

Electrokinetic Remediation of Nickel From Low Permeability Soil

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Received: 25 July 2011 / Accepted: 18 August 2011 / Published: 1 September 2011

Electrokinetic remediation of nickel from low permeability soil using titanium electrodes having inter-electrode spacing of 10 cm was carried out in a cylindrical reactor. The influences of current density, voltage gradient and electrolyte pH were investigated upon removal efficiency for 60 h experimental runs. Efficiency improved from 49.3% to 57.2% when the current density was increased from 4.36 mA/cm² to 13.1 mA/cm². Furthermore, an enhancement in efficiency from 38.5% to 54.3% was observed when voltage gradient increased from 1 V/cm to 2 V/cm (at 13.1 mA/cm²). Further increase in voltage gradient to 2.5 V/cm improved efficiency during initial runs. However, an overall reduction of 3.2% was observed after 60 h of operation in comparison to that obtained at 2 V/cm. This may be attributed to precipitation and localized accumulation of metallic ions. An inverse relationship between efficiency and electrolyte pH was also observed (at 13.1 mA/cm² and 2 V/cm). Although a removal of 74.1% was achieved at pH = 4.5, the system required optimization as the nickel content in treated soil was above the maximum values given in international standards.

Keywords: Electrokinetic process; Nickel; Low permeability soil; Removal efficiency; Current density.

1. INTRODUCTION

In general, soil contamination is placing human health at a great risk. Soil contamination is becoming a key environmental issue, due to its importance in ecosystems, and the influence it has on the quality of ground water, plants and food [1, 2]. Some of the most common and most damaging types of soil contaminants are metals. Generally, during routine operations or accidental spills in industry soil may be contaminated with metals. Once metal contaminates the soil, it can have complex

interactions with natural binders that can lead to both short (delaying the normal hydration reaction) and long (release of the heavy metals in groundwater) term problems. Presence of heavy metals in soil has great concern with respect to human health and safety [2].

Application of electrokinetic process for the removal of contaminant may vary mainly due to the variation in soil type and type of contaminant in the soil [3, 4]. Electrokinetic remediation can be made more effective by optimizing the operating parameters of the process like applied current, applied voltage, and pH of electrolyte [5]. Remediation of low permeable soils is usually difficult by most traditional methods such as soil washing [6]. Electrokinetic remediation method, on the other hand, is a very effective technique when applied to fine-grained soils and soils with low hydraulic conductivity for the removal of pollutants [7, 8]. Electrokinetic remediation uses electric current to extract a variety of organic and inorganic pollutants from low permeable soils. Extensive research has been done on directing the contaminants migration to where remediation may be more easily achievable [5]. A combination of electrokinetic techniques with other processes such as electro-Fenton, bioremediation and phytoremediation has been tested to enhance pollutant removal [9 - 14]. In order to improve the transport of contaminants and process efficiency various additives such as solvents, chelating agents and surfactants have been used in other studies [14 - 16]. In addition, these researchers have indicated the need to explore the influence of operating parameters on the removal efficiency of the process.

Maximum contaminant level (MCL) of metals that could be present in soil is presented in Table 1. It can be seen from Table 1 that permissible concentration limits for metals in soil is very low which, in turn, reflects the toxicity level and hazards associated with these metals [2, 17].

Table 1. Maximum permissible concentration of metals in soil [2, 17].

Metal	Max limit in Soil (mg/kg)	
	US-EPA	Dutch Standards
Arsenic (As)	14	29
Selenium (Se)	1.6	0.7
Nickel (Ni)	32	35
Cobalt (Co)	20	9
Cadmium (Cd)	1.6	0.8
Chromium(Cr)	120	100
Copper (Cu)	100	36
Lead (Pb)	60	85
Mercury (Hg)	0.5	0.3
Zinc (Zn)	220	140

For instance, it is well known that nickel is toxic [18] and nickel compounds, for example nickel sulphide, are known or suspected to cause cancer [19, 20]. Some researchers have studied the remediation of nickel contaminated soils using electrokinetic technology [17, 18, 20] but their focus was on the removal of a series of heavy metals, in which, nickel was also a constituent. A direct

electrokinetic remediation of nickel from low permeable soil appears to be limited in the literature (especially for the South Asian region, i.e., Pakistan) considering the fact that levels of nickel present in soils from the Sindh region are beyond the recommended limit as reported by Yawar et al. [21].

Some studies conducted in Pakistan have shown higher concentrations of nickel in water and sediment samples collected from various localities along Karachi's coast (as a consequence of discharges from tanneries, refineries and power stations). Mangrove habitats in the vicinity of Karachi serve as a sink for nickel and a variety of other heavy metals [22, 23]. The sediments act as major traps for metals followed by mangrove plants. Detrital silicates and sulphides are the principal carriers of iron and nickel thereby making sediments a long term contaminant sinks.

The aim of the present work is to study the influence of some operating parameters on the removal of nickel from a low permeability soil in Karachi (Pakistan) using electrokinetic process. The effects of studied process variables are discussed in detail.

2. MATERIALS AND METHOD

2.1. Description of the soil

Low permeability soil was collected from the Hawks bay beach in Karachi. The soil sample was classified as sandy soil (97.6% sand, 2% silt and 0.4% clay) by the Unified Classification System procedure (based on ASTM D-2487) with 6.17% of organic matter (OM) and a cation exchange capacity (CEC) of 25.2 mmol/kg. The soil was passed through a 2 mm sieve to remove stones, branches and any other coarse material. The soil sample was then washed with distilled water followed by 2% commercial sulphuric acid (Merck, Pakistan) to remove organic components from the soil. Rinsing with distilled water was repeated. Properties of the soil such as pH and moisture content were determined in the laboratory using standard methods [24]. An initial concentration of 200 mg/kg of nickel was detected in the soil sample, which was beyond the limits specified by Yawar et al. [21]. Hydraulic conductivity of the soil was measured in the laboratory as reported in the literature [25] and was found to be in the range of 10^{-10} to 10^{-9} m/s. Initial pH of the soil was 5.5 as shown in Table 2.

Table 2. Properties of soil used

Parameter (units)	Value
Moisture content, %	20 – 25
Particle size, mm	< 2
Soil pH (except in pH experiments)	5 – 5.5
Soil temperature, °C	28 – 30
Hydraulic conductivity, m/s	10^{-10} – 10^{-9}

2.2. Reactor Design

The experimental set-up (Fig. 1) was very similar to that reported by Al-Shahrani and Roberts [26]. A multi-compartment Perspex cell was constructed with a cylindrical shaped sample vessel and two electrode compartments. The sample vessel had an inside diameter of 50 mm, and a length of up to 30 cm. The sample vessel was divided into compartments, each 3 cm in length and vinyl gaskets were used to prevent leakage between the compartments. Each compartment had a hole sealed with a rubber bung, which could be removed during experiments in order to measure the local pH and electrical potential [26].

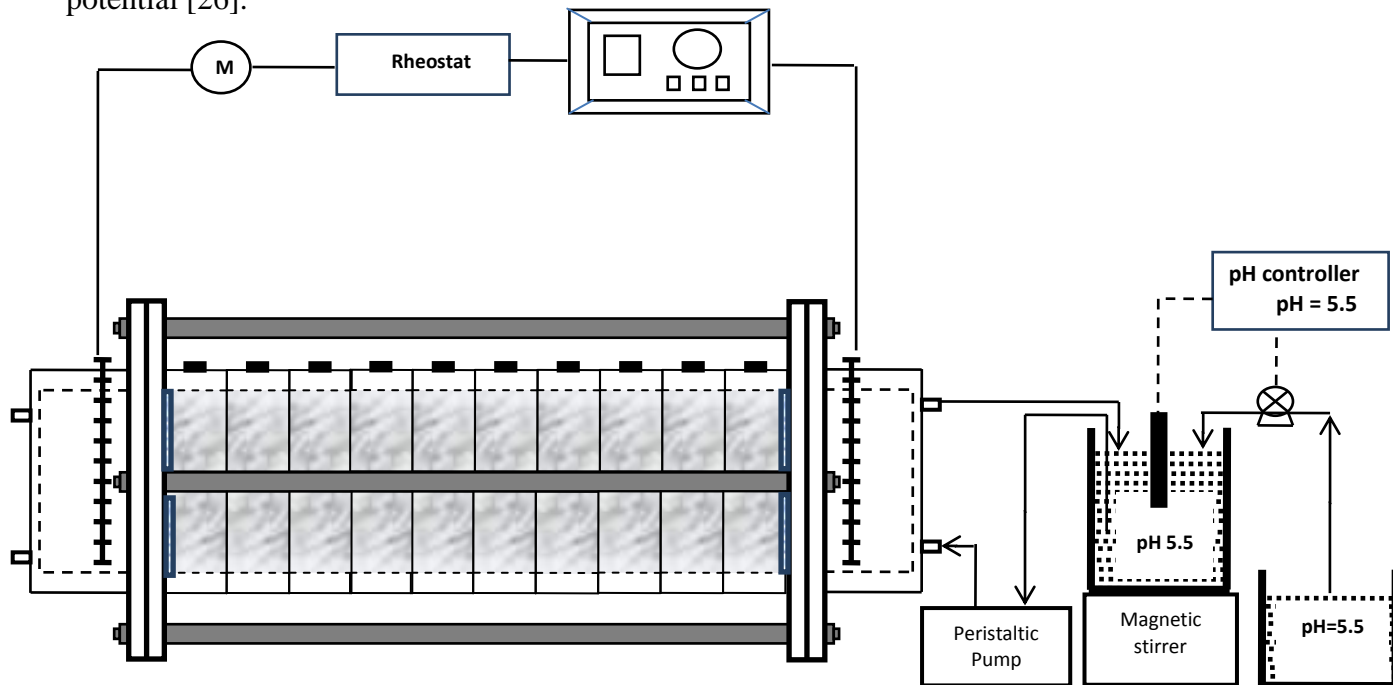


Figure 1. Schematics of electrochemical set-up [26].

The electrode compartments had the same inside diameter as the specimen vessel and were 50 mm in length. The top of each electrode compartment was open to allow insertion of the electrodes, enable the release of any gases generated at the electrodes and for measurement of the catholyte and anolyte pH. Two tubes were fitted to the top and the bottom of the catholyte compartment to enable continuous circulation and pH control of the catholyte. Both electrodes were made of titanium and had diameters of 50 mm. The soil specimen was separated from the electrode compartment using two circular micro-porous flat sheet membranes consisting of ultrahigh molecular weight polyethylene and amorphous silica (Daramic®) with an average pore size of 0.1 μm. This membrane was chosen due to its low cost, high conductivity and stability under acidic condition [26]. The contaminants could pass through the pores of the membrane during the extraction process, but the soil particles were separated from the electrolytes. The electrode compartments were initially filled with deionised water. The cathode compartment fluid was recycled using a peristaltic pump through a reservoir which was maintained at pH = 5.5. The electrodes were connected to an uninterrupted DC power supply (MAXIREG 761) along with a rheostat (FVRB, MFPR, USA) and a digital multi-meter (8846A,

Fluke, USA). Inter-electrode spacing was kept at 10 cm in each run. A separate electrolyte tank was used to provide a controlled flow of 0.5 ml/h using a peristaltic pump (Precision BT-50SER, China). Each experimental run lasted for at least 60 h.

2.3. Experimental Procedures

Prior to the start of testing the electrochemical reactor was conditioned (after packing the reactor with soil) by equilibrating it with tap water and applying a zero hydraulic head across it for 24 h. The soil packing procedure was identical to that reported earlier for the electrochemical remediation of caesium [26]. After the electrokinetic cell was conditioned the power supply was turned on and the reactor was set to operate at various different parameters as described in Table 3. All the experiments were performed in duplicate to evaluate test reproducibility in a similar manner to literature reported methods [27]. However, the highest nickel removal efficiencies were reported for both runs under identical conditions.

Each experimental run have been conducted for at least 60 h. Details of the variations in applied current densities and voltage gradients are given in Table 3. Variations in pH at optimum current density and voltage gradient are also shown in Table 3.

Table 3. The process experimental design matrix

Run number	Current density (mA/cm ²)	Voltage gradient (V/cm)	pH
1	4.4	1.5	5.5
1D	4.4	1.5	5.5
2	7.3	1.5	5.5
2D	7.3	1.5	5.5
3	10.2	1.5	5.5
3D	10.2	1.5	5.5
4	13.1	1.5	5.5
4D	13.1	1.5	5.5
5	13.1	1.0	5.5
5D	13.1	1.0	5.5
6	13.1	2.0	5.5
6D	13.1	2.0	5.5
7	13.1	2.5	5.5
7D	13.1	2.5	5.5
8	13.1	2.0	3.0
8D	13.1	2.0	3.0
9	13.1	2.0	4.5
9D	13.1	2.0	4.5
10	13.1	2.0	6.5
10D	13.1	2.0	6.5
11	13.1	2.0	8.0
11D	13.1	2.0	8.0
12	13.1	2.0	10.0
12D	13.1	2.0	10.0

In order to solubilize the metal hydroxide and carbonates formed, or different species adsorbed on the soil particles, as well as to protonate organic functional groups during the electrokinetic process, acetic acid (Merck) is added to the cathodic compartment [18]. Due to possessing negative charges, the organic acids migrate towards the anodic compartment. As a result, sodium hydroxide (Merck) is added into this chamber to neutralize the acid. However, to ensure high nickel removal, water has been used as a purging solution at both the anode and cathode initially, followed by the use of acetic acid as the cathode purging solution and NaOH as the anode purging solution [28].

After calibration with a standard pH solution, the pH of the electrolytes was measured by a pH meter (Istek Inc., Model 76P) in an identical manner to that reported by Al-Shahrani and Roberts [26]. The average value of the two experiment samples was used in a similar manner to the procedure followed in the literature [18].

2.4. Post Run Soil Analysis

At the end of the electrokinetic process anode and cathode end solutions have been collected and all liquid and solid samples are digested according to EPA method 3015 and 3051, respectively [29]. Collected soil samples have been analyzed (in triplicate) for residual nickel concentration by using Atomic Absorption Spectrophotometer (AAS M6, Thermo Fisher Scientific) following standard procedures [24]. This is followed by the measurement of soil pH. Afterwards the total energy consumption and the current efficiency of the electrokinetic process are calculated as given in the literature [30].

3. RESULTS AND DISCUSSION

Some of the properties of soil used in this experimental study are given in Table 2. The XRD based mineralogical phase analyzer indicated that the soil consisted of 68.2% quartz as shown in Table 4. Soil also had about 9.7% of calcite which could have caused buffering effects during electrokinetic treatment.

Table 4. XRD mineralogical phase analysis

Quartz, %	68.2
Calcite, %	19.7
Kaolinite, %	2.3
Albite, %	6.1
Muscovite, %	3.7

3.1. Effect of applied current density on removal efficiency

It was found that in general, the efficiency of the process increased with the increase in applied current density from 4.4 to 13.1 mA/cm² during 60 h of runs (Fig. 2). The removal efficiency was high during the first 10 h but dampened over time. The removal efficiency of nickel was *c.a.* 44.2 %, 45.7 %, 48.1 % and 52.1 % after 48 h of electrokinetic treatment with current densities of 4.4 mA/cm², 7.3 mA/cm², 10.2 mA/cm² and 13.1 mA/cm², respectively. Nickel removal after 60 h of run reached to 49.3%, 51.9%, 56.1% and 57.2% while using current densities of 4.4 mA/cm², 7.3 mA/cm², 10.2 mA/cm² and 13.1 mA/cm², respectively. These percentages are based on the amount of nickel collected in the catholyte, rather than the nickel concentrations measured in the soil at the end of the experiment. A material balance on nickel was performed and the results were summarized in Table 5. A maximum discrepancy of 2.0% indicated that the material balance was sound.

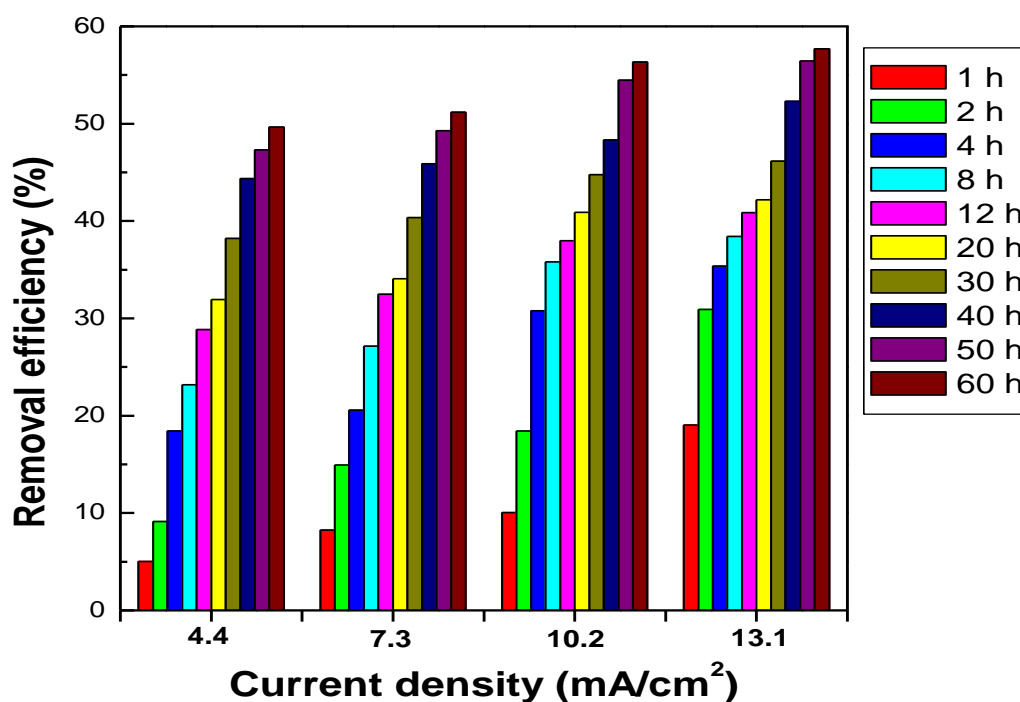


Figure 2. Temporal effect of applied current density on the removal efficiency nickel from soil by means of Electrokinetic process.

Results showed that removal efficiency was dependent on the total energy input to the process (Table 5). The removal efficiency achieved in the present work was better than those achieved under similar conditions in an earlier study [31] and consistent with the current literature [32].

Conductivity was initially high probably due to the presence of more dissolved species in the porous soil matrix. Therefore, measured current increased initially as the dissolved ions and desorbed metals came into the solution phase and transported through the soil matrix in response to electroosmosis and electromigration [17]. However, with the passage of time when little ionic species

and dissolved materials were available in solution phase, conductivity decreased so the rate of removal declined. Higher values of current densities were not applied because previous work indicated that temperature of soil could rise thereby increasing energy usage [7].

Table 5. Material balance of nickel removal experiments, total energy consumption and current efficiency

Run number	Ni collected in anolyte (mg)	Ni remaining in cell (mg)	Ni collected in catholyte (mg)	Total Ni (mg)	Discrepancy in material balance (%)	Energy usage (kWh)	Current efficiency (%)
1	< 0.1	100	97	17	1.5	0.00389	105.7
1D	< 0.1	100	98	198	1.0	0.00389	105.7
2	< 0.1	96	103	199	0.5	0.00645	63.7
2D	< 0.1	94	102	196	2.0	0.00645	63.7
3	< 0.1	88	111	199	0.5	0.00902	45.6
3D	< 0.1	88	111	199	0.5	0.00902	45.6
4	< 0.1	85	113	198	1.0	0.01158	35.5
4D	< 0.1	84	112	196	2.0	0.01158	35.5
5	< 0.1	122	75	197	1.5	0.00772	35.5
5D	< 0.1	121	75	196	2.0	0.00772	35.5
6	< 0.1	84	112	196	2.0	0.01544	35.5
6D	< 0.1	84	113	197	1.5	0.01544	35.5
7	< 0.1	98	101	199	0.5	0.01930	35.5
7D	< 0.1	97	101	198	1.0	0.01930	35.5
8	< 0.1	53	145	198	1.0	0.01544	35.5
8D	< 0.1	53	145	198	1.0	0.01544	35.5
9	< 0.1	53	144	197	1.5	0.01544	35.5
9D	< 0.1	54	145	199	0.5	0.01544	35.5
10	< 0.1	74	122	196	2.0	0.01544	35.5
10D	< 0.1	75	123	198	1.0	0.01544	35.5
11	< 0.1	112	85	197	1.5	0.01544	35.5
11D	< 0.1	113	86	199	0.5	0.01544	35.5
12	< 0.1	133	63	196	2.0	0.01544	35.5
12D	< 0.1	134	64	198	1.0	0.01544	35.5

3.2. Effect of applied voltage gradient on removal efficiency

It was observed that the applied voltage gradient was positively related to the process efficiency at a constant current density of 13.1 mA/cm². It can be seen from Fig. 3 that the removal of nickel from the soil increased with the increase in applied voltage gradient. However, maximum removal of 54.3% was achieved with 2 V/cm after 60 h of run. Further increase in applied voltage gradient (2.5 V/cm) initially improved the removal efficiency, however, cumulative removal after 60 h of experimental run showed a 3.2% reduction from the efficiency obtained when 2 V/cm was employed. This effect was probably due to the enhanced movement of ions in the soil matrix with the increase in potential difference. However, soil temperature rose with the increase in applied voltage gradient and resulted in the localized accumulation of metallic ions in the soil that reduced mobility.

This in turn resulted in diminishing of soil pore water by thermally induced gradients that may have suppressed the electrokinetic process [7]. Consequently, with the decrease in moisture content in some of the soil pockets, current flow decreased resulting in the reduction of removal efficiency.

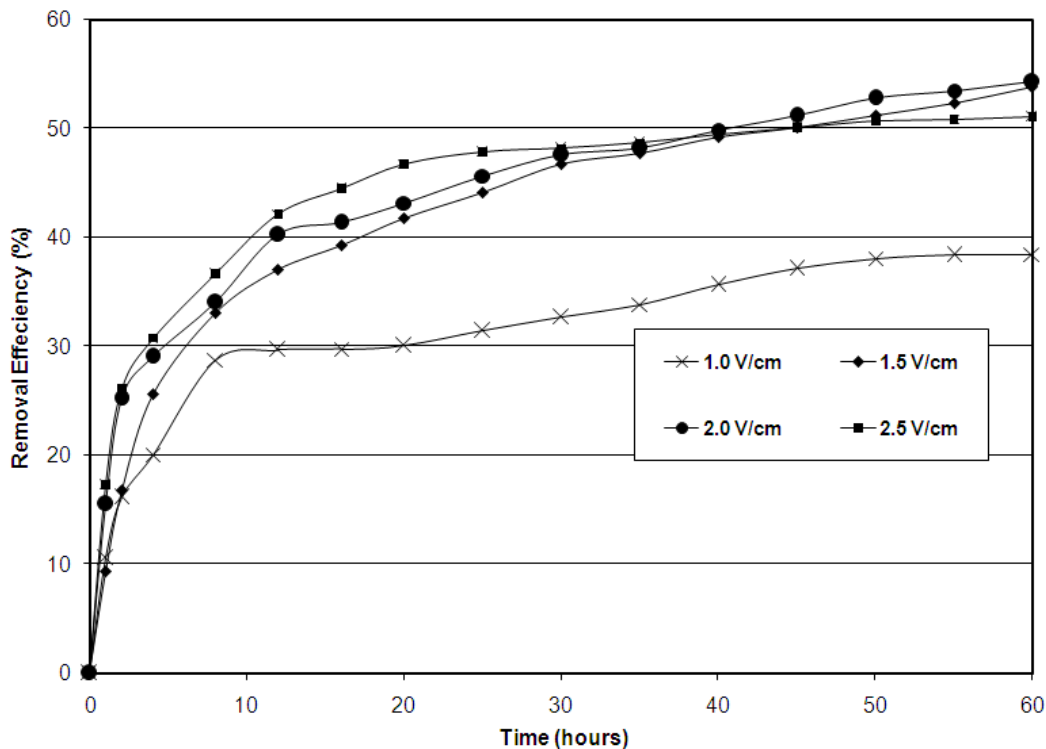


Figure 3. Temporal effect of voltage gradient on the removal efficiency of nickel from soil by means of Electrokinetic process.

3.3. Effect of electrolyte pH on removal efficiency

It was found that the removal efficiency of electrokinetic process decreased with the increase in pH of electrolyte passing through the porous media (at a constant current density of 13.1 mA/cm^2 and voltage gradient of 2 V/cm). Maximum removal efficiency of 74.1% was noted at a pH value of 4.5, however, further reduction in pH did not improve the efficiency significantly as shown in Fig. 4. Result was in line with the fact that generally at a pH of 8.0 nickel has a solubility of 70 mg/L and at a pH of 10.2 the solubility is 0.1 mg/L [33, 34]. It was evident from Fig. 4 that the removal efficiency of the electrokinetic process decreased drastically when the pH value increased from 6.5 and showed removal efficiency of only 33.1% at a pH of 10. Reduction in removal efficiency at higher pH of electrolyte may be attributed to alkali fronts near the cathode which produces non-conductive precipitates. These can retard or stop the migration of ions which in turn results in reduction of removal efficiency. The formation of a highly resistive band influences the remediation as it causes the voltage gradient, and hence the pollutant migration, to decrease across the soil. Further work is required in order to optimize the electrokinetic process. In addition, catholyte conditioning and pre-treatment of the soil with nitric acid would enhance the removal efficiency as reported by other workers [32].

Since the pH of the catholyte was controlled at constant values, it is not immediately clear how the acetic acid used affects the pH distribution in the soil. The explanation is probably that the associated anion added with the acid migrated in the electric field into the soil, thus modifying the speciation in the pore fluid. In particular, the acetate ions will buffer the acid front migrating from the anode. In addition, these ions will interact with other adsorbed and dissolved species, so that the overall effect is complex and difficult to predict. The weaker and more mobile acetate would be expected to have a stronger buffering effect than other stronger acids, which is consistent with results reported in the literature [32]. As a consequence a pH distribution was not reproduced in this work.

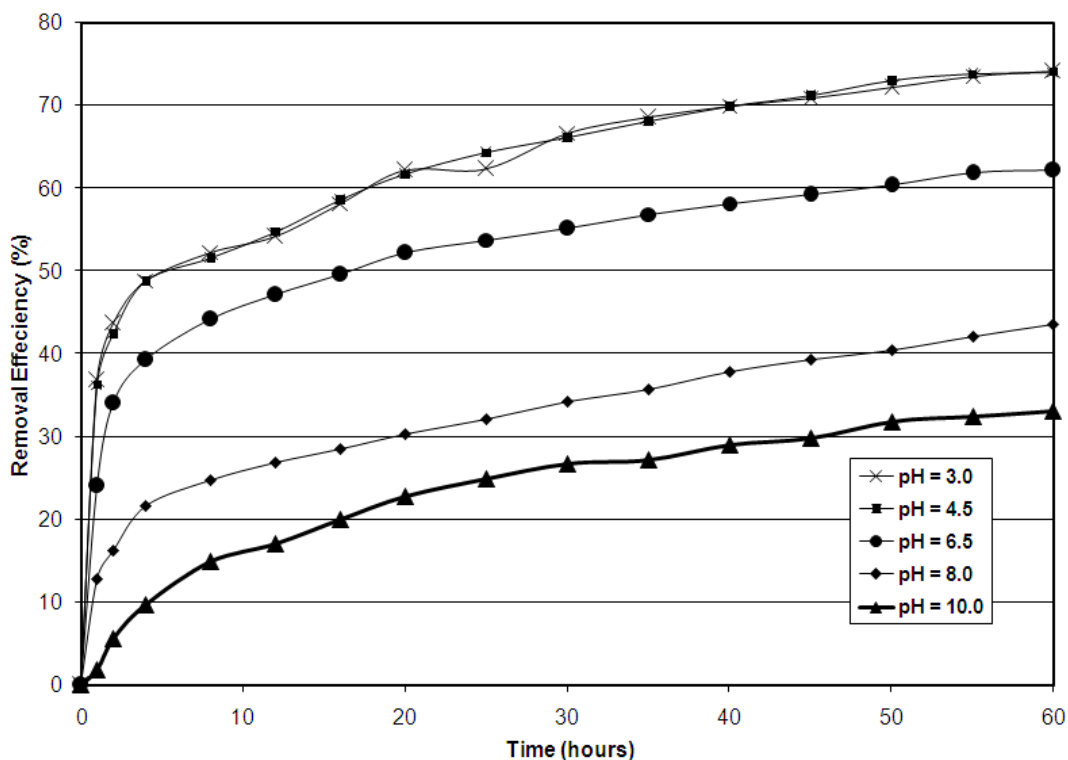


Figure 4. Temporal effect of electrolyte pH on the removal efficiency of nickel by means of Electrokinetic process.

4. CONCLUSIONS

The following specific conclusions are drawn on the basis of results obtained during the present study:

- Temporal increase in nickel removal using electrokinetic process is observed during each 60 h of experimental runs. High removal rates during initial 10 h may be attributed to the higher conductivity due to more dissolution of species in the porous soil matrix.
- Nickel removal is positively related to the applied current density; however, increase is up to 7.9% when applied current density is increased from 4.4 mA/cm² to 13.1 mA/cm².

- An enhancement in removal efficiency up to 15.9% is observed when voltage gradient is increased from 1 V/cm to 2 V/cm but further increase doesn't improve the removal efficiency.
- An inverse relationship between the removal efficiency and the pH of electrolyte solution is observed. It is found that removal of nickel by electrokinetic technology is better with electrolytes having low pH values as reported in the literature. It is probably due to desorption of metal ions which is greatest at lower pH and decreases with the increase in pH. Maximum removal efficiency of the process (74.1%) is achieved at a pH value of 4.5. However, further decrease in soil pH doesn't improve the removal efficiency.
- From the experimental results obtained, it may be concluded that the optimum conditions for electrokinetic remediation of nickel from low permeable soil in Karachi are $i = 7.3$ mA/cm², voltage gradient = 1.5 V/cm and a pH = 7.

ACKNOWLEDGEMENTS

Authors are grateful to acknowledge the help and support provided by the Karachi Institute of Power Engineering and University of Malaya (Bright Sparks Funding) during the study period.

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