PILOT SCALE REMOVAL OF HEAVY METALS FROM SODIC-SALINE CLAY SOIL USING HYBRID ELECTROKINETIC-ADSORPTION TECHNIQUE

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ABSTRACT

Electrokinetic remediation (EKR) technologies for contaminated soils are faced with significant technical challenges, especially for sodic-saline soils which inherently exhibit characteristics that render them difficult in getting remediated from mixed contaminants. The feasibility of the remediation of saline-sodic clay heavily contaminated with mixed contaminants at lab scale has been recently reported. However, these studies limit understanding of the feasibility of the process treatment of the contaminated soil at larger scale. In this study, remediation of saline-sodic clay contaminated with Zn, Pb, Cu, Cd, Cr and Hg, kerosene and phenol (initial concentration ranged 8.82-76.5 mg/kg) at pilot scale using hybrid electrokinetic-adsorption (HEKA) cell. The HEKA cell was ran continuously for 35 days at fixed voltage gradient of 0.2 v/cm and the soil pH, water content, organic carbon, electrical conductivity and electro-osmotic flow were monitored. At estimated energy expenditure at 4.70 kWh/kg or 1187.65 kWh/m3 of the treated soil, the achievable removal efficiencies of the heavy metals were estimated at 31.9, 38.1, 55.7, 36.0, 70.2 and 47.4%, respectively. The pilot scale results obtained were found to be comparable to the bench scale results, though at the expense of drastic increase in cumulative energy consumption

Keywords: Saline-Sodic soil remediation, mixed contaminants, heavy metals, pilot scale, electrokinetic-adsorption

1. Introduction

Remediation technologies for soils and groundwater contaminated with heavy metals and organic pollutants have received increased attention in recent decades [1]. Of particular interest is coupling of EKR with other techniques due to their increased remediation efficiencies [1-3]. This is so considering the synergetic effect successfully recorded by integration of EKR with adsorption for remediating soils contaminated multiple contaminants at field, pilot and bench scales [1-4]. Electrokinetic remediation is the application of low DC voltage to mobilize and transport contaminants from the contaminated section to the treatment zones which is affected by applied voltage gradient, soil type, migration of acid/ base fronts, dissolution/ precipitation of metallic ions, redox reactions, complexation/speciation [1, 2, 4]. Saline-sodic soils have been identified to possess electrical conductivity greater than 4 dS/m, pH greater than 8.2 and exchangeable sodium percentage greater than 15 [5]. These soil types are characterized by large amount of dissolved salts and minerals in the pore fluid leading to high electric current flow, excessive soil heating, process fluid consumption and rapid corrosion of electrodes [8,9]. These render sustaining optimal voltage gradient for effective remediation challenging [10,8]. Lukman *et al* [2, 6] reported successful remediation of heavily contaminated saline-sodic clay using HEKA cell on bench scale, thereby limiting understanding the feasibility of implementing the process at larger scale. Moreover, directly utilization of the lab scale findings into real treatment of contaminated soils or sites becomes more implausible. Hence, to overcome this limitation, this study further experimentally investigated the remediation of saline-sodic clay contaminated with mixed heavy metals and organics at pilot scale.

Figure 1: Pilot Scale HEKA

Table 1: Initial Concentrations of the Heavy Metals in the HEKA Cell, mg/Kg

Chamber Matrix	Heavy Meal					
	Zn	Pb	Cu	Cd	Cr	Hg
Natural Clay (B & D)	10.61	3.09	5.05	0.09	13.04	0.2
Contaminated Clay (C)	76.5	48.93	51.85	72.3	57.78	8.82
AC (F and G)	5.85	0.92	7.18	0.05	10.87	0.05

2. Materials and methods

2.1. Pilot Scale Reactor

The pilot scale reactor as shown in Figure 1 has seven (7) compartments (A, B, C, D, E, F and G as per Table 1) with overall dimensions of 196 cm x 97 cm x 50 cm (Figure 1). Compartments A and B housed the anolyte and catholyte, respectively.

2.2. Clay Characterization and Experimental Procedure

Details physical and chemical characteristics of the clay and GAC used were reported earlier [2, 6]. Approximately 65 kg of the clay was placed in each of the reactor's chambers B, C and D. The soil in chamber C was artificially spiked with Cu, Cr, Cd, Pb, Zn and Hg, kerosene and phenol and thoroughly mixed with water (≈40% moisture) and allowed for 24 hours to ensure homogeneity. The initial measured concentrations of the heavy metals as placed in the different chambers of the cell are given in Table 1. The cell anode and cathode were connected to DC voltage supply (AMETEK, Sorenson) and portable data logger (TDS - 303, Tokyo Sokki) for real-time data monitoring. The two electrode compartments as well as the middle GAC chambers were isolated from the soil zone by a porous Geotextile material (Alyaf Industrial., Saudi Arabia). The processing fluids used in the electrode chambers are; anolyte (2 N NaOH) and catholyte (1 N HNO$_3$), while two(2) graphite electrodes served as the anode and cathode. The two GAC treatment zones cut across the cell vertically bracketing the spiked soil compartment. For the test that lasted for 5 weeks, , fractions of the soil were taken at different points at specified time interval to determine the residual concentrations of the contaminants, soil pH, water content, organic carbon and electrical conductivity as detailed by Lukman *et al.* [2] and Essa *et al* [6].

3. Results and discussions

3.1. Electrolyte pH and Electro-Osmotic Flow Volume

Figure 2(I) and 2(II) show the pH variability with treatment time in the electrolytes and soil, respectively. Throughout the five(5) weeks run, soil pH was within the alkaline range (pH 8.5 to

13) implying that both contain appreciable soluble salts that easily hydrolyse [5]. The rise in the soil pH may be attributed to the level of voltage applied which increased electrochemical decomposition of electrolyte producing more OH- ions that migrated into the soil. There was significant continuous decay and rise of anolyte and catholyte pH respectively as demonstrated in the bench scale by Lukman *et al* [2, 6]. This necessitate continuous utilization of processing fluids, NaOH and HNO3, to stabilize the pH due to the rapidly generated H+ and OH- ions at the anode and cathode respectively. As such, the electrolytes pH were monitored every 12 hours and replaced as they degraded or refilled as the required amount is lost via electro-osmotic flow. Due to inherent nature of high buffering capacity of the tested soil, the H+ was suppressed while OH- was more susceptible to migrating from the anode via electro-osmosis to the soil, thereby keeping the soil within the alkaline condition. The electro-osmotic flow volume as depicted in Figure 2(III) clearly shows that the flow was predominantly in the direction from the anode towards the cathode which buttresses the decline in the anolyte pH. This suggests that the heavy metals removal was mainly via electro-osmosis. The continuous induced electro-osmotic flow led to increase in the volume of the catholyte and rapid degradation necessitating much more frequent replacement rather than refill which suppressed the impending rise in the catholyte pH (Figure 2(I)). The electro-osmotic flow maintaining a unidirectional pattern was corroborated to the fact that high soil pH values are recorded which ranges between pH 8-12. Salihu el al[10] has reported similar observations at bench scale. Due the soil moisture content relevance in EKR [2], it was monitored within the three(3) compartments which showed very slight variation (3%) throughout the test run for the continuous refill and replacement of the degraded process fluids.

3.2. Energy Consumption

To avoid excessive energy consumption experienced during the bench scale experiments [2, 6], the pilot scale run was conducted at low voltage gradient of 0.2 v/cm. However, as result of increase resistance to the electro-osmotic flow, the needed current to sustain the voltage gradient increased gradually from 0.2A to 0.4A for the first 15 days. Thereafter, the current rapidly increase until it reached about 1.8 A at the end of the 35th day. Hence, there was continuous in increase in both the daily and cumulative energy consumption as depicted in Figure 2(IV). With the total energy consumed at the end of the test run estimated at 4.70 kWh/kg or 1187.65 kWh/m^3. The smooth trends of the two energy consumptions fitted into linear and quadratic models given in Figure 2(IV) with R^2 of 0.997 and 0.998, respectively. Considering that the electrical conductivity decreased from the first week and didn't increase throughout the test run in the all the chambers, suggest that the increase in the cell current (which is responsible for the energy rise) was due to the electro-osmotic flow resistance as result of the stable low soil moisture (30-38%). Additionally, in related work reported earlier, higher current flow during EKR test led to the rapid electrolyte degradation which led to higher energy consumption [6],hence suggesting using buffered electrolyte during EKR.

3.3. Efficiency of Heavy Metals Removal

Figure 3 shows significant removal for most of the contaminants in all the tests, especially in the contaminated soil in chamber C. In such chamber, the initial concentrations were high, obviously depicting consistent decrease in the concentrations with time in the soil for all the heavy metals. At the end of the 35 days test run, the achievable removal efficiencies of Zn, Pb, Cu, Cd, Cr and Hg were 31.9, 38.1, 55.7, 36.0,70.2 and 47.4%, respectively. The lowest percent removal was observed in Zn ions, though Zn had the highest initial concentration in the contaminated chamber. Even though, Lukman *et al.* [7] observed that Zn has the highest removal (during bench scale studies) due to its least selectivity to adsorption by the tested soil in competitive alkaline aqueous medium (which predominates the pH during the pilot test. On the other hand, considering the concentration of the heavy metals in the GAC chambers (Figure 3), it appeared that migration of the metals from the contaminated chamber C to the GAC chambers (F & G) and their subsequent entrapment was farfetched despite the recorded osmotic flow volume collected, especially at the cathode chamber. Figure 3(III) and 3(IV) which

depicts the concentrations profiles for these metals in chambers B and D, natural unspiked chambers. The contrast between these two chambers clearly indicated lower residual concentrations of the heavy metals in chamber D (which is adjacent to the anodic chamber) compared to chamber B. At the chamber D, good removals were recorded, particularly for Pb, Cu and Cr, while Zn has the lowest. Evidently, this shows that the heavy metals were flushed by the electro-osmotic flow predominantly towards GAC chamber to cathode. Based on the forgone, it was postulated that the contaminants from both the contaminated and the uncontaminated were trapped at the geosynthetic materials as such couldn't pass through to reach the GAC chambers.
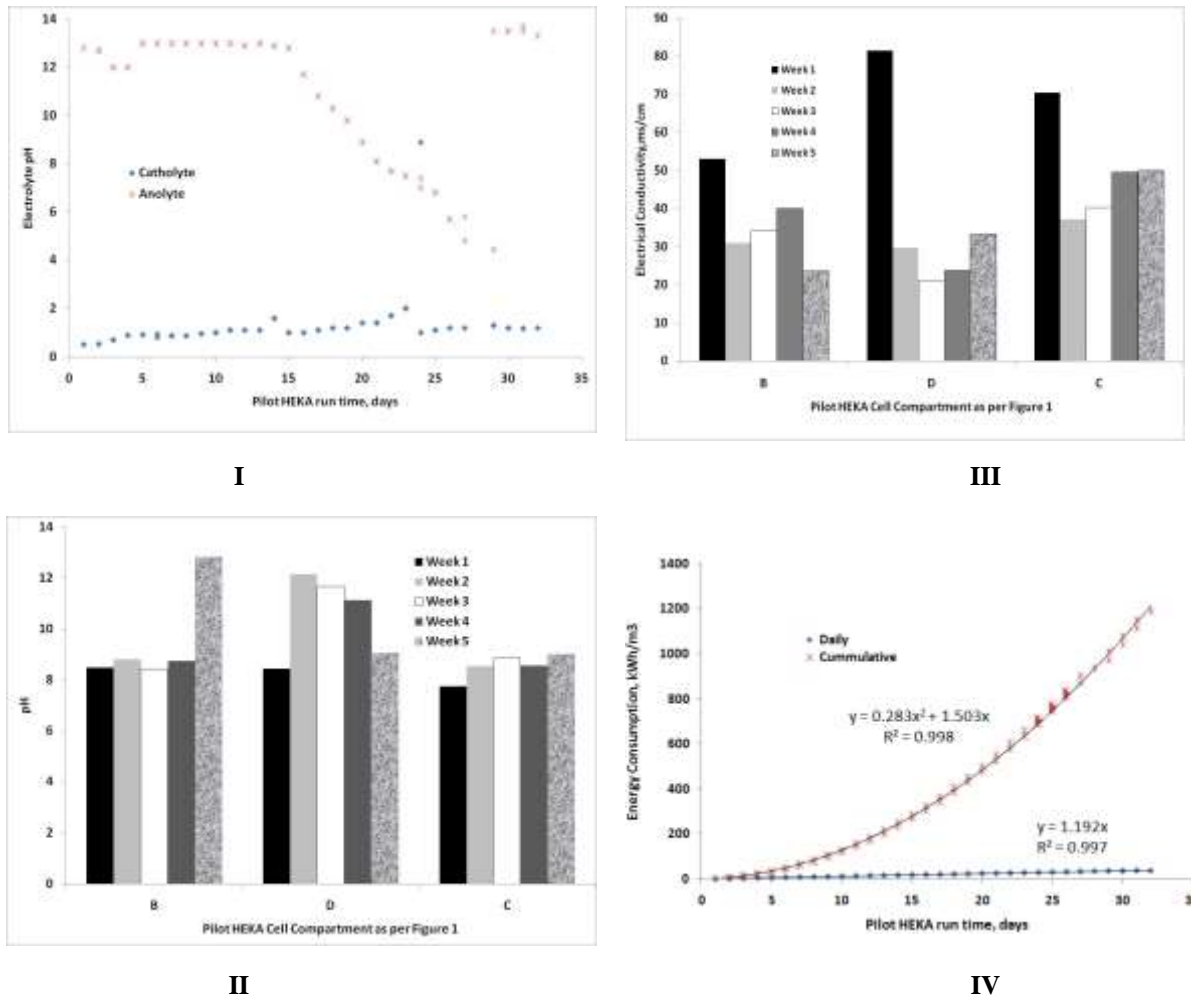

I

III

II

IV

Figure 2: Changes in pH for the (I) Electrolytes and (II) HEKA compartments . (III) Changes in electrical conductivity HEKA chambers and (IV) the overall daily energy during the test run

4. Conclusions

Hybrid electrokinetic-adsorption (HEKA) cell was tested Pilot scale for the removal of Zn, Pb, Cu, Cd, Cr and Hg from saline-sodic soil. The cell was run for 35 days at fixed voltage gradient of 0.2 vcm^{-1} and the soil pH, water content, organic carbon, electrical conductivity and electro-osmotic flow at the electrode chambers were monitored. At estimated energy expenditure at 4.70 kWh/kg or 1187.65 kWh/m^3 of the treated soil, the achievable removal efficiencies of the heavy metals were estimated at 31.9, 38.1, 55.7, 36.0,70.2 and 47.4%, respectively. At longer remediation time, the pilot scale results obtained were found to be comparable to the bench scale results, though at the expense of drastic increase in cumulative energy consumption. Increase of the cost of the HEKA technology at larger scale attributed to the rapid degradation of the electrolyte fluids suggesting using buffered processing fluid.
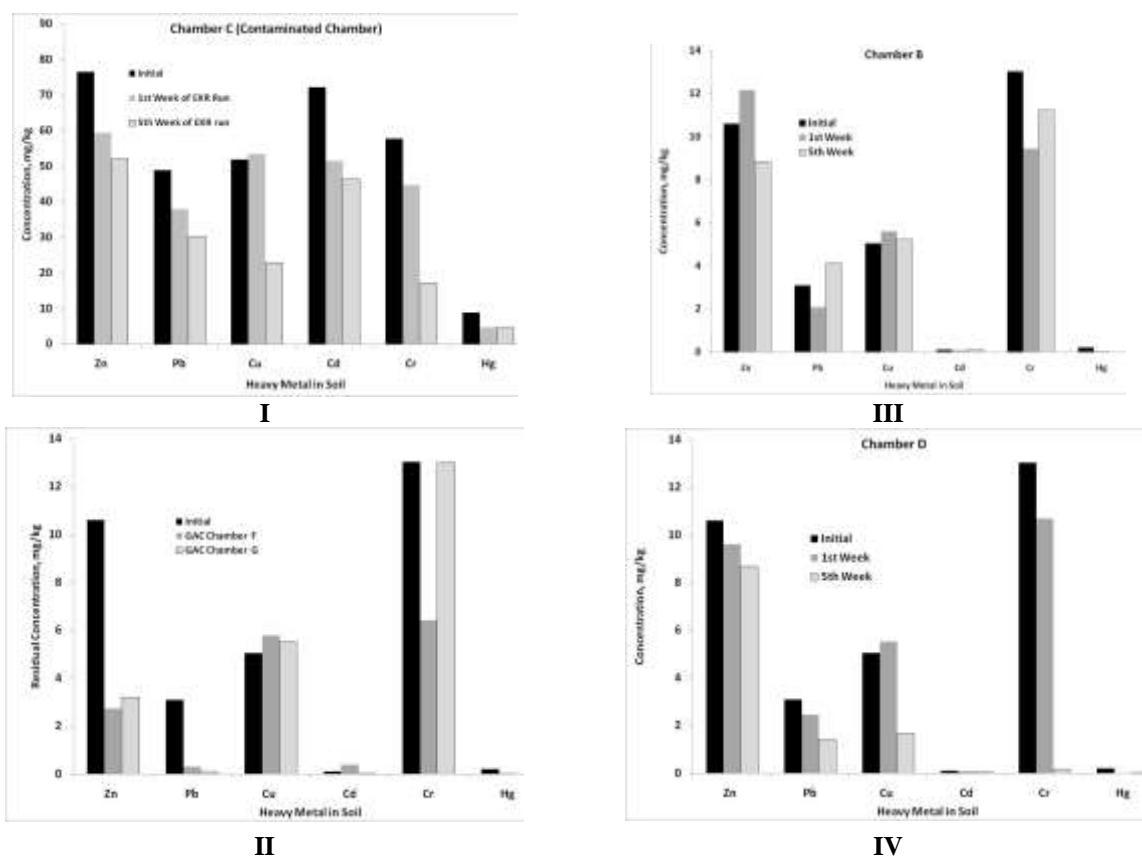
Figure 3: Average residual concentration of the heavy metals in the different chambers HEKA cell

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