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Review Article

ELECTROKINETIC REMEDIATION OF HEAVY METAL CONTAMINATED SOIL

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Heavy metal contamination is a major social issue in the era of urbanization and industrialization. Industries are practicing open dumping since it is an economic means of waste disposal. Wastes which contain heavy metal will contaminate soil as well as ground water. So soil remediation is nowadays gaining importance. Not only industries, but also households and vehicles cause heavy metal contamination. A number of methods are available for soil contamination. But 100% removal is not possible. But electrokinetic remediation method removes heavy metals effectively because en external energy is applied in the form of current. This method does not cause any secondary pollution. Various enhancement techniques are available to increase the removal efficiency. This article provides a brief description of different remediation techniques available and various enhancement techniques practiced in electrokinetic remediation.

Keywords: Heavy metal, Contaminated soil, Remediation Techniques, Electrokinetic Remediation, Enhancement techniques

INTRODUCTION

Due to rapid industrialization and urbanization, soils are increasingly getting polluted. Many industries are generating wastes which contain heavy metals. Nowadays, industries are practicing open dumping, since it is an economical means of waste disposal. Waste, which contains heavy metal, either in liquid or solid form, will pollute soil and ground water, when it gets disposed off to the soil. It has become a major social issue. So removal of heavy metal from soil or decontamination of soil is now gaining importance.

Heavy metals consist of group of metals and metalloids. Their atomic density is more than 5 times that of water. Heavy metal contamination of soil is a common occurrence in industrial areas and in areas with high traffic volume. Heavy metal contamination of soil occurs during mining, manufacturing, and the use of synthetic products such as pesticides, paints, batteries, industrial waste, and land application of industrial or domestic sludge (USDA NRCS, 2000).

Old landfills with industrial wastes dumped get contaminated. Fields and orchards

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sprayed with insecticides with arsenic, past applications of waste water or municipal sludge, areas in or around mining waste piles and tailings, industrial areas with chemicals may have been dumped on the ground, or in areas downwind from industrial sites (USDA NRCS, 2000).

The density of heavy metal is more than 5 g/cm^3. Most common problem causing heavy metals are Lead, Mercury, Cadmium, Arsenic, etc. Other problems associated with heavy metals is, it is non-biodegradable. Unlike carbon based molecules, it remains in the soil for decades (Giannis *et al*., 2009). So it is important to have an effective and economical soil remediation technique.

REMEDIATION TECHNIQUES

A number of technologies have been developed in response to address increasing environmental problems. A particular contaminated site requires a combination of different technologies (Khan *et al*., 2004). Soil remediation techniques can broadly be divided into physical, chemical and biological remediation (Zhitong Yao *et al.,* 2012). It can also be divided into in-situ and ex-situ techniques. In many site physical, chemical and biological methods are used in conjunction with one another to reduce the contaminant level (Khan *et al*., 2004).

Solidification/Stabilization

Solidification or stabilization technique is used to remediate soil as well as sludge. It can also be used to treat hazardous residues of any industrial activity. By this method the metal mobility is decreased by physically restricting the contact between the contaminant and the ground water or the chemical properties of the contaminants are altered to restrict the contact. Thus waste will be converted to a less mobile form (Evanko and Dzombak, 1997). Though these immobilization methods cannot remove metal from sediment, due to their low cost and fast remediation effect, they are still popularly applied (Peng *et al.*, 2009).

Soil Washing

Soil washing is relatively a simple method which is adopted to decontaminate soil. Washing water is added to remove the contaminant from the soil (Peng *et al*., 2009). Commonly used washing agents are, surfactant, chelating agents, acids, etc. (Zhitong *et al.*, 2012). Inorganic acids such as sulphuric acid and hydrochloric acid chelating agents such as ethylene diaminetetra acetic acid (EDTA) and nitrilotriacetate (NTA) organic acids such as acetic acid, citric acid etc., are examples of washing agents used. This method alone is sometimes used for removal of heavy metals. But more often it is combined with other technologies as a pretreatment or post treatment technique (Jankaite and Vasarevicius, 2005).

Vitrification

This is also an immobilization technique. A strong energy source is applied to melt soil or other hard material (600-1200^{o}C). By this method, organic contaminants are destroyed by pyrolysis and inorganic contaminants are immobilized (Acar and Alshawabkeh, 1993). The contaminants/metals may get volatilized due to high temperature and that is collected for treatment or disposal. Though in-situ processes are preferred due to lower energy consumption, it can be performed both ex-situ and in-situ. Typical stages in ex situ vitrification processes may include excavation, pretreatment, mixing, feeding, melting and vitrification, off-gas collection and treatment, and forming or casting of the melted product (Evanko and Dzombak, 1997). Energy for heating can be applied by means of fossil fuel burning or using electrodes, through arc, plasma and microwave energy in case of ex-situ remediation. Electrodes inserted in the soil provide the required heat in case of in-situ process (Zhitong *et al.*, 2012).

Flotation

This is a separation method for hetero phase system. Gas bubbles are attached to dispersed phase to form aggregates. Then these aggregates are floated, and thus separated from the dispersing medium. This method is mainly used in mining industry to separate valuable metals (Peng *et al.*, 2009).

Isolation

This is an in-situ remediation technology to prevent the movement of contaminant to the ground water where other methods are not applicable. The contaminated site is isolated from ground water by containing the contaminant in a designated area (Evanko *et al.*, 1997).

Electrokinetic Remediation

This method can be used either in-situ or ex-situ. This is one of the most promising technologies to remove the heavy metals from the contaminated soils. Remediation is possible by the application of low voltage electric field across the soil. An acid front is generated in the positively charged anode electrode and a base front is generated in the negatively charged cathode electrode. The acid and base fronts are formed because of the electrolysis reaction and are explained by given equations (Orcino *et al.*, 1998).

$$2H_2O - 4e^- \rightarrow O_2 + 2OH^-$$

$$2H_2O + 2e^- \rightarrow O_2 + 2OH^-$$

Capping

The surface water infiltration into contaminant is restricted to prevent further release of contaminant into ground water. This barrier also controls gas and odor emission, improves aesthetics and provides a stable structure. Dermal contact of contaminant is also eliminated by this method (Evanko et al., 1997).

Biological Remediation

This method involves the utilization of microorganisms or plants. Organisms or plants were used to decontaminate soil, water, air and sludge. Pollutants are accumulated as biomass. Traditional methods available for soil remediation are expensive. That leads to the introduction of bioremediation. Broadly speaking, bioremediation involves all the processes necessary for the transformation of a contaminated environment to its original form.

The indigenous microorganisms will be stimulated for this. Microorganisms can bring changes in valency of the heavy metal (e.g., hexavalent Cr to trivalent Cr). Thus they can convert it to a less toxic form. Also they can bio accumulate heavy metals on their surfaces. Some bacteria like sulphate reducing bacteria convert sulphate to hydrogen sulphide and this hydrogen sulphide precipitates heavy metals as sulphides (e.g., Zn, Cd). In some cases bacteria may volatilize the heavy metal and remove the heavy metal from matrix. But only a few heavy metals can be removed by volatilization (e.g., Hg). But the heavy metals are not actually removed from the site. Though they are converted into less toxic form, they persist in the soil. In this context, phytoremediation is practiced to extract the heavy metal from soil (Garbisu and Alkorta, 2003).

Phytoremediation is a novel technology without the application of any chemical. Sunflower, Indian Mustard, etc., are commonly used for phytoremediation of soil (Prasad, 2007 and Falciglia and Vagliasindi, 2013). Sunflower (*Helianthus annuus* L.) is capable to extract heavy metals from soil as its phytoextraction coefficient is very high. So it is now commonly used for environment studies and remediation. Uranium contaminated soil was remediated using Sunflower and the Uranium was concentrated in roots of the plant (Prasad, 2007). But this method can't be considered as an ultimate cleaner technology as its efficacy depends on the contaminant concentration and availability of contaminant to the root (Falciglia and Vagliasindi, 2013). But this method is very cheaper as the cost of growing plants in the field is lesser than soil removal and replacement. The main energy source for this method is sun, which also reduces the cost (Marques *et al*., 2009).

ELECTROKINETIC REMEDIATION

Electrokinetic Remediation (EKR) is a green remediation technology which has the following advantages; (1) decreases on spot pollution; (2) reduces the remediation time; (3) lowers the cost; and (4) capable of treating low permeability soil. So this method is now gaining importance. A large number of studies have been conducted on electrokinetic remediation (Huang *et al.,* 2012). Reuss (1808) identified the movement of water towards the cathode under the influence of electric field. Geotechnical engineers identified the use of electrokinetics for soil stabilization, slope stabilization and drainage in the late 1930's. But the use of this technology for soil remediation has been identified in 1980's only (Azzam and Oey, 2000).

EKR involves the application of a low voltage DC across the soil by means of positive and negative electrodes. Under the applied electric field following processes take place; electroosmosis, electromigration, electrophoresis. Electroosmosis is the movement of pore fluid which contains ions towards the cathode. Electroosmosis is the movement of water molecule in applied electric field. Electromigration is the movement of dissolved ionic species to the respective electrodes. Ions produced by water electrolysis are also migrated (i.e., H^+ and OH^-). Electrophoresis is the movement of charged soil particles towards the respective electrodes (Acar *et al*., 1995 and Hansen *et al.*, 1996).

First attempt of removal of heavy metal by electrokinetics was done in 1980's (Hansen *et al.,* 1996). Henceforth a number of studies had been conducted in laboratory under controlled condition on synthetic spiked soil. But a few experiments had been done directly on polluted site. The success of this method depends on the type of soil, carbonate content, cation exchange capacity, applied current/

voltage, pH of soil, duration of the experiment, use of complexing agents and surfactants (Hansen *et al*., 1999 and Jensen *et al*., 2007).

Ions are produced at anode and cathode by water electrolysis. H^+ ions are generated at the anode and OH^- ions are generated at the cathode. H^+ ions generate at the anode migrate to negatively charged cathode and OH^- ions migrate towards positively charged cathode. Thus an acidic front moves towards cathode and basic front towards anode. H^+ ions are smaller than OH^- ions. So the movement of H^+ ions will be faster than that of OH^- ions. Acidic front solubilizes the metal ions and causes its movement towards cathode by electroosmosis or electromigration. On the other hand the basic front forms precipitate with metal ions. Metal removal will be impeded by this reaction. In order to prevent the generation of basic front at cathode, cathode can be acidified. Electrolyte conditioning improves the removal efficiency (Orcino and Bricka, 1998).

RESEARCH WORKS AND DEVELOPMENTS

Electrodialytic remediation (EDR) is a modification of EKR in which the electrode compartment is separated from the soil by means of ion selective membrane. When current is applied to the soil, ion selective membranes prevent the entry of ions generated at the electrodes to the soil compartment. Thus current wasted for carrying highly mobile ions from anode to cathode can be reduced and the competition between highly mobile ions and metal ions also can be minimized (Hansen *et al.*, 1996).

Jensen *et al*. (2007) studied the effect of soil type in EDR. They conducted the study on ten industrially polluted lead contaminated soils. They observed that the insoluble organic matter and stable compounds reduce the removal efficiency. They used cylindrical plexiglass tank and platinum coated electrodes for their tests. A constant current (0.2 mA/cm^2) was maintained in the reactor. If the polluting metal species is very high, remediation proceeds very slowly. Soil which contains less organic matter can easily be remediated by this method. In carbonate rich soil, dissolution of carbonates takes place first. Thus the carbonate content of pore fluid increases.

Precipitation and dissolution of metal ions affect the removal efficiency. Due to water electrolysis, H^+ ions are generated at anode and OH^- ions are generated at cathode. If the buffering capacity of the soil is high, the movement of hydrogen ions will be retarded. The presence OH^- ions will increase the pH (10-12). Metal ions will get precipitated as hydroxide reducing the removal efficiency. Enhancing agents can be used to increase the removal efficiency. Enhancing solutions can form complexes with metal and these complexes can be removed easily. But some enhancing solutions change the physicochemical properties (such as pH, redox potential) of soil and thus giving improved removal efficiency (Hosseini *et al*., 2011). Hosseini *et al.* studied the effect of chelating agents (EDTA, ammonium citrate) on the removal of Zn and Pb from the soil. They collected soil samples from a mine site. Electrokinetic experiments were conducted in a 40 × 10 × 10 cm plexiglass box with graphite electrodes (25 V DC). The soil they used was categorized as clay. Initial pH of the soil was 7.6 pH changed considerably with water and EDTA as electrolytes. But pH didn't vary much with citric acid. Use of complexing agent increased the removal efficiency. EDTA forms negatively charged complex with metal ions and this complex can be collected at anode. EDTA is more effective in the removal of lead. Removal of zinc was more than lead in their experiment.

Giannis *et al*. (2009) also studied the effect of chelating agents in EKR. They carried out an extensive experimental program to remove Pb, Cd and Cu from contaminated soil. They used nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA) and ethyleneglycoltetraacetic acid (EGTA) as washing solutions under different pH conditions and concentrations. They got the optimum pH and concentration of washing agent from batch study results. They used a 17 cm long soil cell with 10 cm × 10 cm cross section. The working electrodes were cylindrical graphite electrodes. A neutral pH was maintained in the cell. Results showed that the extraction efficiency for Cd in decreasing order was NTA > EGTA >DTPA, while for Pb and Cu it was DTPA > NTA >EGTA. They observed that, higher washing agent didn't necessarily increase the removal efficiency. The observed removal efficiency for Cd was 65-95%, for Cu 15-60%, but for Pb was less than 20%.

Solar energy can also be used for EKR experiment (Yuan *et al*., 2009). Yuan *et al.* used solar cell for supplying energy required for EKR. They conducted three set of experiments. One was conducted on a sunny day and another on a cloudy day and the third one with normal DC power supply. They conducted studies on Cd spiked soil. They used a reactor cell with an inner size of length 11.1 cm × width 5.4 cm × height 5.0 cm. Graphite sheets were uses as anode and cathode. A solar cell of 30.6 cm length and 21.5 cm width was used to supply power. The study results indicated that the current achieved by was comparable with DC power. Out potential of solar cell depended on daytime and weather conditions.

The H^+ ions and OH^- ions migrate towards cathode and anode respectively. During their migration they meet at a point were focusing of heavy metal takes place. At this point heavy metal accumulates and the removal efficiency will be slackened. Use of complexing agents, electrolyte washing and use of ion selective membrane are practiced to overcome this difficulty. But these methods are deployed to change the pH. Li *et al.* introduced an approaching anode method to migrate the focusing point to anode in a step by step manner. They used a rectangular tank reactor. The reactor was made of Plexiglass with an inner length of 43 cm, a width of 10 cm, and a height of 10 cm. Graphite electrodes were used as working electrodes. They conducted 4 sets of experiment, 2 with fixed electrodes and 2 with variable electrodes. Acetic acid and citric acid were used as electrolyte. They conducted tests on Chromium contaminated soil. Citric acid removed more Cr than acetic acid. Approaching cathode experiments showed higher removal efficiency and. The accumulation of chromium was also decreased.

Sun and Ottosen (2012) studied the effects of pulse current on energy consumption and removal of heavy metals during electrodialytic soil remediation. They conducted eight experiments with constant and pulse current on industrially polluted soils. Electrokinetic cell with 3 compartments was used for tests. Ion selective membranes were also used. Platinum coated electrodes were used as working electrodes. A constant current was maintained across the soil in constant current test. A power supply timer instrument was used to provide pulse current. Electrolyte used was $NaNO_3$ adjusted to pH 2 with HNO_3. Results of this study indicate that the power consumption decreased at high current density with pulse current and the removal efficiency also increased.

Chung and Kamon (2004) studied the coupled effect of electrokinetics and ultrasonic (US) technique in cleanup of contaminated soil. Electrokinetic method removed heavy metal and ultrasonic technique removed the organic matter. Natural clay contaminated with Pb and phenanthrene was used as the test specimen. Two types of tests were carried out. Tests included EKR and EKR+US. Graphite electrodes were used as anode and cathode. A constant current of 50 mA was applied. The test chamber is made of a plexiglass and it has a 10 cm wide, a 10 cm height and a 20 cm length. Inlet and outlet tubes were also installed at both the ends. Outflow was collected and tested regularly. The water and contaminant flowed under the effect of electric field and acoustic flow by sound waves. The accumulated outflow and contaminant removal were enhanced by sonication effect. The removal rates of Pb and phenanthrene are average 88% and 85% for electrokinetic test and average 91% and 90% for electrokinetic and ultrasonic test, thus the removal efficiencies in electrokinetic and ultrasonic process are increased about 3.4% for Pb and 5.9% for phenanthrene by the coupled effects of electrokinetic and ultrasonic phenomena comparing with simple electrokinetic process.

CONCLUSION

Electrokinetic remediation is an effective method for the remediation of heavy metal contaminated soil. This method mainly depends on the soil type, soil pH, applied current, presence of carbonates, buffering capacity of soil. Generation of acid front in the cathode compartment impedes the removal efficiency. This situation can be alleviated by certain enhancement technique. With the support of enhancement technique it is possible to achieve comparatively high removal efficiency. A brief description of some enhancement techniques is given in this paper and other available remediation techniques are also explained.

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