at near the anode. During the EK5 process, heavy metals residual concentrations in the S3 and S4 sections were higher than other sections (S1, S2 and S5). Because heavy metal ions migrated from anode to cathode in the sludge. With generation of H^+ at the cathode chamber, the sludge pH gradually increased at near the cathode. At the high pH region, heavy metals ions may be form $M(OH)_n$ precipitate in the S3 and S4 sections. At the end of EK5 experiment, heavy metal obtained a high removal

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efficiency. Cu, Zn, Cr, Pb, Ni, Mn, Fe and Hg removal efficiencies were 53.20%, 62.00%, 53.00%, 52.40%, 56.20%, 59.20%, 37.00% and 45.00%, respectively. As can be seen in Fig. 7, through the summary of heavy metals removal efficiencies in the different treatment times, which can be indicated that longer treatment times can enhance heavy metals migration at near the anode and cathode region.

3.4. Comparison of heavy metals residual contents distribution after the different EK treatments

Fig. 8 indicated that heavy metals residual concentrations in the different five sections at the end of electrokinetic experiments. As can be observed Fig. 8, the result demonstrated that EK tests have ability to remove heavy metals from the sludge.

As can be seen Fig. 8, at the end of EK tests, Cu obtained the highest removal efficiency (75.00%) at near to the anode in the EK3 experiment. Whereas, the lowest removal efficiency (27.00%) at near to the anode in the EK1 experiment. The nitric acid was applied to control catholyte pH in the EK2 test, Cu obtained removal efficiency (47.00%) higher than EK1 experiment at near to the anode. Rhamnolipid, saponin and sophorolipid were used to pretreat sludge during the EK process. Compared with the EK2 experiment, these biosurfactants obtained an effective removal efficiency in the biosurfactant-enhanced EK tests (EK3, EK4 and EK5). Cu total removal efficiencies were 25.20%, 32.00%, 55.80%, 59.00% and 53.20% for EK1, EK2, EK3, EK4 and EK5, respectively. EK3, EK4 and EK5 obtained removal efficiencies were higher than EK2 and EK1. It may be form rhamnolipid-Cu,

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saponin-Cu and sophorolipid-Cu complexes that can ameliorate heavy metals mobility in the direct electric field [20, 22, 25].

As shown in Fig. 8, Zn removal efficiencies in the EK1 and EK2 experiments were lower than other enhanced EK tests (EK3, EK4 and EK5), which indicated that biosurfactants and nitric acid can enhance Zn removal from the sludge. In the EK3 experiment, Zn total removal efficiency was 73.80%, and the Zn residual concentrations increased from S1 to S3 section, then decreased from S3 to S5 section, which formed a parabolic shape. It may be due to insufficient remediation time in the EK3 tests. In the EK2, EK4 and EK5 experiments, Zn residual concentrations increased from anode to cathode, due to Zn migration from anode to cathode in the constant electric field. Zn total removal efficiencies were 66.40% and 62.00% in the EK4 and EK5 experiments, respectively. In the EK3 experiment, Zn had the highest removal efficiency, because the more soluble metal-complexes of rhamnolipid, and the stronger react with the carboxyl and hydroxyl than sophorolipid and saponin [21].

Fig. 8 demonstrated Cr residual concentrations in the different five sections during the EK process. Cr residual concentrations decreased from S1 to S5 section. Also, Cr obtained high removal efficiencies in the cathode sections. Cr total removal eficiency was more than 53.00% in the biosurfactants enhanced EK tests, and removal efficiencies were 64.00%, 60.60% and 53.00% in the EK3, EK4 and EK5 tests, respectively, which these removal efficiencies were higher than EK1 and EK2.

As shown in Fig. 8, at the end of EK tests, Pb removal efficiency was only

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30.80% in the EK1 test. Whereas, Pb removal efficiencies were 37.20%, 51.60%, 57.40% and 52.40% in the EK2, EK3, EK4 and EK5 tests, respectively. These results demonstrated that rhamnolipid, saponin and sophorolipid and catholyte conditioning pH can promote Pb removal from the sludge in the enhanced EK remediation.

Ni removal efficiencies were 33.20% and 47.80% in the EK1 and EK2 tests, respectively. As presented in Fig. 8, rhamnolipid, saponin and sophorolipid were used to pretreated the sludge in the EK tests. The result indicated that Ni residual concentrations significantly decreased in the enhanced EK tests, and Ni removal efficiencies were 60.80%, 58.40%, and 56.20% for EK3, EK4 and EK5 tests, respectively.

As can be observed Fig. 8, Mn, Fe and Hg residual concentrations decreased in the EK tests, which demonstrated that Mn, Fe and Hg were removed from the sludge. At the end of EK tests, the Mn, Fe and Hg removal efficiencies were 27.60%, 30.00% and 30.00% in the EK1 tests, due to high pH value at the cathode region. Mn removal efficiencies were 41.20%, 56.00%, 56.20% and 59.20% in the EK2, EK3, EK4 and EK5 tests, respectively, Fe removal efficiencies were 39.00%, 41.00%, 38.00% and 37.00% in the EK2, EK3, EK4 and EK5 tests, respectively, Hg removal efficiencies were 32.00%, 35.00%, 40.00% and 45.00% in the EK2, EK3, EK4 and EK5 tests, respectively. These results indicated that rhamnolipid, saponin and sophorolipid can enhance heavy metals removal from the sludge in the EK tests.

3.5. Discussion on biosurfactants roles in the electrokinetic experiments

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In this work, the nitric acid was used to control catholyte pH, and three biosurfactants (rhamnolipid, saponin and sophorolipid) were used to enhance heavy metal removal from sludge in the EK tests. According to the 3.4 section, results demonstrated that heavy metals removal efficiencies in the EK2 test were higher than EK1, because heavy metals could be easily released into the liquid phase from sludge particles in the acidic condition [5, 8]. Therefore, heavy metal can migrate and remove in the electromigration effect [13, 30]. In the EK3, EK4 and EK5 tests, rhamnolipid, saponin and sophorolipid were used to pretreat the sludge, which can enhance heavy metals removal from sludge.

Rhamnolipid, saponin and sophorolipid have many functional groups, such as carboxy, hydroxyl and phenolic hydroxyl [17, 18, 21]. The carboxy pH value less than 7.0, phenolic hydroxyl also played an important role in heavy metal removal process. Compare with carboxyl, the phenolic hydroxyl formed deprotonated at high pH value [7, 17, 18]. In the high pH condition, these functional groups deprotonating process occurs, and these process as negatively charged portions, reacting with heavy metal ions [35]. In the pretreatment process, functional carboxyl (-COOH) groups mainly reacted with heavy metal ions, and gradually dissociated at the low pH value to form the carboxylate ($-COO^-$) group [17]. On the contrary, the other functional groups, the phenolic hydroxyl (-OH) group reacted with less heavy metal ions, because it dissociated at the high pH value [21, 36]. During the enhanced EK tests, the anolyte and catholyte pH were lower than 7.0, and the sludge pH were less than 8.0, in these

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conditions, the carboxyl can deprotonate in heavy metals complexes and the phenolic hydroxyl groups are partially active [37]. In the EK3 experiment, Zn, Cr, Ni and Fe obtained removal efficiencies were higher than other EK tests, that may be the rhamnolipid carboxyl content is higher than saponin and sophorolipid. Therefore, the carboxyl was considered as main functional group, which chelated with heavy metal ions (M^{2+}), it conclude that the carboxylic (-COOH) of rhamnolipid, saponin and sophorolipid and heavy metal ions can react and formed heavy metals complexes, which can form positive charge, and migrate toward the cathode chamber in the direct electric field [7, 30].

3.6. Effect of heavy metals removal process with COD and BOD of sludge.

In the electrokinetic experiments, heavy metals removal efficiencies were affected by the chemical oxygen demand (COD) and biochemical oxygen demand (BOD) concentrations of the sludge. The COD of sludge is mainly composed of low molecular weight organic compounds, such as proteins, amino acids, lipids, carbonhydrates, polyphenols and simple aliphatic acids. These organic compounds can form soluble complexes with heavy metals, which prevent heavy metals adsobing or complexing to the solid phase in the sludge, therefore, increasing dissolved heavy metals concentrations as heavy metals complexes [38].

In the different EK times (24, 48, 96, 144 and 192 h), the COD and BOD of sludge changed greatly, which were 700-7300 mg/L and 110-390 mg/L, respectively. During the electrokinetic experiments, heavy metals removal process can be affected

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by the COD and BOD of sludge, and correlations of COD and BOD with heavy metals residual concentrations (C/C_0) in the sludge are shown in Fig. S2 and Fig. S3. It obviously seen that a siginificant negative relationship between COD, BOD and metals residual concentrations, indicating heavy metals removal from the sludge is the dominant process. These results demonstrated that heavy metals residual concentrations decreased as the COD and BOD increased, because the generated H^+ and biosurfactants can enhance heavy metals removal from sludge, and the H^+ can disintegrate the sludge matrix and bio-macromolecules [39]. Therefore, with the COD and BOD of sludge increasing, heavy metals removal efficiencies decreased. Depending on heavy metals fractions in the sludge, metals are reacted with particles competitively, and some metals with low affinity to particle surfaces might form metal-macromolecule complex with a specific stability constants [40]. The reaction may be reversed by competitive metals binding to macromolecule, while some metals with low affinities.

3.7. Electric energy consumption

During the electrokinetic experiments, the electric energy expenditure is directly related to the experiment time. Fig. S4 indicated the calculated energy consumption of treated sludge in all of the electrokinetic experiments conducted in the work. In these five EK experiments, the EK5 had the highest electric energy expenditure (0.209 KWh), while EK1 had the lowest electric energy expenditure (0.045 KWh). Because the sludge saturation has different electric conductivity, the deionized water has lower

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electric conductivity, while rhamnolipid, saponin and sophorolipid have higher electric conductivity. Compared with heavy metals total removal efficiencies in the EK experiments, the EK3 and EK4 obtained total higher removal efficiencies (Table 3). Cu, Zn, Cr, Pb, and Ni obtained the highest removal efficiency, which were 59.0±3.56%, 66.4±3.11%, 64.0±5.11%, 57.4±2.11%, 60.8±2.12%. However, the EK3 and EK4 have low electric energy expenditure. These results indicated that electrokinetic experiments have higher energy utilization rate. Therefore, using biosurfactants enhanced electrokinetic experiment is economical and promising for heavy metal removal from the sludge.

4. Conclusions

In this work, rhamnolipid, saponin and sophorolipid were used to pretreat the sludge, and the nitric acid was used to control catholyte pH in the EK tests, which were used to enhance heavy metal removal from the sludge in the novel enhanced EK technique. Results demonstrated that heavy metal can effectively remove from the sludge in the enhanced EK tests. Heavy metals removal efficiencies in the biosurfactants enhanced EK tests (EK3, EK4 and EK5) were higher than unenhanced EK (EK1) and acid-enhanced EK (EK2) tests. Rhamnolipid, saponin and sophorolipid have chelating and binding ability in acid conditions, these characteristics can enhance heavy metal removal from sludge in the EK tests. The positively charged metal-complexes and free heavy metal cation can migrate toward the cathode chamber by electromigration. The results demonstrated three biosurfactants can

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effectively enhance heavy metals removal from the sludge in the electrokinetic tests.

Acknowledgement

This research was supported by the Major Science and Technology Program for Water Pollution Control and Treatment of China (No. 2014ZX07202-011-004), Program of International S&T Cooperation (No. 2016YFE0123400) and National Natural Science Foundation of China (NSFC, No. 51778179).

References

[1] Y. Xu, C. Zhang, M. Zhao, H. Rong, K. Zhang, Q. Chen, Comparison of bioleaching and electrokinetic remediation processes for removal of heavy metals from wastewater treatment sludge, Chemosphere. 168 (2017) 1152-1157.

[2] Y. Liu, J. Chen, Z. Cai, R. Chen, Q. Sun, M. Sun, Removal of copper and nickel from municipal sludge using an improved electrokinetic process, Chem. Eng. J. 307 (2017) 1008-1016.

[3] G. Yang, G. Zhang, H. Wang, Current state of sludge production, management, treatment and disposal in China, Water Res. 78 (2015) 60-73.

[4] B. Dong, X. Liu, L. Dai, X. Dai, Changes of heavy metal speciation during high-solid anaerobic digestion of sewage sludge, Bioresour. Technol. 131 (2013) 152-158.

[5] X. Wang, J. Chen, X. Yan, X. Wang, J. Zhang, J. Huang, J. Zhao, Heavy metal chemical extraction from industrial and municipal mixed sludge by ultrasound-assisted citric acid, J. Ind. Eng. Chem. 27 (2015) 368-372.

ACCEPTED MANUSCRIPT

ACCEPTED MANUSCRIPT

[6] M. Vocciante, R. Bagatin, S. Ferro, Enhancements in ElectroKinetic Remediation Technology: Focus on water management and wastewater recovery, Chem. Eng. J. 309 (2017) 708-716.

[7] J. Tang, J. He, T. Liu, X. Xin, H. Hu, Removal of heavy metal from sludge by the combined application of a biodegradable biosurfactant and complexing agent in enhanced electrokinetic treatment, Chemosphere. 189 (2017) 599-608.

[8] R. Fu, D. Wen, X. Xia, W. Zhang, Y. Gu, Electrokinetic remediation of chromium (Cr)-contaminated soil with citric acid (CA) and polyaspartic acid (PASP) as electrolytes, Chem. Eng. J. 316 (2017) 601-608.

[9] G. Peng, G. Tian, Using electrode electrolytes to enhance electrokinetic removal of heavy metals from electroplating sludge, Chem. Eng. J. 165 (2010) 388-394.

[10] P.P. Falciglia, D. Malarbì, F.G.A. Vagliasindi, Removal of mercury from marine sediments by the combined application of a biodegradable non-ionic surfactant and complexing agent in enhanced-electrokinetic treatment, Electrochim. Acta. 222 (2016) 1569-1577.

[11] N.M. Zhu, M. Chen, X.J. Guo, G.Q. Hu, D. Yu, Electrokinetic removal of Cu and Zn in anaerobic digestate: Interrelation between metal speciation and electrokinetic treatments, J. Hazard. Mater. 286 (2015) 118-126.

[12] O. Hanay, H. Hasar, N.N. Kocer, Effect of EDTA as washing solution on removing of heavy metals from sewage sludge by electrokinetic, J. Hazard. Mater. 169 (2009) 703-710.

ACCEPTED MANUSCRIPT

[13] M. Bahemmat, M. Farahbakhsh, M. Kianirad, Humic substances-enhanced electroremediation of heavy metals contaminated soil, J. Hazard. Mater. 312 (2016) 307-318.

[14] L. Yuan, X. Xu, H. Li, Q. Wang, N. Wang, H. Yu, The influence of macroelements on energy consumption during periodic power electrokinetic remediation of heavy metals contaminated black soil, Electrochim. Acta. 235 (2017) 604-612.

[15] Z. Huang, Q. Wu, S. Liu, T. Liu, B. Zhang, A novel biodegradable beta-cyclodextrin-based hydrogel for the removal of heavy metal ions, Carbohydr. Polym. 97 (2013) 496-501.

[16] A. Salmani Abyaneh, M.H. Fazaelipoor, Evaluation of rhamnolipid (RL) as a biosurfactant for the removal of chromium from aqueous solutions by precipitate flotation, J. Environ. Manage. 165 (2016) 184-187.

[17] J. Tang, J. He, T. Liu, X. Xin, Removal of heavy metals with sequential sludge washing techniques using saponin: optimization conditions, kinetics, removal effectiveness, binding intensity, mobility and mechanism, RSC Adv. 7 (2017) 33385-33401.

[18] J. Tang, J. He, T. Liu, X. Xin, Extraction and environmental risk assessment of heavy metal in the municipal dewatered sludge using rhamnolipid treatment, Hum Ecol. Risk. Assess. 23 (2017) 1522-1538.

[19] S. Ozturk, T. Kaya, B. Aslim, S. Tan, Removal and reduction of chromium by

ACCEPTED MANUSCRIPT

Pseudomonas spp. and their correlation to rhamnolipid production, J. Hazard. Mater. 231-232 (2012) 64-69.

[20] W.-C. Chen, R.-S. Juang, Y.-H. Wei, Applications of a lipopeptide biosurfactant, surfactin, produced by microorganisms, Biochem. Eng. J. 103 (2015) 158-169.

[21] X. Mao, R. Jiang, W. Xiao, J. Yu, Use of surfactants for the remediation of contaminated soils: a review, J. Hazard. Mater. 285 (2015) 419-435.

[22] M.T. Ammami, F. Portet-Koltalo, A. Benamar, C. Duclairoir-Poc, H. Wang, F. Le Derf, Application of biosurfactants and periodic voltage gradient for enhanced electrokinetic remediation of metals and PAHs in dredged marine sediments, Chemosphere. 125 (2015) 1-8.

[23] S. Wang, C.N. Mulligan, Rhamnolipid biosurfactant-enhanced soil flushing for the removal of arsenic and heavy metals from mine tailings, Process. Biochem. 44 (2009) 296-301.

[24] S. Tang, H. Yin, S. Zhou, S. Chen, H. Peng, Z. Liu, Z. Dang, Simultaneous Cr(VI) removal and 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) biodegradation by Pseudomonas aeruginosa in liquid medium, Chemosphere. 150 (2016) 24-32.

[25] Z.M. Gusiatin, E. Klimiuk, Metal (Cu, Cd and Zn) removal and stabilization during multiple soil washing by saponin, Chemosphere. 86 (2012) 383-391.

[26] M. Ye, M. Sun, J. Wan, Y. Feng, Y. Zhao, D. Tian, F. Hu, X. Jiang, Feasibility of lettuce cultivation in sophoroliplid-enhanced washed soil originally polluted with Cd, antibiotics, and antibiotic-resistant genes, Ecotoxicol. Environ. Saf. 124

ACCEPTED MANUSCRIPT

(2016) 344-350.

[27] Y. Asci, M. Nurbas, Y. Sag Acikel, Investigation of sorption/desorption equilibria of heavy metal ions on/from quartz using rhamnolipid biosurfactant, J. Environ. Manage. 91 (2010) 724-731.

[28] J. Gao, Q. Luo, C. Zhang, B. Li, L. Meng, Enhanced electrokinetic removal of cadmium from sludge using a coupled catholyte circulation system with multilayer of anion exchange resin, Chem. Eng. J. 234 (2013) 1-8.

[29] J. Wu, J. Zhang, C. Xiao, Focus on factors affecting pH, flow of Cr and transformation between Cr(VI) and Cr(III) in the soil with different electrolytes, Electrochim. Acta. 211 (2016) 652-662.

[30] L. Yuan, X. Xu, H. Li, N. Wang, N. Guo, H. Yu, Development of novel assisting agents for the electrokinetic remediation of heavy metal-contaminated kaolin, Electrochim. Acta. 218 (2016) 140-148.

[31] H. Xu, M. Ding, K. Shen, J. Cui, W. Chen, Removal of aluminum from drinking water treatment sludge using vacuum electrokinetic technology, Chemosphere. 173 (2017) 404-410.

[32] M. Cherifi, N. Boutemine, D.F. Laefer, S. Hazourli, Effect of sludge pH and treatment time on the electrokinetic removal of aluminum from water potabilization treatment sludge, C.R. Chim. 19 (2016) 511-516.

[33] J. Gao, Q.S. Luo, J. Zhu, C.B. Zhang, B.Z. Li, Effects of electrokinetic treatment of contaminated sludge on migration and transformation of Cd, Ni and Zn in

ACCEPTED MANUSCRIPT

various bonding states, Chemosphere. 93 (2013) 2869-2876.

[34] S.-R. Ryu, E.-K. Jeon, K. Baek, A combination of reducing and chelating agents for electrolyte conditioning in electrokinetic remediation of As-contaminated soil, J. Taiwan Inst. Chem. Eng. 70 (2017) 252-259.

[35] W. Zhou, J. Yang, L. Lou, L. Zhu, Solubilization properties of polycyclic aromatic hydrocarbons by saponin, a plant-derived biosurfactant, Environ. Pollut. 159 (2011) 1198-1204.

[36] J. Hou, S. Zhang, Z. Qiu, H. Han, Q. Zhang, Stimulatory effect and adsorption behavior of rhamnolipids on lignocelluloses degradation system, Bioresour. Technol. 224 (2017) 465-472.

[37] J. Zhang, L. Bing, G.A. Reineccius, Comparison of modified starch and Quillaja saponins in the formation and stabilization of flavor nanoemulsions, Food Chem. 192 (2016) 53-59.

[38] H. Zhang, J. Yang, W. Yu, S. Luo, L. Peng, X. Shen, Y. Shi, S. Zhang, J. Song, N. Ye, Y. Li, C. Yang, S. Liang, Mechanism of red mud combined with Fenton's reagent in sewage sludge conditioning, Water Res. 59 (2014) 239-247.

[39] X. Tian, C. Wang, A.P. Trzcinski, L. Lin, W.J. Ng, Interpreting the synergistic effect in combined ultrasonication-ozonation sewage sludge pre-treatment, Chemosphere. 140 (2015) 63-71.

[40] S.S. Yang, W.Q. Guo, G.L. Cao, H.S. Zheng, N.Q. Ren, Simultaneous waste activated sludge disintegration and biological hydrogen production using an

ACCEPTED MANUSCRIPT

ozone/ultrasound pretreatment, Bioresour. Technol. 124 (2012) 347-354.

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Figure and Table captions

Table captions

Table 1 Heavy metals contents in the sludge compared to Chinese legal standard.

Table 2 Experimental conditions of the five electrokinetic experiments.

Table 3 Heavy metals average removal efficiencies after the EK treatment.

Figure captions

Fig. 1. Electric current variation during the EK process.

Fig. 2. Sludge pH variation during the EK process.

Fig. 3. Heavy metals residual concentrations with time and space variations in the different five sections during the EK1 process.

Fig. 4. Heavy metals residual concentrations with time and space variations in the different five sections during the EK2 process.

Fig. 5. Heavy metals residual concentrations with time and space variations in the different five sections during the EK3 process.

Fig. 6. Heavy metals residual concentrations with time and space variations in the different five sections during the EK4 process.

Fig. 7. Heavy metals residual concentrations with time and space variations in the different five sections during the EK5 process.

Fig. 8. Heavy metals residual concentrations distribution in the different five sludge sections after EK tests.

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Table 1

Heavy metals contents in the sludge compared to Chinese legal standard.

Parameters (unit)	Value	Acid soil (pH＜6.5)[a]	Alkaline soil(pH≥6.5)[a]	Environmental soils[b]
pH	7.21±0.45			
Water content (%)	79.35±3.32			
Cu (mg kg^{-1})	1352.11±11.21	250	500	400
Zn (mg kg^{-1})	731.58±8.98	500	1000	500
Cr (mg kg^{-1})	202.52±6.27	600	1000	300
Pb (mg kg^{-1})	52.50±6.52	300	1000	300
Ni (mg kg^{-1})	175.11±4.12	100	200	200
Mn (mg kg^{-1})	1033.33±25.22	-	-	-
Fe (mg kg^{-1})	989.45±15.56	-	-	-
Hg (mg kg^{-1})	18.12±2.32	5	15	1.5

"-": not mentioned

[a]National Standard of the People's Republic of China GB 4284-84: Control standards for pollutants in sludges from agricultural use.

[b]National Standard of the People's Republic of China GB 15618-1995: Environmental quality standard for soils.

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Table 2

Experimental conditions of the five electrokinetic experiments.

Test	Anolyte	Sludge saturation	Catholyte	Time (h)	Electric potential (V cm^{-1})
EK1	Deionized water	Deionized water	Deionized water	48, 96, 144, 192	1
EK2	Deionized water	Deionized water	0.1 mol L^{-1} HNO_3	48, 96, 144, 192	1
EK3	Deionized water	2.0 g L^{-1} Rhamnolipid	0.1 mol L^{-1} HNO_3	48, 96, 144, 192	1
EK4	Deionized water	2.0 g L^{-1} Saponin	0.1 mol L^{-1} HNO_3	48, 96, 144, 192	1
EK5	Deionized water	2.0 g L^{-1} Sophorolipid	0.1 mol L^{-1} HNO_3	48, 96, 144, 192	1

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Table 3

Heavy metals average removal efficiencies after the EK treatment.

EK tests	Cu	Zn	Cr	Pb	Ni	Mn	Fe	Hg
EK1	25.2±2.31	42.4±2.11	39.8±4.31	30.8±2.42	33.2±2.31	27.6±1.22	30.0±2.56	30.0±3.11
EK2	32.0±3.45	39.6±2.67	47.0±3.21	37.2±4.23	47.8±3.42	41.2±3.21	39.0±3.21	32.0±2.13
EK3	55.8±5.46	73.8±6.23	64.0±5.11	51.6±5.32	60.8±2.12	56.0±3.21	41.0±2.12	35.0±2.12
EK4	59.0±3.56	66.4±3.11	60.6±3.22	57.4±2.11	58.4±4.22	56.2±3.21	38.0±3.21	40.0±3.21
EK5	53.2±4.12	62.0±4.32	53.0±3.23	52.4±4.56	56.2±4.23	59.2±4.21	37.0±1.23	45.0±3.45

Average C=(C_{S1}+ C_{S2}+ C_{S3}+ C_{S4}+ C_{S5})/5

Average removal efficiency of total heavy metals in whole sludge cell = [(C_0-average C)/ C_0]×100%.

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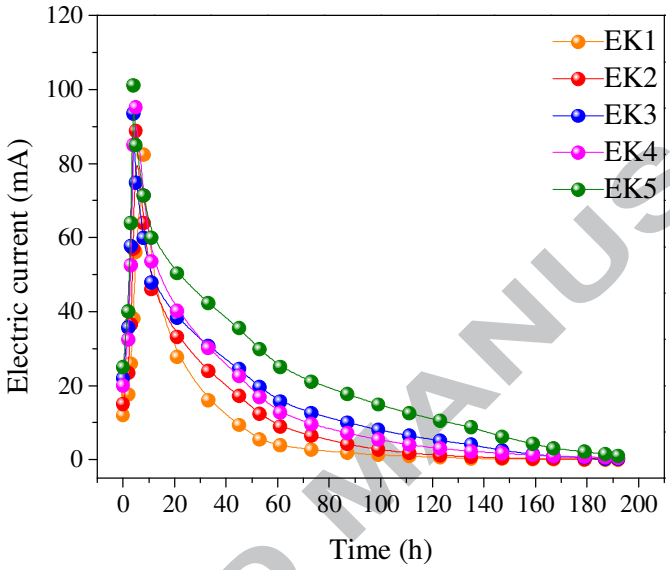

Fig. 1. Electric current variation during the EK process (EK1: Unenhanced EK; EK2: Acid-enhanced EK; EK3: Rhamnolipid-enhanced EK; EK4: Saponin-enhanced EK; EK5: Sophorolipid-enhanced EK).

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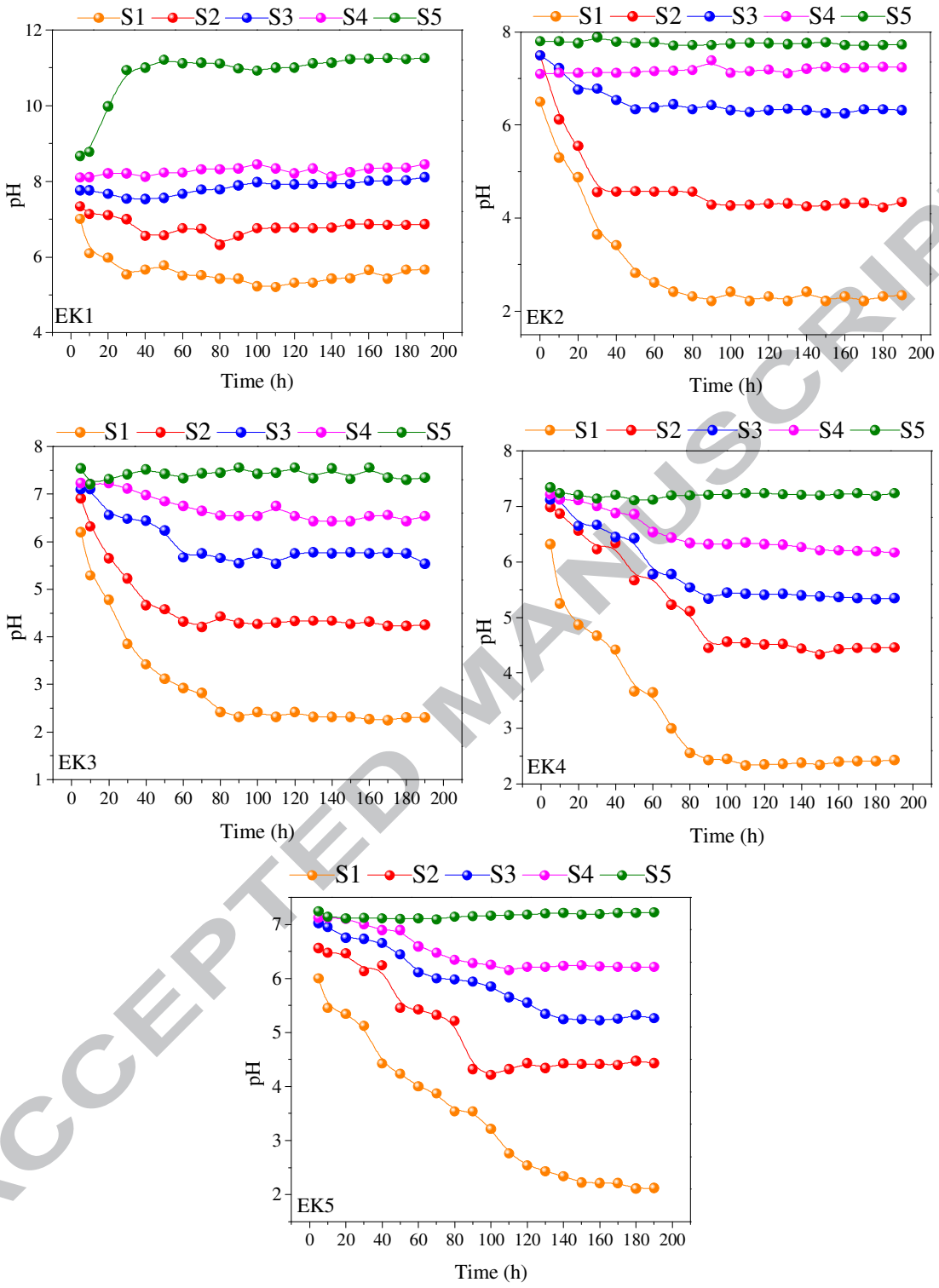

Fig. 2. Sludge pH variations during the EK process. EK1: Unenhanced EK; EK2: Acid-enhanced EK; EK3: Rhamnolipid-enhanced EK; EK4: Saponin-enhanced EK; EK5: Sophorolipid-enhanced EK.

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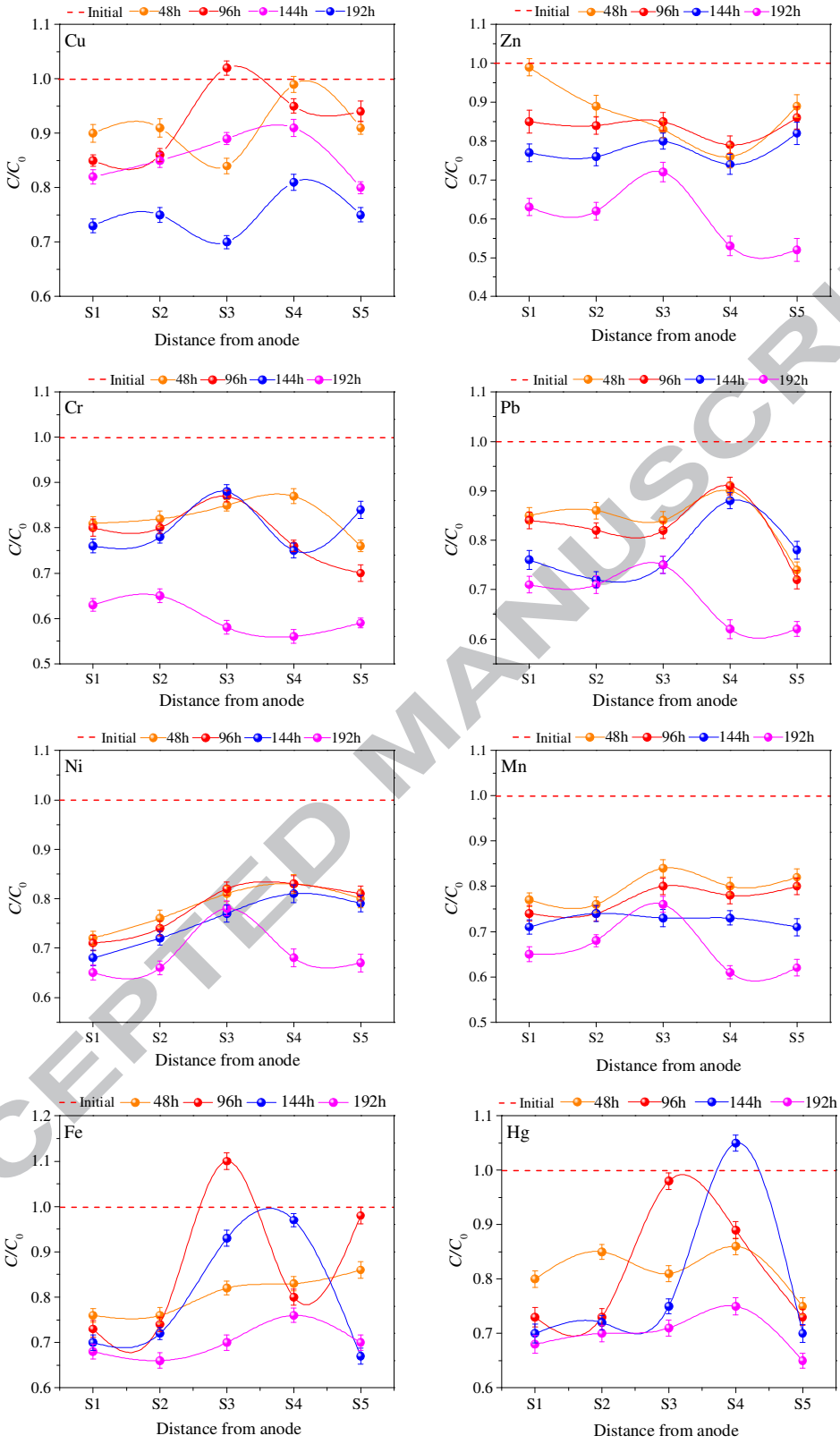

Fig. 3. Heavy metals residual concentrations with time and space variations in the different five sections during the EK1 process.

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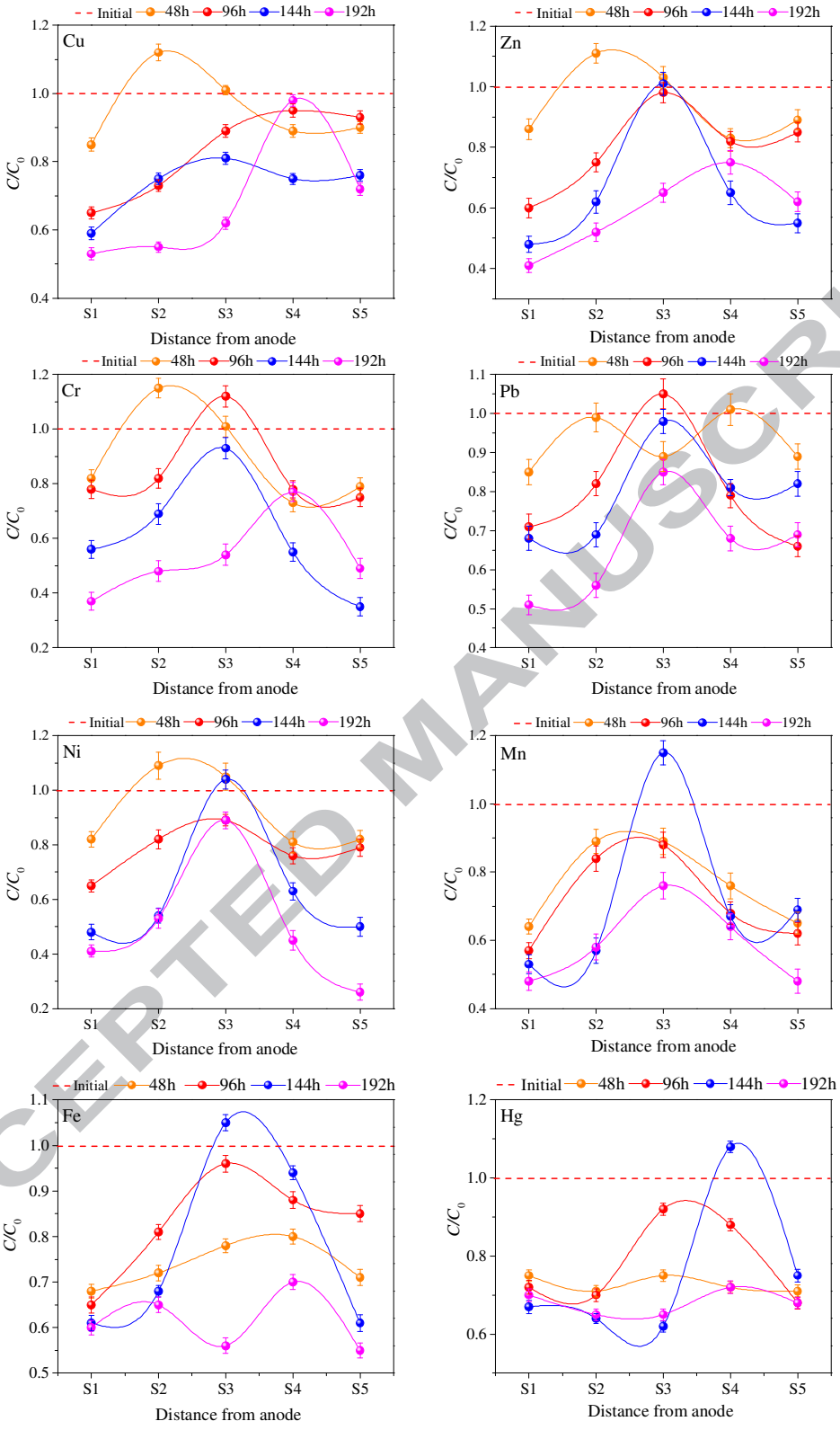

Fig. 4. Heavy metals residual concentrations with time and space variations in the different five sections during the EK2 process.

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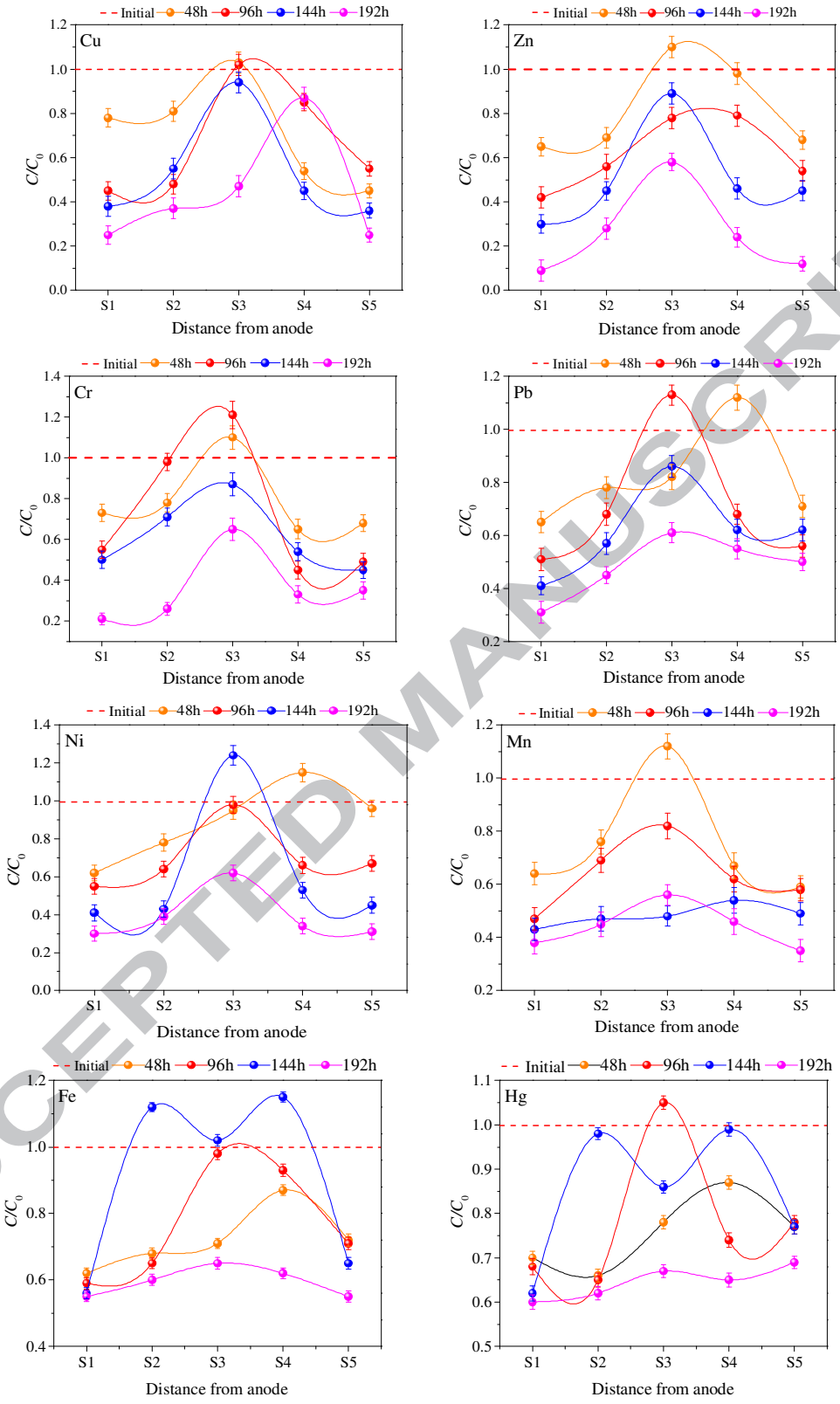

Fig. 5. Heavy metals residual concentrations with time and space variations in the different five sections during the EK3 process.

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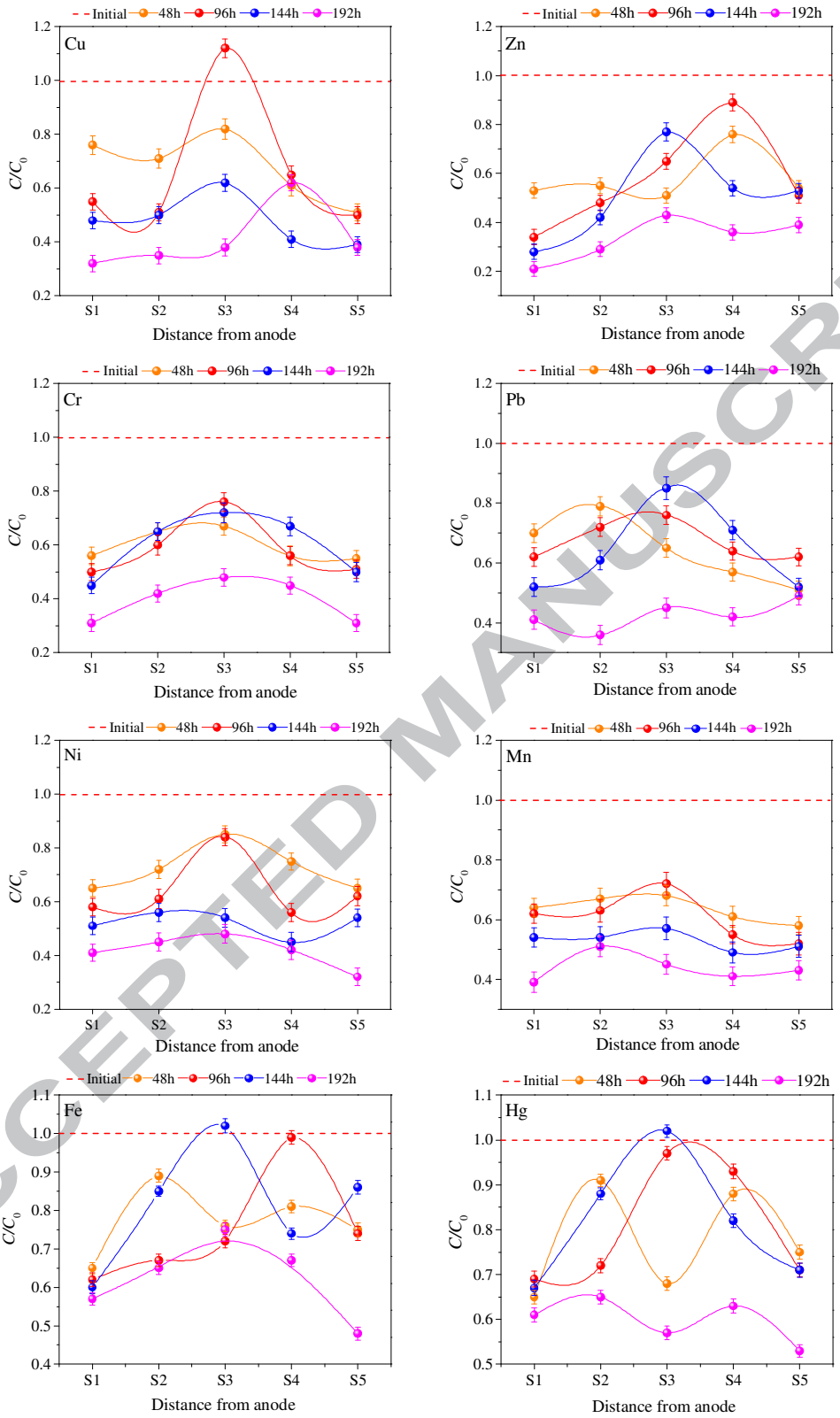

Fig. 6. Heavy metals residual concentrations with time and space variations in the different five sections during the EK4 process.

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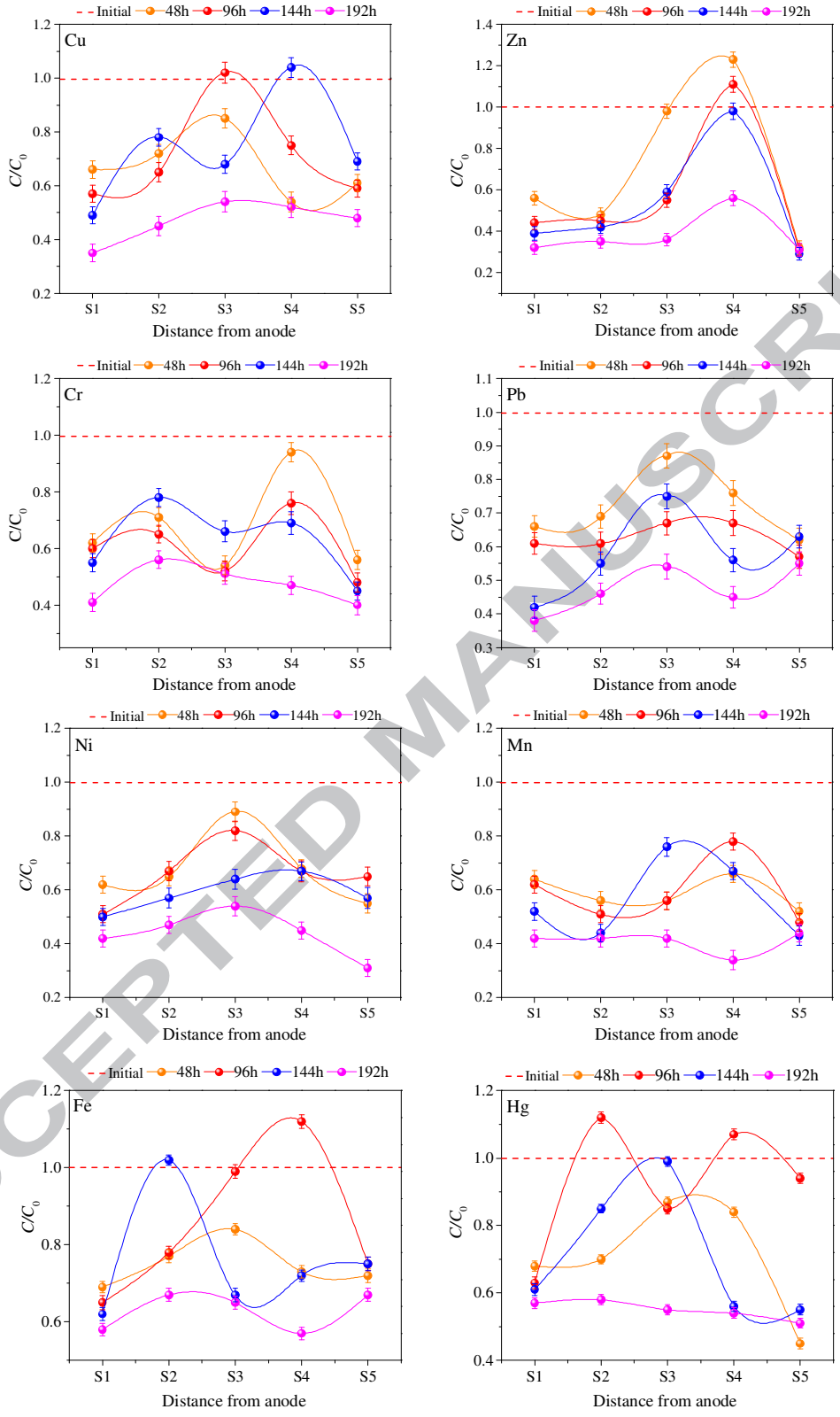

Fig. 7. Heavy metals residual concentrations with time and space variations in the different five sections during the EK5 process.

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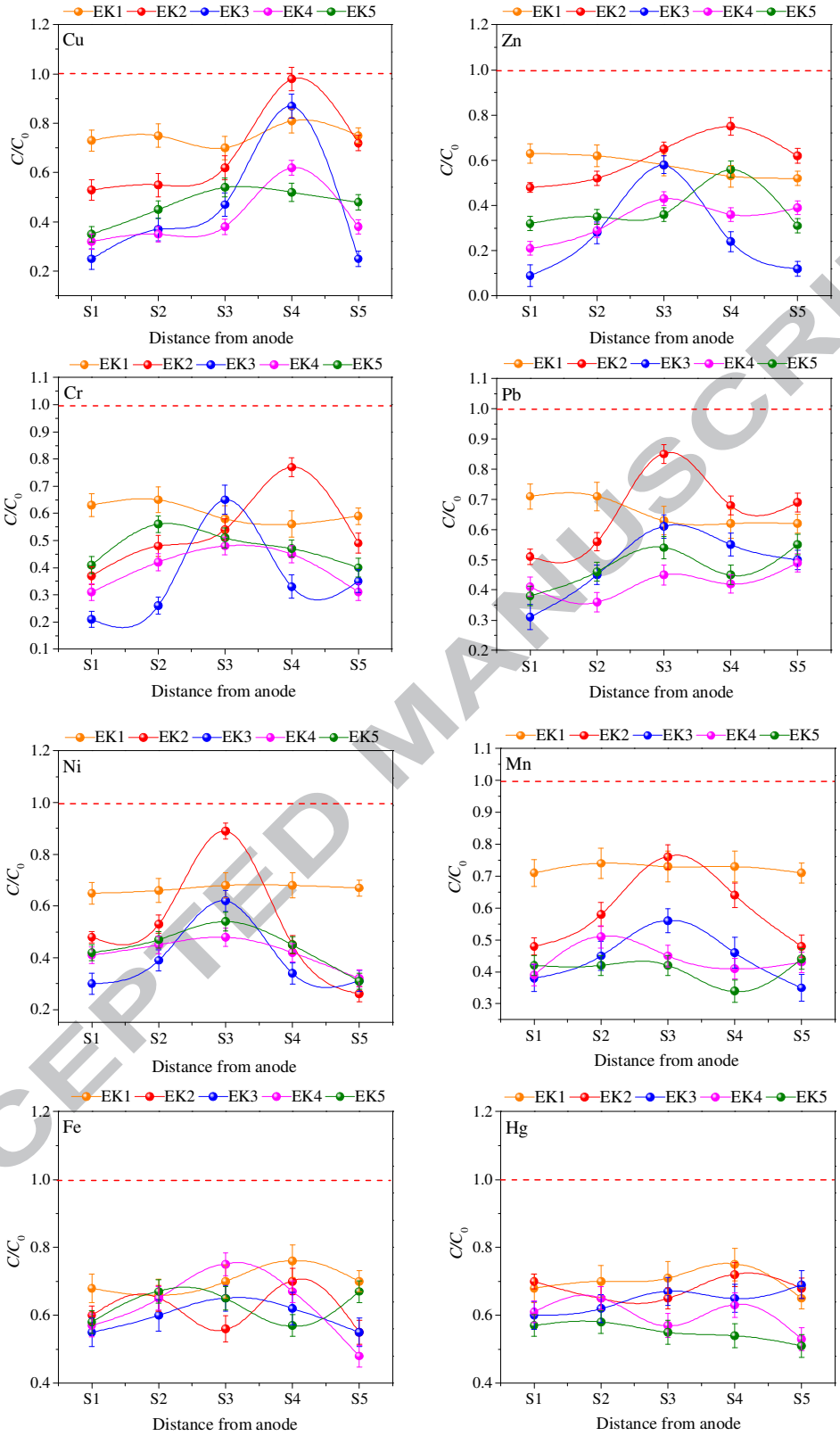

Fig. 8. Heavy metals residual concentrations distribution in the different five sludge sections after EK tests.

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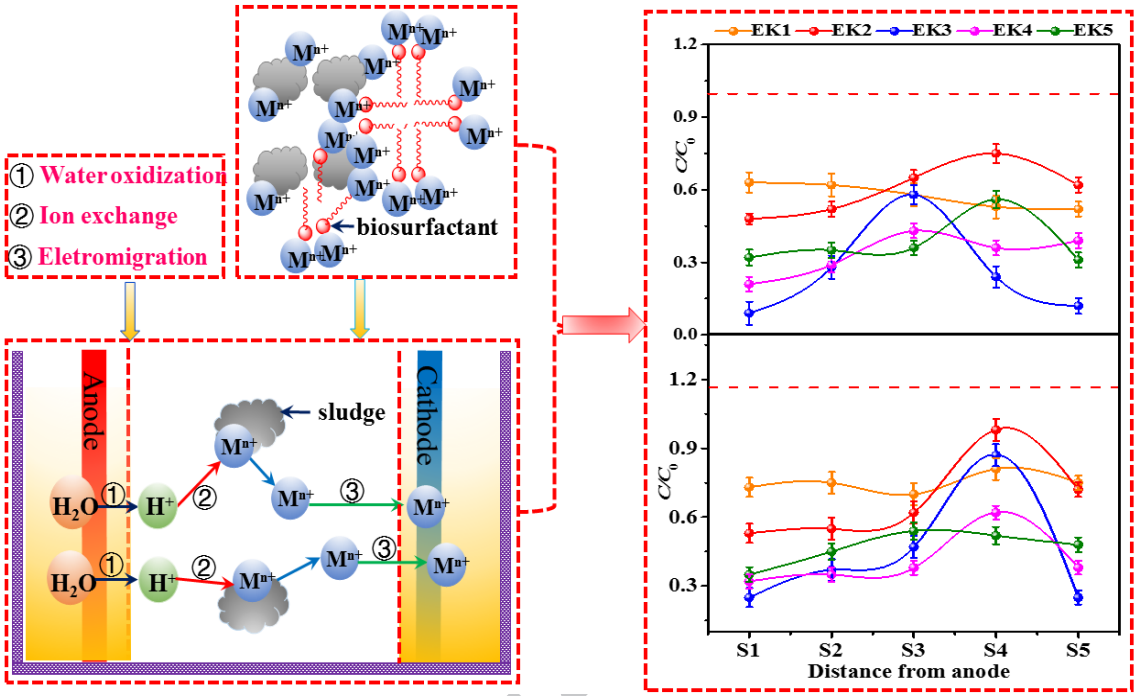
Graphical Abstract



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- Using rhamnolipid, saponin and sophorlipid as chelating agents to enhance EK efficiency.
- Biosurfactant-enhanced EK efficiency was greater than the unenhanced EK.
- Rhamnolipid obtained the highest heavy metals removal efficiency.
- Results demonstrated that the suitability of biosurfactant-enhanced EK removal heavy metals from sludge.

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