# Electrokinetic Reactor for Heavy Metals removal from Industrial Wastewater Sludges : Design Aspects

## Vihangraj V. Kulkarni[1], Animes Kumar Golder[2], Pranab Kumar Ghosh[3]

[1]Department of Civil Engineering, GEC Banswara, Rajasthan, India
[2]Department of Chemical Engineering, [3]Department of Civil Engineering, IIT Guwahati, India
Email: vinaykulkarni7@gmail.com, animes@iitg.ac.in, pkghosh@iitg.ac.in

*Abstract: The ill effects of heavy metals are well known and proved to be even cacogenic for human beings. The industries are the major source of heavy metal pollution and emits heavy metals by generating wastewater and sludge. Industrial sludges are the most concentrated heavy metallic waste and considered as hazardous one. Decontamination of such sludges is practiced in many ways, one of them is through Electrokinetic migration of heavy metals. However, the designing a reactor has to address numerous critical points such as voltage across, electrode material, current density, initial water content, space-time yield,reactor sizes, and serviceability of reactor. This paper covers all the design aspects of Electrokinetic reactor.*

*KEYWORDS: Industrial Sludge, Electrokinetic migration, heavy metal, Electrokinetic reactor*

## Introduction

Heavy metals removal from industrial wastewater is conventionally carried out by hydroxide and carbonate precipitation. It suffers from generation of toxic heavy metallic sludge [1, 2]. The sludge disposal practices includes incineration, landfilling, ocean dumping and lagooning[3]. Incineration pollutes air with toxic gases, hence required expensive off gas treatment [4]. The heavy metals present in sludge finally leach outs and contaminates soil as well as groundwater ultimately affecting human health. The best disposal practice could be utilization of the sludge in agricultural or nonagricultural lands by minimizing the metal loading.

In recent years, researches are going on to reduce metal content of sludge for its utilization for agricultural purpose. It includes chemical extraction of heavy metals using organic and inorganic acids, bioleaching, Electrokinetic (EK) treatment and supercritical extraction [5, 6].

The basic EK treatment of sludge, sediment, soil or any solid waste containing heavy metals includes application of low voltage direct current through embedded electrodes. It is also referred as electrochemical remediation, electro-remediation, and electro-reclamation [6]. The application EK treatment is accepted as one of the most effective treatment for in-situ remediation of metal contaminated soils [7]. The application of voltage makes electric current to flow through applied media altering its physicochemical properties. The changes in media properties are result of electric current induced reactions such as electrolysis of water, oxidation-reduction, mineral decomposition and physicochemical sorption [8]. As a result, heavy metals from contaminated media gets distorted through different coupled mechanisms viz. electromigration, electro-osmosis and electrophoresis along with water electrolysis [6, 9, 10]. Electrolysis of water produces oxygen gas and $H^+$ in the anode compartment, while hydrogen gas and hydroxyl anions are formed at the cathode. This also

could cause contaminants to be desorbed and/or dissociated, and results in an initiation of electromigrationi.e transport of ions and polar molecules under the influence of the applied electric field. In addition, an acid front is generally produced at the anode during the electrolysis of water and moves towards the cathode [10, 11].

## Electrokinetic migration of heavy metals for sludge decontamination

Electrokinetic migration is technique in which potential applied across electrodes acts as driving force for migration of charged particles towards oppositely charged electrode. Essentially, electrokinetics involves the installation of electrodes into the subsurface surrounding the contaminants. After the electrodes are in place, a low electrical potential is applied across the anode(s) (positively charged electrode) and the cathode(s) (negatively charged electrode). As a result of the electrical gradient, contaminant transport occurs due to various coupled mechanisms such as electromigration, electroosmosis and electrophoresis, which take place together with the electrolysis of water at electrodes [6, 10]

These phenomenon can be further explained as

i. The transport of ions and ion complexes toward the electrode of opposite charge under the application of DC voltage as driving force is termed as electromigration. [9].

ii. Electroosmosis is the movement of sludge moisture, which generally takes place from the anode to the cathode and is due to the existence of a space-charge on the solution side of the particle/solution interface. In consideration of the fact that ionogenic groups, like silanols, are ionized above pH 3 affording a negative charge to the solid surface, the space charge on the solution side is positive. Its migration toward the cathode causes solution displacement too, thus generating a cathode-directed electroosmotic flow [6]

iii. Electrophoresis is the transport of charged particles or colloids under the influence of an electric field; contaminants bound to mobile particulate matter can be transported in this manner [10]

Apart from these, electrolysis of water expected to happen in electrokinetic cell. Electrolysis of water produces oxygen gas and $H^+$ in the anode compartment, while hydrogen gas and hydroxyl anions are formed at the cathode. This causes contaminants to be desorbed and/or dissociated, and results in an initiation of electromigrationi.e transport of ions and polar molecules under the influence of the applied electric field. In addition, an acid front is generally produced at the anode during the electrolysis of water and moves towards the cathode. This front can be used to inject acidity to sludge, solubilize basic metal hydroxides, carbonates or adsorbed species, and protonate electron-rich organic functional groups in order to

give molecules a more cationic character and promote their migration across the electric field thus facilitating their removal [10, 11].

Electrokinetic migration of nickel (II) through synthetically prepared nickel (II) contaminated sludge was studied by [9]. 5 x 5 x 25 cm reactor with initial concentration of 300 mg/kg of sludge was used. Rate of migration of nickel ions observed to be increased from anode to cathode with increasing voltage from 5-25 V. Lowest concentration of 42 mg/kg and highest concentration of 678 mg/kg at a normalized distance of 20% and 80%, respectively, from the anode were observed after 14 h of operation at an applied voltage of 25 V. Maximum of 13.1 and minimum of 4, pH was noticed at normalized distance of 20% and 80% from anode with application of maximum voltage of 25 V. The study concluded feasibility of electrokinetic migration of heavy metals through contaminated sludge. Effects of other parameters such as initial water content, current density, space-time yield were not studied. Migration of copper and iron from anaerobic granular sludge in open and closed cell was studied by [12]. The drastic change in pH was observed in open cell which was absent in closed cell as reason of conditioning of cathode with $HNO_3$ in closed cell. Adjustment of initial pH of catholyte in acidic range increased migration of copper as well as iron towards cathode, as, in acidic range copper and iron carry positive charges, in result electrokinetic migration was enhanced. About 20% and 5% higher concentrations of copper and iron than initial concentrations were observed at cathode when initial pH was adjusted in acidic range at 2.5. Addition of Chelating agents such as EDTA formed negatively charged compounds with heavy metals. With initial pH of 12.5 addition of EDTA didn't induced any mobility, contrary when pH was 7.7 migration of copper towards anode occurred indicating formation of $CuEDTA^{2-}$ complexes. The open cell given higher migration than closed cell as some inactive electric field areas present in the soil/sludge when using the 'closed' cell layout [12, 13]. The study failed to calculate net removal efficiencies of copper and iron from the sludge cake. Hence, the accumulation and distribution were presented as the major electrokinetic treatment assessment tool.

Similar results were observed in study carried out by [14] in which acidification of sludge increased mobility of heavy metals inducing higher electrokinetic migration of heavy metals towards cathode. The influence of acidification of sewage sludge on the heavy metals mobility was studied in deep, within the pH range from 2.7 to 7.1, mobility of heavy metals followed the sequence: Ni, Zn, Cu, As, Cr, Pb similar results were observed by [15]. The acidification study showed that acidification of sewage sludge changed the distribution of heavy metals by transfer of their different fractions into more mobile forms. Effects of initial water content and temperature were studied by [10] which concluded that initial water content does affect electrokinetic process but do not significantly influence migration and removal of total aluminum. Temperature rise reported to be beneficial in electrokinetic sludge processing increasing rate of migration and reducing processing time.

Application of electrochemical process is not limited to heavy metals removal, but treatment of different industrial wastewaters such as dyes and pigments [16], textile industries [17, 18],

Lead frame nickel-plating [19, 20] by electrodeposition were also studied. Reduction of organics by using electrochemical treatment is also reported by various researchers [21].

The electrokinetic migration has many advantages viz. low power consumption, capability of removing wide range of pollutants, less running cost, control over flow of water as well as contaminants in wastewater/sludge, and higher rate of removal. But there are some aspects those needs to be addressed to make optimum use of the process; which includes complexity of media, surface interactions, chemical and electrodic reactions and low solubility of target pollutants [11, 12].

The overall efficiency of the electrokinetic migration process depends on many factors, including the contaminant ion concentration, hydration of ions, mobility of the ions, viscosity of the wastewater/sludge, the temperature investigation, effect of increasing the voltage gradient, remediation times, current density and initial moisture content [10].

Thus considering dynamicity of Electrokinetic process with different operating conditions, higher efficiency of electrikinetic migration process can be achieved by designing reactor system which is given by [21]. The key parameters for designing a reactor are mass transfer coefficient $Km$, specific electrode area $a_e$ and reactor is space-time yield $(\rho)$. The removal of metal ions $Me^{z+}$ from waste water is based on the cathodic metal deposition as:

$$Me_{sol}^{z+} + ze^- \leftrightarrow Me$$
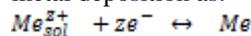
From a thermodynamic point of view, the Nernst equation predicts that it should be possible to decrease the $Me^{z+}$ concentration in solution to an arbitrarily low level, if the potential $E$ of the $\frac{Me}{Me^{z+}}$ electrode is maintained sufficiently negative with respect to the standard potential $E°_{Me/Me^{z+}}$.

$$C_{Me^{z+}} = C^+ \exp\left[\frac{zF}{RT}\left(E - E^o_{Me/Me^{z+}}\right)\right]$$

However, at extremely low concentrations, the rate of the mass transport controlled process strongly decreases. In practice, electrolysis at concentrations below 0.05 ppm is no longer economical due to increasing electrolysis time and unacceptable space–time yield. Since the current densities at low metal ion concentrations are small, the specific energy demand for an electrochemical waste water purification process is generally quite low. More relevant are the specific investment costs, which are inversely proportional to the space–time yield ρ of the reactor. For cathodic deposition in an electrochemical reactor of volume V, the space time yield is defined as the amount of metal deposited $dm$ deposited in time $dt$ :

$$\rho = \frac{1}{V}\frac{dm}{dt}$$

According to Faraday's law, $dm$ is proportional to the electrolysis charge $A\emptyset^e i\, dt$

$$dm = A\emptyset^e i\, dt\, \frac{M}{2F}$$

Where $\emptyset^e$ is the current efficiency, $A$ the actual electrode area, and $M$ the molecular weight of the metal deposited. The optimal process conditions are met when the rate of the heterogeneous reaction attains its maximum at the limiting diffusion current density, $i = i_l$

$$i_l = -ZFD_{Me^{z+}}\frac{C_{Me^{z+}}}{\delta} = -ZFk_m C_{Me^{z+}}$$

Where $D_{Me^{z+}}$ is the diffusion coefficient, d the Nerst diffusion layer thickness, and $k_m = \frac{D}{\delta}$ is the mass transport coefficient.

On replacing the current density $i$ in Eq. (4) by $i_l$, the space–time yield can be expressed as:

$$\rho = \emptyset^\theta M A_e k_m C_{Me^{z+}}$$

This is the key formula for the design and construction of an electrochemical reactor for waste water treatment and metal recovery. For a given metal ion concentration $C_{Me^{z+}}$ a high mass transfer coefficient $k_m$ and a large specific electrode area $a_e = A/V$ are essential to obtain high space–time yields.

## Conclusion

The paper demonstrated the various mechanisms of the heavy metal transport through industrial sludge under the application of the voltage drop. The three mechanisms i.e. electromigration, electroosmosis, and electrophoresis were well explained with the scientific reasons and the type of mechanism for removal of heavy metals bound to organic, inorganic and Fe-Mn bound is explained. The design parameters for an Electrokinetic migration reactor such as voltage across, electrode material, current density, initial water content, space-time yield, reactor sizes, and serviceability of reactor are elaborated, the current density being the most critical for heavy metal migration.

## References

i.      Barakat, M.A., New trends in removing heavy metals from industrial wastewater. Arabian Journal of Chemistry, 2011. **4**(4): p. 361-377.

ii.     Dahodwalla, H. and S. Herat, Cleaner production options for lead-acid battery manufacturing industry. Journal of Cleaner Production, 2000. **8**(2): p. 133-142.

iii.    Metcalf, Eddy, and G. Tchobanoglous, Wastewater engineering: treatment disposal reuse. 1979: McGraw-Hill.

iv.     Babel, S. and D. del Mundo Dacera, Heavy metal removal from contaminated sludge for land application: A review. Waste Management, 2006. **26**(9): p. 988-1004.

v.      Pathak, A., M.G. Dastidar, and T.R. Sreekrishnan, Bioleaching of heavy metals from sewage sludge: A review. Journal of Environmental Management, 2009. **90**(8): p. 2343-2353.

vi.     Ferri, V., et al., Electrokinetic extraction of surfactants and heavy metals from sewage sludge. Electrochimica Acta, 2009. **54**(7): p. 2108-2118.

vii.    Ammami, M.T., et al., Simultaneous electrokinetic removal of polycyclic aromatic hydrocarbons and metals from a sediment using mixed enhancing agents. International Journal of Environmental Science and Technology, 2014. **11**(7): p. 1801-1816.

viii.   Gao, J., et al., Effects of electrokinetic treatment of contaminated sludge on migration and transformation of Cd, Ni and Zn in various bonding states. Chemosphere, 2013. **93**(11): p. 2869-2876.

ix.     Ghosh, P., S. Balagurunathan, and C. Basha, Electrokinetic Migration of Nickel [Ni(II)] in Contaminated Sludge. Journal of Hazardous, Toxic, and Radioactive Waste, 2012. **16**(3): p. 201-206.

x.      Cherifi, M., S. Hazourli, and M. Ziati, Initial water content and temperature effects on electrokinetic removal of aluminium in drinking water sludge. Physics Procedia, 2009. **2**(3): p. 1021-1030.

xi.     Rajeshwar, K., J.G. Ibanez, and G.M. Swain, Electrochemistry and the environment. Journal of Applied Electrochemistry, 1994. **24**(11): p. 1077-1091.

xii.    Virkutyte, J., M. Sillanpää, and P. Lens, Electrokinetic copper and iron migration in anaerobic granular sludge. Water, Air, and Soil Pollution, 2006. **177**(1-4): p. 147-168.

xiii.   Turer, D. and A. Genc, Assessing effect of electrode configuration on the efficiency of electrokinetic remediation by sequential extraction analysis. Journal of Hazardous Materials, 2005. **119**(1–3): p. 167-174.

xiv.    Wang, J.-Y., et al., Evaluation of electrokinetic removal of heavy metals from sewage sludge. Journal of Hazardous Materials, 2005. **124**(1–3): p. 139-146.

xv.     15.     Iqbal, M. and R.G.J. Edyvean, Biosorption of lead, copper and zinc ions on loofa sponge immobilized biomass of Phanerochaete chrysosporium. Minerals Engineering, 2004. **17**(2): p. 217-223.

xvi.    Modirshahla, N., M.A. Behnajady, and S. Kooshaiian, Investigation of the effect of different electrode connections on the removal efficiency of Tartrazine from aqueous solutions by electrocoagulation. Dyes and Pigments, 2007. **74**(2): p. 249-257.

xvii.   Aouni, A., et al., Treatment of textile wastewater by a hybrid electrocoagulation/nanofiltration process. Journal of Hazardous Materials, 2009. **168**(2–3): p. 868-874.

xviii.  Radha, K.V., V. Sridevi, and K. Kalaivani, Electrochemical oxidation for the treatment of textile industry wastewater. Bioresource Technology, 2009. **100**(2): p. 987-990.

xix.    Chen, C.-S., Y.-J. Huang, and Y.-H. Huang, Treatment of lead frame nickel-plating wastewater with newly designed electrodeposition reactor. Sustain. Environ. Res, 2011. **21**(6): p. 341-345.

xx.     Hunsom, M., et al., Electrochemical treatment of heavy metals (Cu2+, Cr6+, Ni2+) from industrial effluent and modeling of copper reduction. Water Research, 2005. **39**(4): p. 610-616.

xxi.    Jüttner, K., U. Galla, and H. Schmieder, Electrochemical approaches to environmental problems in the process industry. Electrochimica Acta, 2000. **45**(15–16): p. 2575-2594.