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Electrokinetic Remediation of Copper Contaminated Soils using EDTA

Rahul Dasgupta[1], Dr. K. Venkatesh[2], Dr. R.P. Tiwari[3]

[1]Ph.D scholar, Civil Engineering Department, M.N.N.I.T. Allahabad, U.P., India
[2]Assistant Professor, Civil Engineering Department, M.N.N.I.T. Allahabad, U.P., India
[3]Professor, Civil Engineering Department, M.N.N.I.T. Allahabad, U.P., India

Abstract: *Electrokinetic remediation is the one of the most promising soil decontamination processes that have high removal efficiencies for metal ions being and time effectiveness with electroosmosis and electromigration. The present experimental study is aimed to investigate the effect of initial copper concentration and applied voltage on transport and removal of copper from typical clayey soil by eletrokinetic remediation and to examine the copper removal efficiency under various experimental conditions. The experimental results were also analyzed on enhanced process using purging solution at anode end. Laboratory 1-D tests were performed on typical clayey soil under the influence of direct current (DC) electric field. The purging fluids EDTA and zero valent iron powder were used as reactive barrier which enhanced the electrokinetic remediation. The removal of copper was increased from 66.55% to 74.85% respectively. The increased removal efficiency indicates that zero valent iron powder as reactive barrier can be successfully utilized for electrokinetic remediation of copper contaminated soils.*

Keywords: *Electrokinetic, Eletroosmosis, EDTA, Zero valent iron powder.*

1. INTRODUCTION

Soil contamination usually arises from the split of underground storage tanks, relevance of pesticide, percolation of contaminated surface water to subsurface strata, oil and fuel discarding, discharge of wastes from landfills or direct discharge of industrial wastes in the soil. The most widespread chemicals mixed up are petroleum hydrocarbons, solvents, pesticides, lead and other heavy metals. Due to soil contamination, undesirable effects may appear to both soil organisms and plants in situ that are present, menacing soil ecology and agricultural production[1].

For removal of soil contamination whether it is in situ or ex situ, electrokinetic remediation is one of the most effective methods, as it has high removal competence and time usefulness in soil with low permeability[2]. Basically, the electrokinetic remediation involves applying a low DC current or an electric current to electrodes inserted in the medium[2],[3]. For amputation of heavy metals from soil, DC current applies from corner to corner to the electrodes in saturated soil ensuing in transport by electroosmosis and ionic movement. Electroosmosis mobilizes the pore fluid to wash out the soil system, generally toward the cathode, while ionic movement effectively separates the negative and positive ionic variety by their transport to the anode and cathode, correspondingly[4]. In electrokintic technique, electromigration, electroosmosis, electrophoresis are three primary mechanisms. Present work show the significant result achieved by use of zero valent nano iron particle as permeable reactive barrier and support the use of permeable reactive barrier technologies in various remediation technique. The design of PRB is depend on geotechnical and geochemical properties of soil [6] . In previous research work it shows that the Ethylene-diamine-tetra-acetic (EDTA) is the best desorbing agent among other like ammonia sodium acetate and distilled water[7]. Thus if we use 0.5M EDTA and zero valent nano iron particle as permeable reactive barrier then combination of both will give the maximum removal efficiency. It is also possible that further increased experimental time may induce a higher removal efficiency of copper.

2. OBJECTIVE

The overall goal of the present study is to evaluate electrokinetic remediation system without enhancement and with enhancement for the efficient removal of the copper from clayey soil collected from field.

To accomplish this objective, five goals are following:

(i)To determine the physical and chemical properties of the soil.

(ii) To experimentally investigate the feasibility of using electrokinetic remediation technique to remove copper from clayey soils.

(iii) To determine the overall effect of the purging chemicals on the removal of copper from soil.

(iv) Enhance the Electrokinetic remediation process by use of nano iron powder as a permeable reactive barrier and study the change in metal removal efficiency.

Table 1: *Physical and chemical properties of soil*

Sr. No.	Property	Value
1.	Particle Size Distribution	
	Gravel (%)	5.60
	Sand (%)	17.4
	Silt (%)	52.0
	Clay (%)	21.0
2.	Atterberg Limits	
	Liquid Limit (%)	40
	Plastic Limit (%)	22
	Shrinkage Limit (%)	13
	Plasticity Index (%)	30
3.	Activity	1.87
4.	Specific gravity	2.62
5.	Maximum Dry Unit Weight (kN/m^3)	14.68
6.	Optimum Moisture Content (%)	17.4
7.	Hydraulic Conductivity (m/sec)	4×10^{-9}
8.	Specific Surface Area (m^2/g)	0.18
9.	Cation exchange capacity (USEPA) (meq/100 g)	22
10.	pH	8.52
11.	Organic Content (%)	6.25
12.	Loss on Ignition (LOI) (%)	9.93
13.	$CaCO_3$ (%)	2.5
14.	Soil classification (USCS)	CL
15.	Cu (mg g^{-1})	0.5
16.	Silica-Sesquioxide ratio (SSR)	5.74

3. MATERIALS AND METHODS

For the present study, field soil was obtained from an agricultural field site of Meja village, Allahabad district (Uttar Pradesh, India) at a depth of 1-2 m. After collection, the soil sample was air dried first. Pebbles, stones, and plant roots were hand-picked and discarded. Soil sample was further washed through 0.425 mm sieve to obtain fine grained soil. Physical and chemical properties of virgin soil are presented in Table 1.

3.1 Electrokinetic System

A schematic experiment unit used in this experiment is shown in **Fig. 1**. The test set up consists of cylindrical cell prepared by Perspex material containing sample compartment of 6.9 cm inner diameter and 35 cm in length having two electrode compartments **(Fig. 2)** with an anode reservoir and cathode reservoir. At each end of the soil cell, a cork with nylon net is used as strengthening. It is right away provided next to filter paper to prevent spreading of fine soil particles from inflowing into the reservoir. Gas vents were provided in both the electrode compartments to exceed gases generated from the electrolysis progression. Graphite anode and cathode were fitted at the end of reservoir were attached by a direct-current power supply. Along the longitudinal axis of the cylindrical cell, five auxiliary electrodes were tidy for the function of electric field distribution along the sample. The unit was powered by 12 V batteries 40 AH of 4 nos. and current of 40 A outputs. The voltage, current and various incremental voltages of the unit were monitored and logged physically by means of digital millimeters at regular intervals.

3.2 Experimental procedure

Soil was chosen to be contaminated with copper at maximum sorption value found in sorption studies. To minimize the discrepancy between the fields contaminated soil and the laboratory contaminated soil, the latter had to be aged before EK extraction process. The uncontaminated soil sample was spiked with a solution containing copper. The suspension was aged for 3 days. The contaminated soil was then dried in an oven and thoroughly mixed to ensure maximal homogeneity, before EK experiments were carried out. Finally, the concentration of copper was also confirmed by both soil digestion processes. The copper contaminated soil with moisture content 40% (approaching to liquid limit value) was maintained for full saturation behaviour and the equilibrium soil sample was then placed in the electrokinetic cell in uniform layers.

3.3 Contaminant Concentration in Soil

The concentration of copper of EK treated soils was determined using atomic absorption spectrophotometer (Perkin Elmer).

The digestion procedure followed weighing 3.0 g of soil sample into a bottle, then adding 30 ml of 2 M nitric acid (HNO_3). The mixture was kept in shaker and shaken for 24 h. The sample was extracted, centrifuged and filtered and finally concentrations were measured using AAS. Precautions were taken in order to ensure the accuracy and repeatability of the test results.

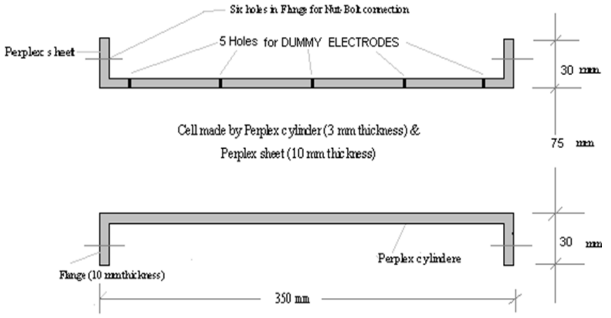

Fig 1: *Details of middle cell.*

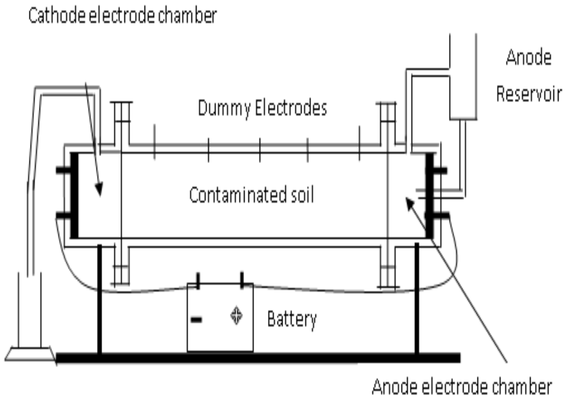

Fig 2: *Schematic diagram of EK test setup*

3.4 Electrokinetic Testing

A total of 3 different experiments were conducted to evaluate the removal efficiency of desorbing agents. All experiments were conducted once soil was saturated with de-ionized water and EDTA was used as purging solution in the electrode compartments. For each Electrokinetic test, approximately 2 kg of dry soil were saturated with 40 % of water i.e. 800 ml water and filled into EK cell. A constant DC electric potential was then applied across the specimen in all the experiments for a treatment time of 7 days. When it was necessary, the loss of liquid due to evaporation or the electrolysis reactions was compensated with the addition of desorbing agent in the anode compartment by creating a small constant external hydraulic gradient of 0.3 across the cell. A variety of physicochemical parameters were measured at regular time intervals during the experiment. Current and voltage at each 1 hour interval was measured at every section of cell like A-1, A-2, A-3, A-4, A-5, A-C.

After finishing the experiments the soil was segmented into slices from anode towards cathode. The number of slices was 6, and the length of slices at anode to section 1 and cathode to section 5 was 15 mm thick. The middle slices lengths were 80 mm thick. For each of these slices the copper concentration measured by AAS.

Use Zero valent nano iron particle as barrier 10 gm of sand and 10 gm of iron particle are used as barrier material.

ZVI powder as a following type of specification

Minimum assay = 98.5 %

Arsenic = 0.0005 %

Copper = .01%

Sulphate = .02 %

Lead =0.002 %

Mesh size = 300 mesh

Mesh is designated by the number of openings per linear inch in the sieve.

Mesh was further calculated and converted into micron and the size of zero valent nano iron particle was 47 micron.

X mesh =1/x inches

300 mesh = 47 micron

Thickness of barrier

Thickness of barrier was calculates by following formula:

$(\Pi/4)$ x d^2 x h = weight of barrier / (density of iron and sand)

Where d = internal diameter of cell

H = thickness of barrier

$(\Pi/4)$ x 6.5^2 x h = 20 /9.402

Iron density = 7.8 gm /cc

Sand density = 1.602 gm /cc

After calculating

H = 6 mm thick barrier was used.

3.5 Experimental Results:

Table 3: *Water content, Voltage and pH variation after 7 days EK test with deionised water*

Compartments		A-1	A-2	A-3	A-4	A-5	A-C
7 Days with deionised water	Water content, %	39.49	38.32	35.05	36.87	40.72	40.29
	Voltage, V	6.4	7.5	10.4	14.6	29.7	43.2
	pH	5.69	6.98	7.18	7.98	8.15	9.02

Table 4: *Water content, Voltage and pH variation after 7 days EK test with 0.5M EDTA.*

Compartments		A-1	A-2	A-3	A-4	A-5	A-C
7 Days with 0.5M EDTA	Water content, %	40.32	35.53	38.25	41.29	39.09	35.91
	Voltage, V	10.8	14	17.2	23.5	27	42.8
	pH	5.74	6.89	6.03	5.74	7.59	7.75

Table 5: *Water content, Voltage and pH variation after 7 days EK test with 0.5M EDTA and zero valent nano iron powder*

Compartments		A-1	A-2	A-3	A-4	A-5	A-C
7 Days with 0.5M EDTA and Zero valent nano iron powder	Water content, %	42.5		35.30	39.75	34.55	40.40
	Voltage, V	7.4		8.3	9.3	10.3	11.6
	pH	4.99		5.26	5.20	6.60	6.92

4. RESULTS AND DISCUSSION

Voltage, current and water content variation: The variation in voltage and current is given in **Fig. 3, 4**(7 days test with deionised water), **5, 6**(7 days test with 0.5M EDTA), **7, 8** (7 days test with 0.5M EDTA with nano iron particle). **Fig. 3, 5& 7** shows the time vs. voltage graph which include the variation in voltage between anode and cathode and also between anode and the corresponding dummy electrodes i.e. dummy electrode 1 to 5. And **Fig. 4,6&8** shows the variation of current with respect to time between anode and cathode. Water content variation across the cell is given for the experiment i.e. case of 7 days sorption of soil and its remediation with the help of deionised water **(Fig. 9)**, 0.5M EDTA **(Fig. 10)** and 0.5M EDTA with nano iron particle **(Fig. 11)**. The graphical representation for the water content variation is given in **Fig.9, 10 & 11.**

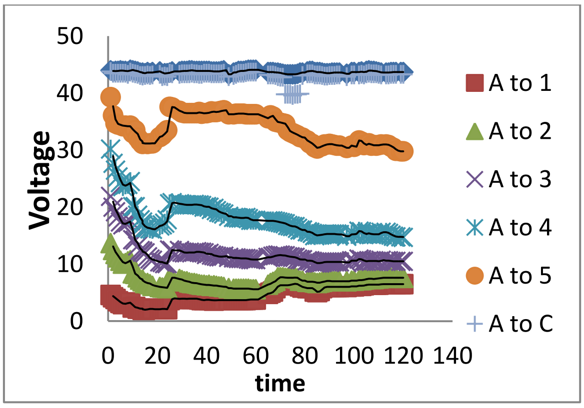

Fig 3: *7 days test with deionised water (Voltage variation)*

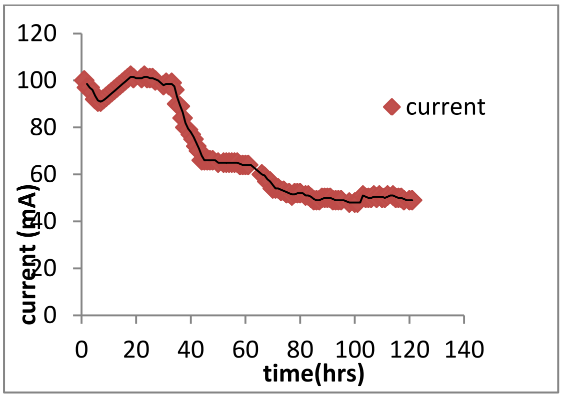

Fig 4: *7 days test with deionised water (Current variation)*

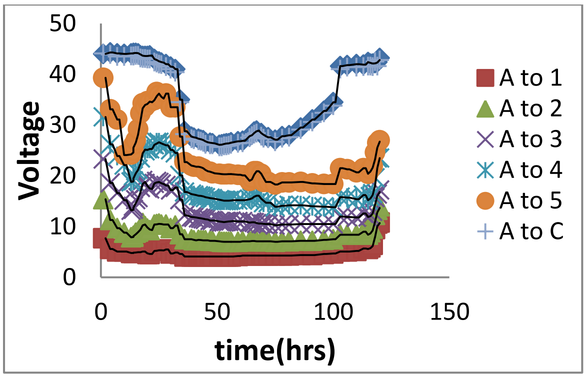

Fig 5: *7 days test with 0.5M EDTA (Voltage variation)*

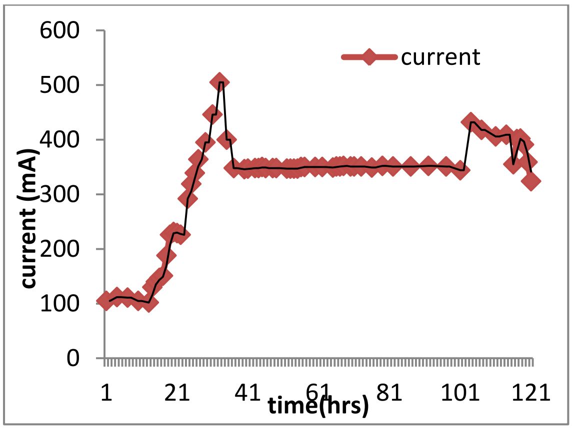

Fig 6: *7 days test with 0.5M EDTA (Current variation)*

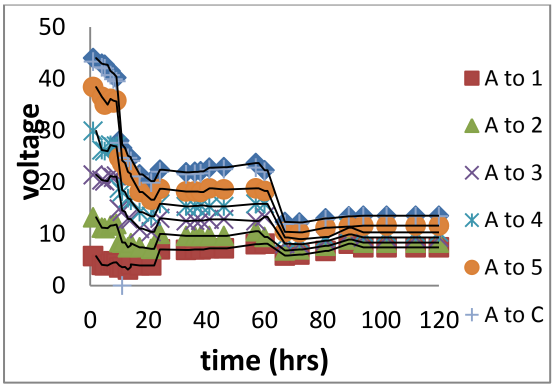

Fig 7: *7 days test with 0.5M EDTA with nano iron particle (Voltage variation)*

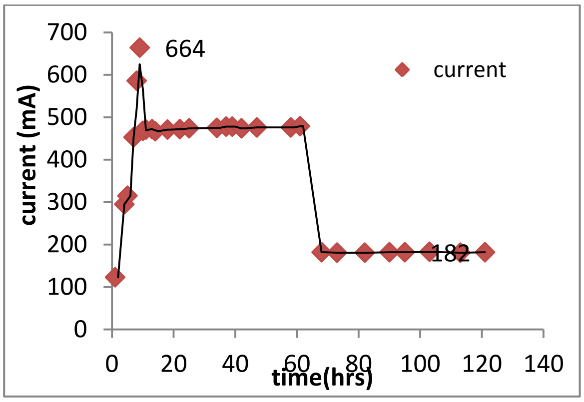

Fig 8: *7 days test with 0.5M EDTA with nano iron particle(Current variation)*

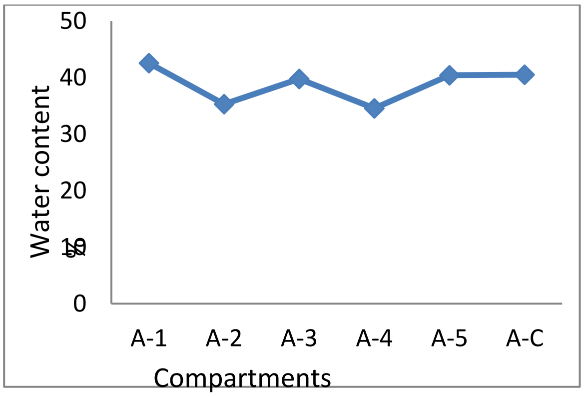

Fig 9: *7 days test with deionised water*

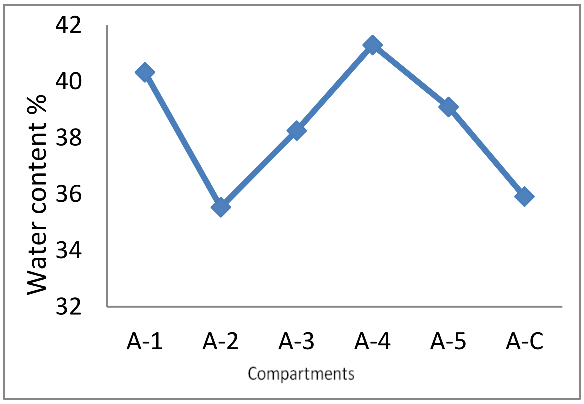

Fig 10: *7 days test with 0.5M EDTA*

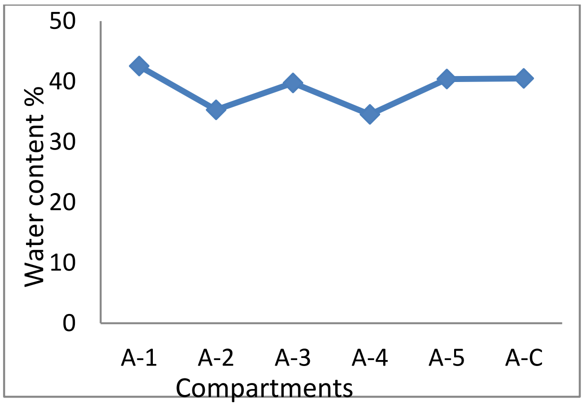

Fig 11: *7 days test with 0.5M EDTA with nano iron particle*

Table 6: *shows removal of copper from copper contaminated soil after 7 days test on electrokinetic with deionesd water*

Compartment	Copper present after removal (mg/g)
	Deionised water
A-1	9.7
A-2	10.83
A-3	13.89
A-4	12.03
A-5	14.95
A-C	39.11
Average	**16.85**

We know initial copper concentration in the soil is 20mg/g of soil. Total copper removed from soil is 3.15mg/g of soil. Hence removal efficiency is 15.75%.

Table 7: *shows removal of copper from copper contaminated soil after 7 days test on electrokinetic with 0.5M EDTA*

Compartment	Copper present after removal (mg/g)
	0.5M EDTA
A-1	1.6
A-2	3.74
A-3	4.85
A-4	3.02
A-5	5.85
A-C	21.08
Average	**6.69**

Again we know initial copper concentration in the soil is 20mg/g of soil. Total copper removed from soil is 13.31mg/g of soil. Hence removal efficiency is 66.55%.

Table 8: *shows removal of copper from copper contaminated soil after 7 days test on electrokinetic with 0.5M EDTA by nano iron particle using as reactive barrier.*

Compartment	Copper present after removal (mg/g)
	0.5M EDTA with nano iron powder
A-1	1.20
A-2	2.72
A-3	3.02
A-4	15.10
A-5	4.34
A-C	3.80
Average	**5.03**

Again initial copper concentration in the soil is 20mg/g of soil. Total copper removed from soil is 14.97mg/g of soil. Hence removal efficiency is 74.85%.

From the analysis of experimental results, it is observed that by use of deionesd water, the EK remediation of copper contaminated soil is least, only 15.75% removal of copper is observed after 7 days sorption. By use of purging solution 0.5M EDTA the removal efficiency of copper is increased to 66.55%. The use of purging solution with nano iron particle is observed still more effective in EK remediation of copper contaminated soil as efficiency of copper removal is increased further to 74.85%. Therefore it is concluded that EDTA with nano iron particle as barrier plays a significant role in EK remediation of copper contaminated soil. Water content and pH value are observed changing with each compartment. The behavior of voltage and current is also seen changing after use of EDTA and nano iron particle.

5. CONCLUSIONS

The important conclusions derived from the present work are as follows:

- It is concluded that eletrokinetic remediation is feasible to remediate the fine grained soil contaminated with copper.
- Results also show the wide variation in removal efficiencies, due to factor like pH, water content and different purging solutions applied.
- From the results obtained by variation of current when 0.5M EDTA and nano iron powder are used, a continuous rising trend of current is seen, which is because of presence of dissolved species and less contaminant migration in the system From the results on use of purging solution deionised water, the EK removal efficiency of copper attained was 15.75% only.
- From the results on use of purging solution 0.5M EDTA, the EK removal efficiency of copper was enhanced to 66.55%.
- From the results on use of purging solution 0.5M EDTA and nano iron powder as a barrier, a maximum EK removal of copper attained was 74.85%.
- Use of zero valent nano iron powder as a permeable reactive barrier shows a remarkable increase in efficiency, and cost of barrier installed was under so economical, thus pilot scale Electrokinetic remediation process is now seems quite feasible.

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