



## Copper Removal Efficiency of EDTA from Laboratory Contaminated Soil

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### ABSTRACT

Contamination of soil is a serious environmental issue from past decades & removal of contaminants from soil may be costly or time taking. The nature of the electrostatic potential near the surface of a particle is known as Zeta Potential. Zeta Potential is determined by measuring the velocity of the particles in a D.C. electric field. The main objective of this study is to analyze the effect of Chemical additive on the Zeta Potential of heavy metal contaminated soil. Copper used as a heavy metal and EDTA as a chemical additive in the present investigation. The sample taken from the field is basically clayey in nature. Various engineering properties of soil determined and the soil is artificially contaminated with Copper in the laboratory. Removal of Cu from artificially contaminated soil analyzed by using solution of EDTA in different concentrations and at different pH. Zeta potential measurements are performed by using Zeta Meter System 4.0. The Zeta Potential of virgin, contaminated and contaminated soil treated with different concentration of EDTA has been calculated at different pH in acidic as well as in basic range. At different pH the zeta potential of the soil changes & it affect the efficiency of removal of Copper from artificially contaminated soil.

**Key words:** Contamination, Copper, EDTA, Zeta potential

### INTRODUCTION

The presence of soil and water into the land cause the relative movement of soil particles and this phenomenon produced the electric potential at the solid-liquid interface. This electric potential produced at the solid-liquid interface known as the zeta potential [1]. The mobility of the soil particles is related to the dielectric constant, viscosity of the suspending liquid and to the electrical potential at the boundary between the moving particle and the liquid.

This potential measured in MilliVolts, may arise by various mechanisms. It may because of the dissociation of ionogenic groups in the particle surface and the differential adsorption of solution ions into the surface region. The ion distribution in the nearby region can be affected by the net charge at the particle surface which may increase the concentration of counter ions close to the surface. Thus, in the region of the particle-liquid interface an electrical double layer is formed. This double layer (upper part of Fig. 1) consists of two parts: an inner region containing ions bounded very tightly to the surface, and an outer region where a balance of electrostatic forces and random thermal motion determines the ion distribution. In this region the potential, decreases with increasing distance from the surface until, at sufficient distance, it reaches the bulk solution value, generally taken to be zero. The lower part of the figure represents this decay and indicates that the zeta potential is the value at the surface of shear. Zeta potential of particles basically indicates their electrical potentials; the higher the zeta potential, the higher the surface potential of charged clay particle. Fig. 1 represents the zeta potential on the diffuse double layer on a charged particle. The boundary between the moving particle and the liquid is called the slip plane and is usually defined as the point where the Stern layer and the diffuse layer meet as shown in Fig. 2. The Stern layer is rigidly attached to the colloid, while the diffuse layer is not. Hence, the electrical potential at this junction is related to the mobility of the particle and is called the Zeta Potential. Although zeta potential is an intermediate value, it is sometimes considered to be more significant than surface potential as far as electrostatic repulsion is concern. Zeta potential can be quantified by tracking the colloidal particles through a microscope as they migrate in a voltage field. The physical properties of colloids and suspensions are strongly dependent on the nature and

extent of the particle-liquid interface; the behaviour of aqueous dispersions being especially sensitive to the electrical and ionic structure of the interface.

The production and stability of colloids and suspensions are both intimately related to the so-called electrical double layer that characterizes the interface. Information relating to stability is therefore of considerable importance. It should be noted that the term stability, when applied to colloidal dispersions, is generally relative in meaning and intended to express the resistance to change of the dispersion with time.

Zeta potential measurements are directly related to the nature and structure of the electric double layer at the particle-liquid interface. pH is very important factor for the zeta potential because it effects on the charge distribution of the particle surface. If we adjust the pH, the particles can produce the zero value of electrical potential while other things remain constant in the system. When there is no charge on the particles it means there are only attractive forces between the particles will be applicable which causing flocculation. The pH value gives zero zeta potential, known as the point of zero charge (pzc). Many researchers has been investigated the significant variation in the pzc of kaolinite and the magnitude of the zeta potential. Williams and Williams (1978), Smith and Narimastu (1993), Vane and Zang (1997), Dzenitis (1997) and Hotta et al (1999) were investigated that the kaolinite gives low value of zeta potential at low pH, as well as pH increases the value of zeta potential increases and the pzc occurred between pH value 2-6[2-6]. Stephan and Chase (2001) recorded their data for pH 3-11 and the zeta potential varies between -8mV to -43mV. There was no PZC recorded for kaolinite by their investigation [7].

Variation in pH alters the zeta potential of soils, the magnitude of the zeta potential controls the fluid flow rate, whereas its sign controls the flow direction. Generally clay has a net negative charge on its surface. The negative surface electric charge of a clay particle is due to the presence of isomorphous substitution and broken structure. The negative charge on the clay surface is balanced by excess positive charge distributed in the fluid zone adjacent to the clay surface. This distribution adjacent to the clay surface is called the diffuse layer as illustrated in Fig 2.

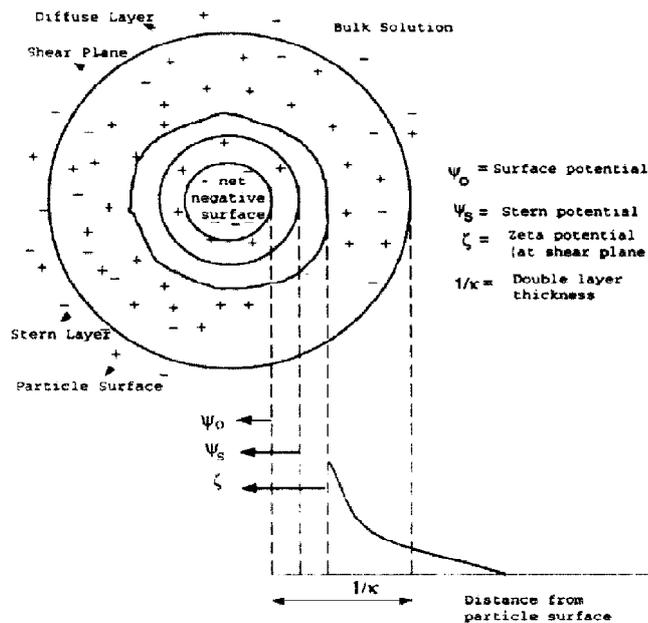


Fig.1 The location of zeta potential,  $\zeta$ , on the electrical diffuse double layer (Yukselen et al [8])

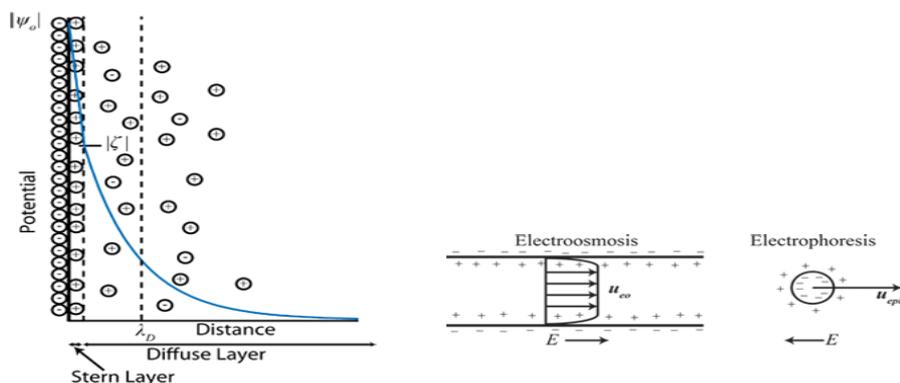


Fig.2 Diffuse layer

However, limited research has been done about the Zeta Potential of soils changes under various chemical conditions. Zeta potential is a function of surface coverage by charged species at a given pH, and it is theoretically determined by the activity of the species in solution. The zeta potentials of particles occurring in soils, such as clay and iron oxide minerals, directly affect the efficiency of the electro-kinetic soil remediation [8].

Zeta potential is therefore a function of the surface charge of the particle, any adsorbed layer at the interface, and the nature and composition of the surrounding suspension medium. It can be experimentally determined and, because it reflects the effective charge on the particles and is therefore related to the electrostatic repulsion between them, the zeta potential has proven to be extremely relevant to the practical study and control of colloidal stability and flocculation processes.

Contamination of soil is a serious environmental issue from past decades. Various remediation techniques has been applied by the researchers, most of the methods are successful but some drawbacks were also there & it was found that the removal of contaminants from soil may be costly or time taking. Immobilization of heavy metals using various chemical additives is very effective for remediation but the most significant drawbacks of immobilization are that: (1) the metal still remains in the soils. The soil does not return to its original state and it is not suitable for further use [9]; and (2) the long-term stability and effects on the bios stem (plant/animal) are unknown [10] and little has been reported by previous studies. Immobilization is thus not a permanent solution. Soil extraction is a relatively new method. Acids and chelating agents are the most popular extractive reagents for soil washing/flushing [10-13].

The objective of this study is to observe the zeta potential of virgin, soil contaminated with different concentration of copper and the contaminated soil treated with different concentration of EDTA.

### MATERIALS AND METHODS

The soil used for the analysis was collected from Meja road, near Allahabad. Engineering properties of the virgin soil were determined in the laboratory and SEM & XRD analysis also has been done for deeply analyse the soil properties. Soil sample was coated with the gold-palladium because of the conductive nature of soil for safety purpose. Then the soil was artificially contaminated in the laboratory by using copper sulphate salt ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). Batch extraction study has been done for the mixing of copper sulphate salt as well as for EDTA for the contamination and remediation purpose respectively. AAS was used for determination of copper present in the contaminated as well as remediated soil. Zeta-Meter System 4.0 was used to determine the zeta potential of virgin, contaminated as well as the remediation soil samples.



Fig.3 Zeta Meter System 4.0

### RESULTS AND DISCUSSION

The properties of the virgin soil has determined in the laboratory. The soil has been classified as clay with intermediate compressibility. Other engineering properties are given in Table. 1. Fig. 4 represents the XRD analysis and Fig. 5 shows the SEM image of the virgin soil.

#### Properties of Soil

Engineering properties of virgin soil and contaminated soil were determined in the laboratory as per the following Table 1. The properties of virgin soil have been altered after contamination.

#### Chemical Properties of Virgin Soil

Some compounds have been predicted by the chemical analysis of the virgin soil as per following Table 2. Silica and alumina were the major compounds.

### XRD Analysis

XRD analysis is mostly done for identification of minerals present in soil. The minerals presents in virgin soil are identified as kaolinite, quartz, calcite, illite [14-16]. Fig. 4 represents the XRD analysis of the virgin soil. The result confirms the clayey nature of soil particles.

### SEM Analysis

SEM analysis is basically done to analyze the texture of the soil. Interweaving bunches assemblage of clay particles shows by SEM image, Fig. 5 of virgin soil [14].

### Zeta Potential Measurements of Virgin Soil, Contaminated Soil and Treated Soil

For measurement of zeta potential, 100mg of soil mixed in 100ml of distilled water to make the soil sample for testing. Table 3 contains the Zeta Potential Measurements of Virgin Soil and contaminated soil at different pH. NaOH and HCl were used to adjust the pH of soil solution. During measuring the zeta potential try to maintain the standard deviation between 1-3 mV. Fig. 6 represents the variation obtained in zeta potential at different pH, for virgin as well as for contaminated soil. From the results, it was found that the zeta potential of contaminated soil was decreased as comparable to virgin soil and the direction of movement was also changed. Three concentrations 0.01M, 0.05M and 0.1M of EDTA has been taken for decontamination of soil. Fig. 7 shows the zeta potential of decontaminated soil with different concentration of EDTA and the results shows that the most effective concentration of EDTA for removal of copper is 0.1M.

### Zeta Potential Measurement of Soil after treating with EDTA

In this study EDTA has been mixed with contaminated soil at three different concentrations and measured the zeta potential by maintaining the solution at four different pH. Table 4-6 shows the contaminated soil treated with different concentration of EDTA and it was found that the optimum concentration of EDTA for treatment of contaminated soil is 0.1M EDTA.

Table-1 Properties of Virgin and Contaminated Soil

Properties	Virgin Soil	Contaminated soil
Liquid limit(%)	44.0	38.0
Plastic limit(%)	20.0	16.0
Plasticity index(%)	24.0	22.0
I.S. Classification of soil	CI	CI
Shrinkage limit(%)	13.90	13.52
Free swell index(%)	23.50	24.22
OMC(%)	16.00	15.70
MDD(gm/ml)	1.20	1.70
UCS(kN/m <sup>2</sup> )	91.87	88.45
pH	7.72	7.81
Specific Gravity	2.66	2.60

Table-2 Chemical properties of Virgin soil

Compounds	Wt. %
SiO <sub>2</sub>	77.10%
Al <sub>2</sub> O <sub>3</sub>	13.99%
MgO	4.88%
Fe <sub>2</sub> O <sub>3</sub>	1.78%
CaO	0.231%
TiO <sub>2</sub>	0.181%

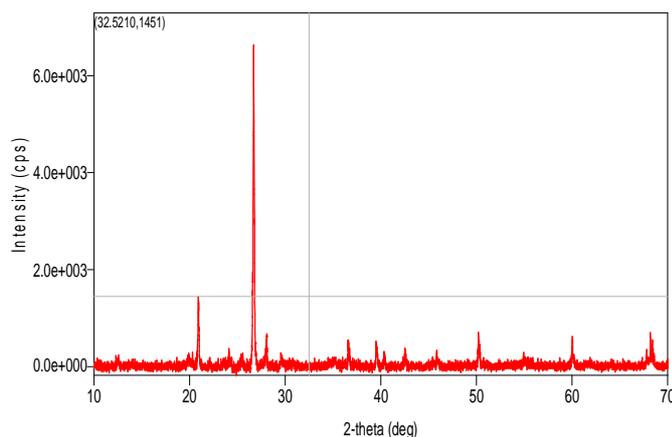


Fig 4 XRD analysis of the Virgin Soil

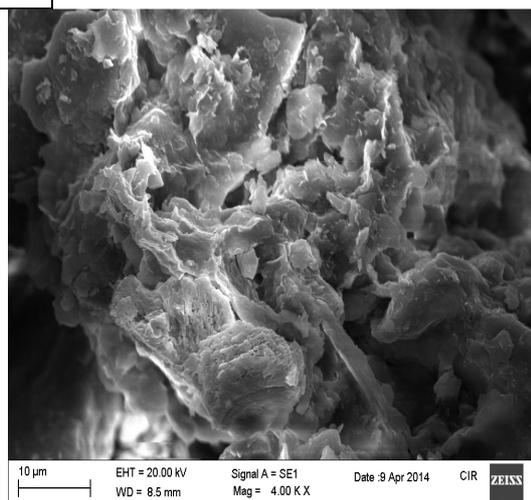


Fig.5 SEM image of Virgin Soil

Table-3 Zeta potential Measurement of Virgin Soil and Contaminated Soil at different pH

S.No	pH of Soil Sample	Virgin Soil		Contaminated Soil	
		Zeta Potential(mV)	Standard Deviation(mV)	Zeta Potential(mV)	Standard Deviation(mV)
1	3	-18.74	2.6	2.14	2.9
2	5	-22.12	1.7	-1.12	1.9
3	7	-25.22	1.9	-5.78	1.1
4	9	-30.02	2.4	-12.24	2.2

Table-4 Contaminated Soil Treated with 0.01M EDTA

S. No.	pH of the sample	Zeta Potential (mv)	Standard Daviation (mv)
1	3	-12.20	1.7
2	5	-14.87	1.2
3	7	-17.21	2.1
4	9	-26.07	2.8

Table-5 Contaminated Soil Treated with 0.05M EDTA

S. No.	pH of the sample	Zeta Potential (mv)	Standard Daviation (mv)
1	3	-14.21	2.2
2	5	-18.78	2.3
3	7	-20.20	1.7
4	9	-27.88	1.8

Table-6 Contaminated Soil Treated with 0.1M EDTA

S. No.	pH of the sample	Zeta Potential (mv)	Standard Daviation (mv)
1	3	-16.21	2.5
2	5	-21.27	1.9
3	7	-23.22	2.3
4	9	-28.76	2.1

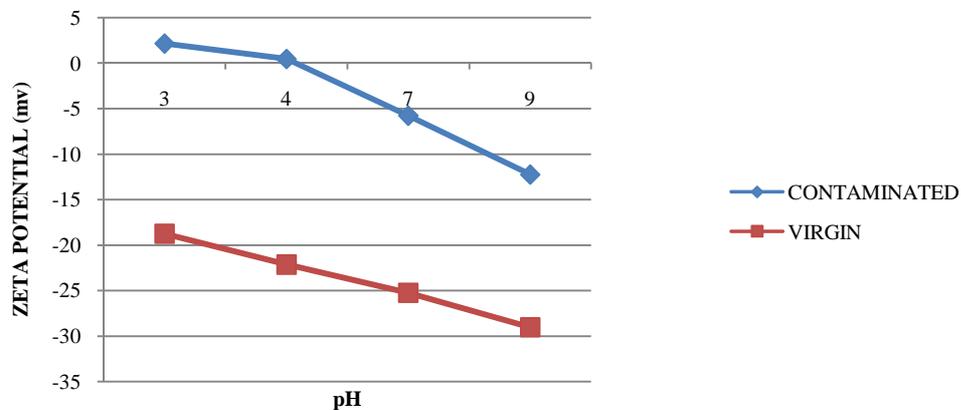


Fig.6 Comparative study of Zeta potential of Virgin and Contaminated Soil

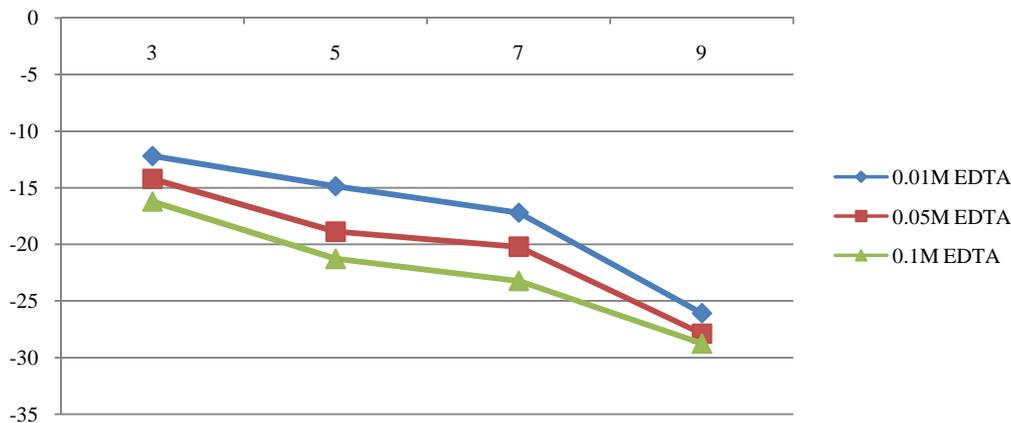


Fig.7 Zeta Potential of decontaminated soil at different EDTA concentration

## CONCLUSIONS

The present study concluded:

- From the engineering properties, virgin soil is classified as CI (clay with medium compressibility).
- From the results obtained, it is inferred that at high pH, Zeta potential is highly negative for virgin soil, which is due to presence of negatively charged ions present in soil, but as the pH is decreased, the Zeta potential reduces to lower negative values.
- The Zeta potential of contaminated soil is observed to be positive at lower pH values, which shows that the soil is highly contaminated with copper. Because copper is a salt made up with strong acid  $H_2SO_4$  and weak base  $Ca(OH)_2$ , hence the amount of positive ions is high at lower pH.

- The results of engineering properties after copper contamination show that Optimum moisture content, Unconfined compressive strength, Specific gravity, Liquid limit, Plastic limit, Plasticity index were decreased and Shrinkage limit, Free swell index and Maximum dry density were increased.
- The results of the Zeta potential of soil extracted with EDTA show that the Zeta potential is different from the Zeta potential of virgin soil. This concludes that copper impurities are still present on EDTA treated soil.
- It is further observed that after adding EDTA the Zeta Potential of soil becomes more negative value as compared to contaminated soil. This may be due to reduction in the surface charge on the soil, thus the flocculent matrix of particles can be formed easily and water can be drained easily. On the other hand, if the surface charge is higher as in the case of contaminated soil, undesirable changes can be developed as flocculent matrix of particles will get weakened.

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