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# Recent Research Trends in the Removal of Heavy Metallic Materials from Contaminated Site Soils: A Review

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**ABSTRACT:** The purpose of the review is to provide the recent research trends in the electrokinetic remediation technologies of heavy metal contaminated soils. However, enhancement techniques are often required to improve the remediation efficiency of the technology. Specifically, an introduction to speciation, chemistry of some important heavy metals and their permissible levels in the environment have been provided. In this paper, laboratory, pilot plant and field-scale investigations on enhanced electrokinetic remediation technologies have been detailed. In addition, recent research findings, limitations and still faces many challenges are also discussed. A comprehensive and future research perspectives are briefly summarized for the researchers who is interested in a particular electrokinetic technologies to perform further study to remediate the heavy metal from contaminated soils, sediments, mining dumps, industrial sludge and ground water.

**KEYWORDS:** Heavy metals, Electrokinetic remediation, Environmental pollution, Chemical Engineering.

## INTRODUCTION

Soil contamination is the incorporation of pollutants into soil environment and causes instability, disorder, harm, or discomfort to the living species including green vegetation. Mismanagement of environment and anthropogenic activities are the major roots of environmental pollution (Shukla & Chandel, 2001 [1]). Soil is the thin layer and composed of organic and inorganic matter, which covers the rocky surface of the earth crust. The topsoil is formed by the decomposition and decayed of organic matter from plants and animal species. The inorganic portion of soil is formed from rock fragments over thousands of years by physical and chemical actions due to weathering of bed rock. Thus, the soil is composed of weathered minerals and varying amounts organic matter. Soils can be contaminated because of spills or direct contact with contaminated waste streams such as mining activities, air born emissions, and mishandling of solid waste or sludge disposal from chemical industries. It was reported that the solubility of metals in soil is influenced by the chemistry of the soil and ground water (Sposito, 2008 [2]).

Electokinetic remediation is a promising technology for in-situ soil removal of environmentally hazardous heavy metals, radio nuclides and organic pollutants from contaminated soil. This technique variably known as electrokinetic soil processing, electroreclamation, electrochemical decontamination, electrorestoration or electrokinetic remediation (Reddy et al., 2006 [3]). Generally, it can be performed in two ways unenhanced electrokintic remediation and enhanced electrokinetic remediation for decontamination of soils.

In this paper, recent laboratory and pilot plant scale investigations have been detailed on electrokinetic technologies. Additionally, research findings and limitations are also discussed. A comprehensive and future research perspectives are briefly summarized to remediate the heavy metal contaminated soils, sediments, mining dumps, industrial sludge and ground water.

## SPECIATION OF HEAVY METALS

Heavy metals are generally occur in the earth's crust in the form of rock fragments and sediments. Furthermore, groundwater can get contaminated with heavy metals from landfill leachate, sewage, leachate from mine tailings particularly in open cast mines, deep well disposal of liquid wastes, and seepage from industrial waste lagoons (Evanko et al., 1997 [4]). Various types of chemical reactions can be occurred in soil environment such as acid and/or base, precipitation and/or dissolution, oxidation and/or reduction, sorption and/or desorption, and ion exchange processes can influence the speciation and migration of metal contaminants. The hazardous of heavy metals depends on their speciation and concentrations, which depends on PH, temperature, moisture, etc., of the weathering conditions. The sequential extraction method is used to determine the speciation of metals in the soils with help of specific extracting which can solubilize the various phases of metals (Evanko et al., 2010 [5]). The maximum permissible concentration levels of mercury in soil 1mg/kg, and in water 0.01 mg/L, therefor this heavy metal is more toxic than others even at low concentrations. The speciation of some of the important heavy metals and their permissible levels in the environment are listed in **Table 1.**

**Table 1: The speciation of some of the important metals and their permissible levels in the environment.**

| Heavy metal | Speciation and chemistry | Maximum permissible level in | Reference |
|---|---|---|---|
| Arsenic (As) | As occurs in -3, 0, +3, +5 oxidation states. In aerobic environments, As(V) is dominant, usually in the form of arsenate $(AsO4)^{3-}$. It behaves as chelate and can coprecipitate with or adsorb into Fe oxyhydroxides under acidic conditions. Under reducing conditions, As(III) dominates, existing as arsenite $(AsO3)^{3-}$ which is water soluble and can be adsorbed/coprecipitated with metal sulphides. | Irrigated water : 0.01 mg/L,<br>Soils: 20 mg/kg<br>Vegetation: - | (Hashim et al., 2011[13];<br>Chiroma et al., 2014 [14];<br>WHO, 2000 [15]) |
| Cadmium (Cd) | Cd occurs in 0 and +2 oxidation states. Hydroxide $(Cd(OH)_2)$ and carbonate $(CdCO_3)$ dominate at high pH whereas $Cd^{2+}$ and aqueous sulphate species dominate at lower pH (<8). It precipitates in the presence of phosphate, arsenate, chromate, sulphide, etc. Shows mobility at pH range 4.5-5.5. | Irrigated water : 0.01 mg/L,<br>Soils: 3 mg/kg<br>Vegetation: 0.1 mg/kg | (Hashim et al., 2011[13];<br>Chiroma et al., 2014 [14];<br>WHO, 2000 [15]) |
| Cobalt (Co) | Cobalt chemistry is dominated by the Co(II) oxidation state in the aqueous phase of terrestrial environments primarily due to the extremely low solubility of Co(III). | Irrigated water : 0.05 mg/L,<br>Soils: 50 mg/kg<br>Vegetation: 50 mg/kg | (Collins& Kinsela, 2011 [16]) |
| Chromium (Cr) | Cr occurs in 0, +6 and +3 oxidation states. Cr(VI) is the dominant and toxic form of Cr at shallow aquifers. Major Cr(VI) species include chromate $(CrO_4^{2-})$ and dichromate $(Cr_2O_7^{2-})$ (especially $Ba^{2+}$, $Pb^{2+}$ and $Ag^+$). Cr(III) is the dominant form of Cr at low pH (<4). Cr(VI) can be reduced to Cr(III) by soil organic matter, $S^{2-}$ and $Fe^{2+}$ ions under anaerobic conditions. The leachability of Cr(VI) increases as soil pH increases | Irrigated water : 0.5 5mg/L,<br>Soils: 100 mg/kg<br>Vegetation: - mg/kg | (Hashim et al., 2011[13];<br>Chiroma et al., 2014 [14];<br>WHO, 2000 [15]) |
| Copper (Cu) | Cu occurs in 0, +1 and +2 oxidation states. The cupric ion $(Cu^{2+})$ is the most toxic species of Cu, e.g. $Cu(OH)^+$ and $Cu_2(OH)_2^{2+}$.In aerobic alkaline systems, $CuCO_3$ is the dominant soluble species. In anaerobic environments | Irrigated water : 0.017 mg/L,<br>Soils: 100 mg/kg | (Hashim et al., 2011[13];<br>Chiroma et al., 2014 [14];<br>WHO, 2000 [15]) |

| | | | |
|---|---|---|---|
| | CuS(s) will form in presence of sulphur. Cu forms strong solution complexes with humic acids. | Vegetation: 73 mg/kg | |
| Manganese (Mn) | Divalent Mn salts are chemically most stable, and Mn(IV), ($MnO_2$) predominates in nature. Water-soluble $MnCl_2$ has been historically used to assess the toxic-kinetic properties of manganese. In a natural water system dissolved manganese will be often in (+II) oxidation state. Mn(II) is predominate in most situation s and it is often the most soluble chemical species of manganese and represented about 91% of the manganese | Irrigated water : 0.2 mg/L,<br>Soils: 2000 mg/kg<br>Vegetation: 500 mg/kg | (Pearson& Greenway,2005 [17];<br>Jabłońska-Czapla,2015 [18]) |
| Nickel (Ni) | In its compounds nickel exhibits oxidation states of −1, 0, +1, +2, +3, and +4, though the +2 state is by far the most common. $Ni^{2+}$. | Irrigated water : 1.4 mg/L,<br>Soils: 50 mg/kg<br>Vegetation: 67 mg/kg | (Wang et al., 2013 [19]) |
| Zinc (Zn) | Zn occurs in 0 and +2 oxidation states. It forms complexes with anions, amino acids and organic acids. At high pH, Zn is bioavailable. Zn hydrolyses at pH 7.0-7.5, forming $Zn(OH)_2$. It readily precipitates under reducing conditions and may coprecipitate with hydrous oxides of Fe or Mn. | Irrigated water : 0.2 mg/L,<br>Soils: 300 mg/kg<br>Vegetation: 100 mg/kg | (Hashim et al., 2011[13];<br>Chiroma et al., 2014 [14];<br>WHO, 2000 [15]) |
| Mercury (Hg) | Hg occurs in 0, +1 and +2 oxidation states. It may occur in alkylated system. $Hg^{2+}$ and $Hg_2^{2+}$ are more stable under oxidizing conditions. Sorption to soils, sediments and humic materials is pH-dependent and increases with pH. | Irrigated water : 0.01 mg/L,<br>Soils: 1 mg/kg<br>Vegetation: - | (Wang et al., 2012 [20]) |
| Lead (Pb) | Pb occurs in 0 and +2 oxidation states. Pb(II) is the more common and reactive form of Pb. Low solubility compounds are formed by complexation with inorganic ($Cl^-$ , $CO_3^{3-}$ , $SO_4^{2-}$ , $PO_4^{3-}$) and organic ligands (humic and fulvic acids, EDTA, amino acids).The primary processes influencing the fate of Pb in soil include adsorption, ion exchange, precipitation and complexation with sorbed organic matter. | Irrigated water : 0.065mg/L,<br>Soils: 100mg/kg<br>Vegetation: 0.3 mg/kg | (Hashim et al., 2011[13];<br>Chiroma et al., 2014 [14];<br>WHO, 2000 [15]) |

## REMEDIATION TECHNOLOGIES

### General remediation technologies

Physical and chemical nature of the metal contaminates in soil or water can influence the selection of appropriate method of remediation method. In case of ex-situ remediation, the contaminated media taking away from its natural place, treating it and placing it back from where it came. Generally, the conventional ex-situ remediation methods are used to remove the heavy metals from the contaminated soil such as excavation, incineration, thermal desorption, soil washing, bioremediation and phytoremediation techniques. These are found to be highly expensive and/ or ineffective. In case of in-situ remediation, treating the contaminated soils in their native places without any involvement of excavation process. However, in-situ remediation of contaminated soils to be preferred due to simplicity and less site disturbance. Hence, a variety of in-situ remediation technologies have been designed and developed but these are less effective in treatment of low permeability and heterogeneous soils (Reddy et al., 2006 [3]).

The sorption of five heavy metal ions [Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II)] were studied in various concentrations of tartaric acid electrolyte at different pH values (Bhavna A. Shah et al, 2010 [6]). The maximum removal efficiency of chromium had been achieved using synthesized polyaniline in water with surface adsorption and reduction process (Riahi Samani et al., 2011 [7]). The red rose waste biomass has a potential to remove heavy metals from aqueous solutions particularly Pb(II) and Co(II) from aqueous solutions (Haq Nawaz Bhatti et al., 2011 [8]). Saxal tree ash powder used for efficient removal of cadmium ions from industrial wastewater with low cost adsorption process (Taghavi Mahmoud et al., 2016 [9]). Electrochemical study performed for S-derivaives of 2-amino cyclopentene 1-dithiocarboxylic acid in aqueous ethanolic media (Safavi Afsanesh&Gholivand Mohammad Bagher, 1997 [10]). A single electrochemical cell used to recover copper (82.1%) during oxidative recovery of copper from industrial effluents (Jonidi Jafari Ahmad, 2004 [11]). The effects of temperature on electrochemical behaviour studied on the potential and current capacity of Al-Zn-In sacrificial anodes (Keyvani Ahmad et al., 2005 [12]).

### Electokinetic remediation technology

Electrokinetic remediation process has emerged a promising technology in the removal and recovering of heavy metals from contaminated soils and sledges (Lee & Kim, 2010 [21]). The principle involved in this process is electrolysis of water, electromigration, electroosmosis and electrophoresis (Wang, 2005 [22]). In the beginning of the EK process, an acidic front with low PH environment will be generated and produce the H+ ions in the electrolysis of water near the anode and move toward to the cathode electrode. As they pass through soil matrix, most of the heavy metals in the soil are desorbed and extracted by ion exchange reactions with H+. The oxidation takes place at anode due to transfer of electrons at high acidic environment and reduction occurred at cathode due to acceptance of electrons at basic environment. These can be observed in equation (1) and (2), simultaneously the alkali front will be generated at the cathode and tends to immobilize the heavy metals by hydroxide precipitation. Then, the heavy metals are removed at acidic conditions of contaminated soils (Liu et al., 2017 [23]).Besides simple transport process, chemical reactions occur at electrode surfaces and compartments. Electro active components are generally present in the soil matrix and pore water. However, the main electrode reaction is the electrolysis of water according the schemes.

Oxidation at anode: $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$ ------------ (1)

Reduction at cathode: $2H_2O + 2e^- \longrightarrow 2OH^- + H_2$ --------------(2)

The application of low level direct current results in both physiochemical compositional changes in the soil mass, and leads to the migration of ionic species by electromigration, electroosmosis, diffusion and electrophoresis (Reddy et al., 2006 [3]; Liu et al., 2017[23]; Srivastava et al., 2007 [24]; Vocciante et al., 2017[25]). The movement and direction of ionic metal species depends on its charge and polarity as well as the magnitude of the electroosmosis induce the flow velocity. In case of non-ionic species, transport along with the electroosmosis induced water flow velocity (ITRC [26]). A numerous studies are performed on electrokinetic remediation with experimental design and overall set up is shown in **Fig.1**.

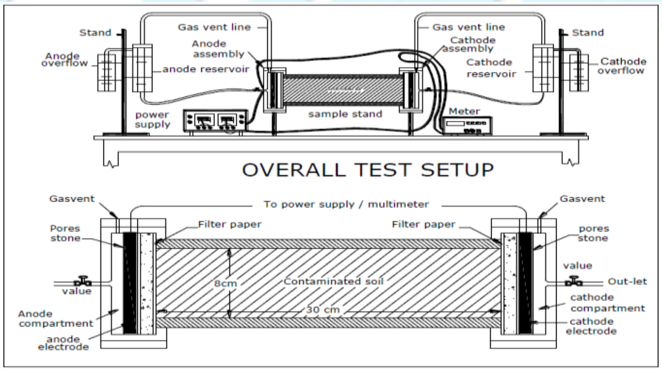

**Fig.1: Schematic of typical bench-scale electrokinetic reactor setup [71].**

The electrokinetic technology is most preferred for the treatment of clay type soils which conduct the electricity well (Alshawabkeh et al., 1999 [27]). The efficiency of the metal removal depends on quantity of metal can be transformed in to a soluble form and its rapid migration (Shapiro & Probstein, 1993 [28]). The migration and direction of metals depend on their concentrations, soil type, and current density in water of soil pores. In order to get an efficient cleaning process, the soil moister level must be maintained above minimum level. The movement of metals depends on moister content, porosity of the soil, mobility of ions, current density of water in pores, metal concentration and total ion concentration. An electric field used to remove metals from clayey soil has been demonstrated in several field applications (Reddy, 2013 [29]). It is extremely difficult to remediate soils with low permeability, high cation exchange capacity, high buffering capacity and expansive nature due to presence of clay minerals of illite or montmorillonite groups. In order to cope up these problems, enhanced electrokinetics has been emerged as viable option for field remediation of such a contaminated soil (Srivastava et al., 2007 [24]).

## Enhanced electrokinetic remediation technology

In many cases, electrokinetic technology alone is not adequate to remediate the contaminated soil to the required acceptance level. Hence, enhanced electrokinetic technology by using enhancement techniques can achieve results that are better than un-enhanced electokinetic technology. For example, the usage of surfactants for the remediation of contaminated soils were more effective than un-enhanced electrokinetic remediation process (Mao et al., 2015 [30]).The impact of electrokinetic treatment on a loamy-sand soil properties are well explained (Pazos et al., 2012 [31]). In case of simultaneous removal of mercury and PAHs from marine sediments using surfactant and MGDA could have enhanced the electrokinetic treatment process (Falciglia et al., 2017 [32]). Recently, supported and unsupported nanomaterials for water and soil remediation was invistigated a prominent solution for worldwide pollution (Trujillo-Reyes et al., 2014[33]). In case of improvement of electrokinetic process for simultaneous mobilization of macro- and trace elements (MTEs) and polycyclic aromatic hydrocarbon (PAH) compounds from soil with a nonionic surfactant and [S,S]-ethylenediaminedisuccinic acid (EDDS) in admixture were succesfully achieved (Wen et al., 2012 [34]). Role of DDL processes had been incorporated during electrolytic reduction of Cu(II) in a low oxygen environment (Brosky et al., 2013 [35]).

Removal of copper and nickel from municipal sludge using an improved electrokinetic process was well explained in laboratory studies (Liu et al., 2017 [36]). Recently, remediation of soils polluted with 2,4-D and heavy metals were effetively removed by electrokinetic soil flushing with facing rows of electrodes (Risco et al., 2016 [37]). Remediation of soil co-contaminated with petroleum and heavy metals invistigated in pilot plant scale by the integration of electrokinetics and biostimulation inorder to enhance the electrokinetic process(Dong et al., 2013 [38]). Recently reported the stabilized nanoscale zero-valent iron for remediation of hexavalent chromium contaminated soil from steel pickling waste liquor(Wang et al, 2014 [39]) and used for the remediation of mercury contaminated sites(Wang et al., 2012 [40]). Recent development in the treatment of oily sludge using enhanced electrokinetic technology was succefully applied for petroleum industry(Hu G & Zeng, 2013 [41). Different pulse frequencies are applied in the pulse current enhanced electrodialytic soil remediation and compared various pulse frequencies for the removal of heavy metals (Sun et al., 2012 [42]).

The Combination of EK with permeable reactive barriers (PRBs) increased Hexachlorobenzene (HCB) removal by a factor of 4 compared with EK alone (Tong & Yuan, 2012 [43]). Multispecies reactive transport modelling mechanism was proposed for enhanced electrokinetic remediation of harbour sediments (Masi et al., 2017 [44]) and multiphysics EK models also Implemented (Vizcaíno et al., 2016 [45]). The advanced microbial fuel cell driving EK technology was proposed for the removal of toxic metals from contaminated soils(Habibul et al., 2016 [46]) and bioremediation also proposed for remediation of organic pollutants such as PAHs (Ortega-Calvo et al., 2013 [47]). Recently, humic substances such as humic acids and fulvin acids are introduced in enhanced electroremediation of heavy metals contaminated soil (Bahemmat et al., 2016 [48]). A gigantic leap in water managemt which was focussed on waste water recovery using ennhanced electrokinetic technology(Voccianteetal., 2017 [49]). It was improved the electrokinetic remediation of organically contaminated soil using oxidation and reduction process (Ren et al., 2014 [50]).

A periodic polarity reversal strategy was proposed to study the effect of electric field on the performance of soil electro-bioremediation in the removal of metal species (Mena et al., 2016 [51]). Comparison studies are performed for fixed anodes and approaching anodes to avoid "focusing" effect during electrokinetic remediation of chromium-contaminated soil (Li G et al., 2012 [52]). Multivariate methods are propsed for evaluating the efficiency of electrodialytic removal of heavy metals from polluted harbour sediments (Pedersen et al., 2015 [53]). The most toxic heavy metal arsenic had successfully removed form As-contaminated soil with a combination of reducing and chelating agents for electrolyte conditioning in electrokinetic remediation process (Ryu et al., 2016 [54]). The coupled and use of hydraulic flushing with EDTA and electrokinetic treatment was investigated for the remediation of silt loam and sandy loam contaminated by both polyaromatic hydrocarbons as well as heavy metals (Reddy et al., 2010 [55]).

## Classification of enhancement techniques

The primary objectives of the enhancement techniques are described as:

1. To solubilize contaminants in soil and to keep them in mobile states.
2. To control the soil pH within a range of values favouring the application of electrochemical remediation.
3. To destruct, breakdown, or transform the contaminants simultaneously or sequentially.

However, these three groups of techniques are inter-related. It was broadly classified enhancement electrokinetic remediation techniques in **Fig.2.** Therefore, the enhancement techniques are broadly classified into three groups:

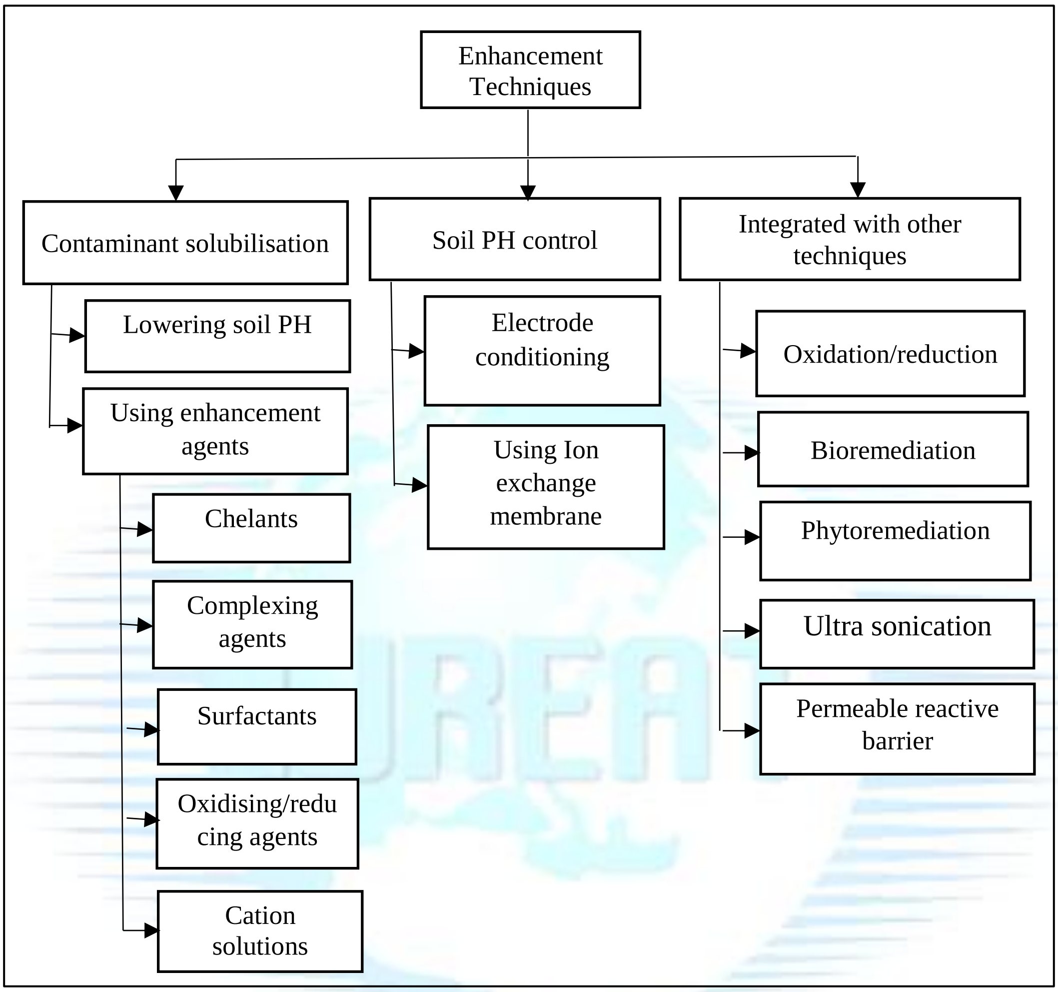

**Fig. 2: Classification of enhancement techniques for electrochemical remediation [56].**

1. Techniques that solubilize contaminants and keep them in mobile states;
2. Techniques that control soil pH;
3. Remediation techniques that can be coupled with electrochemical remediation synergistically to destruct, breakdown, or transform the contaminants simultaneously or sequentially.

In **Table 2** shows the best result obtained in the cited literature, the soil type and origin of pollution are given, as are the initial and final PH of the soil for evaluation of the result. Furthermore the current density and/or voltage gradient and duration of the actual experiment are listed. The results obtained with systems that are enhanced additionally to control pH by, for example, the addition of enhancement solutions for formation of charged complexes that can increase mobilization. This table includes laboratory-scale as well as pilot plant-scale studies, but as may be found from the table, numerous laboratory studies exist, while only very limited pilot or filed-scale studies have been reported. Most of the studies have conducted an electrokinetic technology to enhance the remediation efficiency of electrokinetic process using various enhancement chemical reagents as reported in **Table 2.** Some of the applications are used such as conditioning the catholyte pH, adding chemical reagents to improve metal solubility, using ion-selective membranes to exclude OH− migration from the cathode chamber into the soil, and using an electrolyte circulation to control electrolyte pH. The most preferred electrolytes included acid solutions such as citric acid, acetic acid, oxalic acid, nitric acid, or complexing substances like ethylenediamine tetraacetic acid (EDTA), sodium dodecyl sulfate (SDS) and humic acid are added in enhancement EK process. From **Table 2,** the following observations can be made for each of the specific pollutants:

**Table 2: Recent literature on enhancement electrokinetic remediation technology for the removal of heavy metal contaminated soils**

| **Heavy metal** | **Soil type** | **Origin of pollution** | **Full(F)/ Pilot(P)/ Lab(L)** | **Enhancement** | **Current density(mA/cm$^2$)/Voltage(V/cm)/Duration(days)** | **pH Intial/ Final** | **Concentration(mg/kg) Initial/Final** | **Removed (%)** | **Reference** |
|---|---|---|---|---|---|---|---|---|---|
| **As** | Loamy sand | Rice fields at smelter industrial area | L | 0.1 M EDTA, 0.1 M Oxalate, 0.1 M Citric acid, 0.1 M Ascorbic acid, 0.1 M oxalic acid, 0.1 M dithionite. | -/-/16-22 | 5.5/- | 193/56.4 | 25 | (Ryu et al., 2016 [57]) |
| **Cd** | Loamy sand | Agricultural | L | 0.001M Nitrilotriacetic acid (NTA) ,0.001M Diethylenetriaminepentaacetic acid (DTPA), 0.001M Diaminocycloexanetetraacetic acid (DCyTA) | -/1.23/23 | 5.5/- | 115/- | 85 | (Giannis et al., 2010 [5]) |
| | Loamy sand | Wood land | L | Integrated with activated bamboo charcoal | -/10 | 7.7/7.2 | 500/- | 76 | (Ma et al., 2010 [58]) |
| | Loamy slit | Mine tailing | L | Pulse current frequency | 0.8/-/10 | 7.6/ | 16/- | 16.3 | (Sun et al., 2012 [59]) |
| | Loamy sand | Mine tailing | L | 0.1N Nitric acid,15g/L Humic acid,15g/L Fulvic acid | -/2/20 | 8.20/- | 15.10/- | 38.1/ 58.1/ 66.1 | (Bahemmat et al., 2016 [60]) |
| | Soil | Vegetable garden | L | Microbial fuel cell driven | -/-/143 | 6.73/- | 100/- | 44.1 | (Habibul et al., 2016 [61]) |
| **Co** | Soil | Nuclear power plant | P | 0.01M Nitric acid, 0.01M Acetic acid | 10/-/15 | 6.4/- | 425/- | 98.4 | (Kim et al., 2010 [62]) |
| | Loamy sand | Mine tailing | L | 0.1N Nitric acid,15g/L Humic acid,15g/L Fulvic acid | -/2/20 | 8.20/- | 19.83/- | 29.1/ 38.1/ 38.4 | (Bahemmat et al., 2016 [60]) |
| **Cr** | Sludge soil | Electroplating industry | L | Tap water (TW), 0.024M Sodium dodecylsulfate (SDS) ,1M Citric acid (CA) | -/32/5 | 8.22/- | 70735/- | 69 | (Peng et al., 2010 [63]) |
| | Loamy slit | Industrial waste | L | 0.1M Acetic acid,0.1M Citric acid,0.5M Hydroxylamine hydrochloride,8.8M | -/48/15 | 8.9/- | 71.2/- | 92.5 | (Li et al., 2012 [64]) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Hydrogen peroxide, 1M Ammonium acetate. | | | | | |
| | Sediment soil | Seabed area | L | Stirred suspension(1300 rpm), 2 and 3-compartment cell | 0.04-1/-2-20 | 7.5/1.9-2.3 | 22.1/- | 21/18 | (Pedersen et al., 2015 [65]) |
| **Cu** | Kaolinite | carbonized foods waste | L | 0.05M HCl, 0.05M Acetic acid,0.05M Citic acid, 0.05M EDTA, 0.05M SDS | -/1/10 | 4.5-5.5/1 | 75-150/1 | 53.4 %-84.6 % | (Han et al., 2010 [66]) |
| | Sludge soil | Electroplating industry | L | Tap water (TW),0.024M Sodium dodecylsulfate (SDS) ,1M Citric acid (CA) | -/32/5 | 8.22/- | 3911/- | 34 | (Peng et al., 2010 [63]) |
| | Loamy slit | Mine tailing | L | Pulse current frequency | 0.8/-/10 | 7.6/- | 1117/- | 1.5 | (Sun et al., 2012 [59]) |
| | Sediment soil | Industrial waste | L | Diffuse double layer (DDL) processes | -/1/5 | - | 650/0.05 | - | (Brosky et al., 2013 [67]) |
| | Sediment soil | Seabed area | L | Stirred suspension(1300 rpm), 2 and 3-compartment cell | 0.04-1/-/2-20 | 7.5/1.9-2.3 | 171/- | 67/41 | (Pedersen et al., 2015 [65]) |
| | Sediment soil | Municipal sludge | L | pH of sludge adjusted to 3.8. 0.2M Nitric acid, 0.8 M Sodium nitrate | 2/-/6 | 8/3.8 | 13.91/- | 83.3 | (Liu et al., 2017 [23]) |
| **Hg** | Loamy slit | Marine sediment | L | 5% MGDA, Tween 80, 0.1M EDTA | -/1.2/20 | 8.11 | 28.2/- | 67/71 | (Falciglia et al., 2017 [68]) |
| **Mn** | Sediment soil | Seabed area | L | Stirred suspension(1300 rpm), 2 and 3-compartment cell | 0.04-1/-/2-20 | 7.5/1.9-2.3 | -/- | 37/36 | (Pedersen et al., 2015 [65]) |
| | Loamy sand | Mine tailing | L | 0.1N Nitric acid,15g/L Humic acid,15g/L Fulvic acid | -/2/20 | 8.20/- | 2370/- | 38.3/60.4/64.1 | (Bahemmat et al., 2016 [60]) |
| **Ni** | Loamy sand | Agricultural | L | Nitrilotriacetic acid (NTA), Diethylenetriaminepentaacetic acid (DTPA) and Diaminocycloexanetetraacetic acid (DCyTA) | -/1.23/23 | 5.5/- | 290/- | 80 | (Giannis et al., 2010 [5]) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Sludge soil | Electroplating industry | L | Tap water (TW), 0.024M Sodium dodecylsulfate (SDS) ,1M Citric acid (CA) | -/32/5 | 8.22/- | 639/- | 34 | (Peng et al., 2010 [63]) |
| | Sludge soil | Electroplating industry | L | Tap water (TW), 0.024M Sodium dodecylsulfate (SDS) ,1M Citric acid (CA) | -/32/5 | 8.22/- | 4924.7/- | 42 | (Peng et al., 2010 [63]) |
| | Sediment soil | Seabed area | L | Stirred suspension(1300 rpm), 2 and 3-compartment cell | 0.04-1/-/2-20 | 7.5/1.9-2.3 | 12.7/- | 49/24 | (Pedersen et al., 2015 [65]) |
| | Loamy sand | Mine tailing | L | 0.1N Nitric acid,15g/L Humic acid,15g/L Fulvic acid | -/2/20 | 8.20/- | 103.29/- | 41.7/<br>51.7/<br>70.8 | (Bahemmat et al., 2016 [60]) |
| | Soil | Harbour sediment | L | 0.001M Nitric acid | 4/-/32-120 | 8.32/- | 50.5/- | 42 | (Masi et al., 2017 [69]) |
| | Sediment soil | Municipal sludge | L | PH of sludge adjusted to 3.8., 0.2 M Nitric acid, 0.8 M Sodium nitrate | 2/-/6 | 8/3.8 | 56.37/- | 73.3 | (Liu et al., 2017 [23]) |
| **Pb** | Loamy sand | Agricultural | L | Nitrilotriacetic acid (NTA), Diethylenetriaminepentaacetic acid (DTPA) and Diaminocycloexanetetraacetic acid (DCyTA) | -/1.23/23 | 5.5/- | 1200/- | 90 | (Giannis et al., 2010 [5]) |
| | Loamy sand | Petroleum refinery plant | L | 0.1M EDTA, Tween 80 | -/2/30 | 6.7/- | -/450 | 81.7 | (Dong et al., 2013 [70]) |
| | Sediment soil | Seabed area | L | Stirred suspension(1300 rpm), 2 and 3-compartment cell | 0.04-1/-/2-20 | 7.5/1.9-2.3 | 55/- | 46/34 | (Pedersen et al., 2015 [65]) |
| | Loamy sand | Mine tailing | L | 0.1N Nitric acid,15g/L Humic acid,15g/L Fulvic acid | -/2/20 | 8.20/- | 2500/- | 33.4/<br>41.5/<br>50.6 | (Sun et al., 2012 [59]) |
| | Soil | Vegetable garden | L | Microbial fuel cell driven | -/-/143 | 6.73/- | 900/- | 31 | (Habibul et al., 2016 [61]) |
| | Soil | Harbour sediment | L | 0.001M Nitric acid | 4/-32-120 | 8.32/- | 67.2/- | 48 | (Masi et al., 2017 [69]) |
| **Zn** | Sludge soil | Electroplating industry | L | Tap water (TW), 0.024M Sodium dodecylsulfate (SDS) ,1M Citric acid (CA) | -/32/5 | 8.22/- | 11245/- | 64 | (Peng et al., 2010 [63]) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Sediment soil | Seabed area | L | Stirred suspension(1300 rpm), 2 and 3-compartment cell | 0.04-1/-/2-20 | 7.5/1.9-2.3 | 249/- | 74/71 | (Pedersen et al., 2015 [65]) |
| | Loamy sand | Mine tailing | L | 0.1N Nitric acid,15g/L Humic acid,15g/L Fulvic acid | -/2/20 | 8.20/- | 3330/- | 25.4/<br>45.5/<br>47.4 | (Sun et al., 2012 [59]) |
| | Soil | Harbour sediment | L | 0.001M Nitric acid | 4/-/32-120 | 8.32/- | 893.2/- | 28 | (Masi et al., 2017 [69]) |

In case of Arsenic (As) removal, the acidic enhancement solutions (citric/ascorbic/oxalic acids) are added to ensure that As (III) is present as a charged species or to oxidise the As (III) species to As (V) by addition of chelating agents (EDTA) or treatment of loamy sand soil at initial of pH 5.5. In case of cadmium (Cd) removal, Nitrilotriacetic acid (NTA), Diethylenetriaminepentaacetic acid (DTPA) and Diaminocycloexanetetraacetic acid (DCyTA) are to be suitable leaching and complexing agents when treating with loamy sandy soils. Up to 85% of cadmium was removed when adding these complexing agents compare to other enhancement agents. In case of cobalt (Co) removal, the acidic enhancement solutions (nitric acid and acetic acid) are suitable for reducing the charged cobalt species and up to 98% of cobalt was removed at initial pH 6.4, from nuclear power plant waste disposal soils in a pilot plant scale action. In case of chromium (Cr), even though Cr is one of the most difficult of the heavy metals to remove with the electrokinetic process. Addition of citric acid and hydrogen peroxide as a strong oxidising agents and removed up to 92% in field scale action for industrial waste disposal soils.

In case of copper (Cu), acidic enhanced conditions are more favourable than alkaline conditions to remove copper from municipal sludge waste soils and industrial waste disposals. Citric acid and nitric acid showed a good results. In case of mercury (Hg), 5% MGDA, Tween 80, and 0.1M EDTA are used as enhanced solutions. Up to 71% of mercury is removed from marine sediment soils under initial pH 8.5. In case of manganese (Mn) removal, Nitric acid and humic substances (Humic acid and Fulvic acid) as enhancement chemicals shown good results for mine tailing soils than marine sediment soils under stirred suspension conditions. In case of nickel (Ni) and Lead (Pb) removal, Nitrilotriacetic acid (NTA), Diethylenetriaminepentaacetic acid (DTPA) and Diaminocycloexanetetraacetic acid (DCyTA) are to be suitable leaching and complexing agents when treating with loamy sandy soils. Up to 80% of Ni and 90% of Pb were removed when adding these complexing agents to agricultural loamy sandy soils than mine tailing and marine sediment soils. In case of Zinc (Zn) removal, enhancement of Zn remediation was mainly followed using two strategies: complexation with Sodium dodecylsulfate (SDS) and removal at alakine pH in order to avoid disintegration of soil and lowering of pH with addition of humic acids and citric acid, of these two strategies, the acidic conditions are more favourable than alkaline environment. In addition, the stirred suspension of electrolytes at electrodes showed a good results in laboratory-scale action.

## TECHNICAL CHALLENGES

Currently, the researches on enhanced electrokinetic technologies for metals and organically-contaminated soil remediation mainly rely on laboratory experiments, pilot plant scale level and extending them to real-world practices still faces to many challenges (Reddy, 2010 [71]).These may include:

1. Optimal design and control variables tested in labs may not be suitable for real sites.
2. Pollution situations in field soil may be much complex and thus not match well with the lab condition.
3. The remediation time is too long and the whole operation process is too complicated to be controlled and/or simulated.
4. The electrode conditioning solutions are difficult to inject to get regulatory approval,
5. The corrosion of electrodes and scale formation during EK process. Cost of the process is increased due to replacement of electrodes.
6. The treatment cost is too high (although electricity costs often account for only 15% of the total cost, the breakdown cost for remediation systems needs much more).

## RECENT RESEARCH DEVELOPMENTS AND LIMITATIONS

Most of the previous studies suggested that enhanced conditions and coupled technologies could improve the remediation efficiency of electrochemical remediation as shown in **Table 2.** There are many matured remediation process for heavy metal contaminated soils, and they can potentially be integrated with electrochemical remediation in order to enhance their individual remediation efficiencies synergistically. The research limitations will be the research trends to the researches in the field of electrokinetic remediation technologies for the removal of heavy metals and organic pollutants from contaminated soils and water. The electrodes particularly the anode get corroded over time during electrokinetic remediation process due highly acidic conditions. **Fig. 3** shows the final condition of the anodes used in two experiments A and D in dewatering of oil sands tailings with an electrokinetic geocomposite. The mass loss of anode was 35% for experiment A and 50% for experiment D. It shows that the anodes are highly degraded during electrokinetic remediation experiments (Bourgès-gastaud et al., 2017 [83]). From **Table 3,** the following research findings and limitations are observed for the period of 2008-2017:

**Table 3: Research findings and limitations for the period 2008 to 2017.**

| Year | Methodology | Research findings | Limitations | Reference |
|---|---|---|---|---|
| 2008-2009 | Elececctrokineteic remediation(EKR) | Removal of organic pollutants and metals using non-enhanced electrokinetic conditions in lab-scale actions. The mobility of metal ions in order of Ni>Fe>Zn>Cr>Pb. | Long remediation time (>50d) and lesser removal efficiency (<50%) | [72-82] |
| 2010-2011 | EKR,Electrochemical remediation(ECR) | Removal of organic pollutants and heavy metals using enhanced electrochemical remediation in lab- and pilot plant-scale actions. Improved in removal efficiency up to 85% to 90% in the presence of chelating and reducing reagents. The mobility of ions in order Cr>Zn>Ni>Cu>Pb. | Expensive electrolytes, Long remediation time (>50d). | [55,56,58, 62, 63,66] |
| 2012-2013 | EKR,ECR,Electrodialytic remediation(EDR) | Removal of organic pollutants, heavy metals and radio nuclides in lab-scale and pilot plant-scale actions. Heavy metals removed up to 90% to 95% under stirred suspension. | Long remediation time (>50d), a few metals removed. Power consumption. | [31,34,35, 38,40,43, 47,52,59, 64] |
| 2014-2015 | EKR,ECR,EDR,EK-Bio simulation | Electrokinetic parameters estimation and effects on removal efficiency. Electromigration of metals and osmatic flow related to $P^H$ and zeta potential. | Partial studies on electrokinetic parameters estimation and kinetics. | [30,33,39, 50,53,65] |
| 2016-2017 | EKR,ECR,EDR,EK-coupled with Bioremediation, phytoremediation, MFC, and Surfactants etc., | Completely removed Ni, Zn, Cu, Cd, Pb (>99%) in the presence of chelating/reducing/complexing agents and coupled with phytoremediation methods and bioremediation. Numerical models developed for kinetics. | Environmental issues due to excessive use of chemical agents. Electrokinetic models are partially explained, Cost optimization, Corrosion of electrodes | [32,36,37, 44,45, 46,48,49, 51,54] |

In the period 2008-2009, in the early stage of electrokinetic remediation (EKR) of contaminated soils, the studies focussed on removal of organic pollutants and metals from contaminated soils in laboratory scale action. Most of the studies face the problems of remediation time (more than 30 days) and removal efficiency of metals(less than 50%). The enhanced electrokinetic remediation experiments are carried out in the presence of diluted acids. The mobility of metal ions were found in the order of Ni>Fe>Zn>Cr>Pb.

In the period 2010-2013, the electrochemical remediation (ECR) focussed on removal of organic pollutants and heavy metals from contaminated soils in laboratory scale and pilot plant-scale actions. The enhanced electrochemical remediation experiments are performed in the presence of chelating and reducing agents. The studies faces the problems of usage of expensive electrolytes, long remediation time (>50d) and even in improved in removal efficiency up to 85% to 90%. The mobility of metal ions were found in the order of Cr>Zn>Ni>Cu>Pb.

In the period 2014-2017, the coupled and enhanced electrochemical remediation studies performed particularly in the removal of heavy metals and radionuclides from contaminated soils in laboratory-scale, pilot plant-scale and field-scale actions. Humic substances, microbial, surfactants, complexing, chelating and reducing agents are used as enhancing agents.

The studies faces the problems of power consumption, environmental issues such as soil quality deterioration after treatment, electrokinetics of ionic species are limited, and corrosions of electrodes.

**Fig. 3: The condition of the anodes at the end of the experiments A and D[83].**

## FUTURE PERSPECTIVES

Many significant advances have been developed in establishing of electrokinetic remediation as a practical remediation technology. The field application of this technology lags far behind the laboratory and pilot plant scale studies. The following issues have to be addressed in the filed applications and furthermore to become a generalized commercial technology for the remediation of contaminated soils, sediments, ground water and municipal and industrial waste water. Solar panels/cell, also suggested and used as power supply for electrokinetic remediation process which can greatly reduce power consumption comparative with traditional DC power supply (Yuan et al., 2009 [84]; Krishna R Reddy, 2009 [85]). The following research developments are suggested:

1) The further future research in the enhanced or integrated EK technologies to full-scale implementation should be considered in the point of environmental issues.
2) The coupled EK with advanced techniques may be more effective than unenhancing and enhancing EK under control conditions.
3) Identification of optimal operating conditions such as electrode materials, electrical potential, enhancing electrolytes, range of pH, remediation time using scale up of experimental study from lab scale to field level.
4) Soil deterioration takes place during EK process due to excessive usage of chemical enhancing agents. So that lowest concentrations of chemical reagents are suggested.
5) Assess the impact of electrochemical remediation on soil quality and the environment.
6) Investigate the short-term and long-term effects on electrochemical process.
7) The major problems are raised in the corrosion of electrodes and scale formation during EK process must have accounted to replace the electrodes.
8) Solar power can be suggested to EK process in order to reduce the conventional power consumption and safe to the environmental scenario.
9) Further research need to be focussed on cost estimation, process optimization, electro kinetics and modelling in order to understand the EK remediation process in systematic way.
10) Develop standard protocols/guidance documents for the design, installation, and operation of typical electrochemical remediation systems.

In summary, the importance of enhanced and integrated electrokinetic remediation projects are emphasized. The achievements from these projects are valuable in the identification of advantages and limitations of the electrokinetic technology and need to develop an effective and economical adaptive field systems based on site-specific conditions.

## CONCLUSION

In this review, the state of art on electrokinetic remediation technologies have been provided for heavy metal contaminated soils. However, enhancement techniques are often required to improve the remediation efficiency of the technology. An insight in to recent electrokinetic remediation technologies have been reviewed and reported the recent developments. However, the importance of enhanced and integrated electrokinetic remediation technologies have been emphasized. In this paper, laboratory, pilot plant and field-scale investigations on enhanced electrokinetic remediation technologies have been detailed. A comprehensive, recent advancements, research findings, limitations and still faces many challenges are also provided. A comprehensive and future research perspectives are briefly summarized for the researchers who is interested in a particular electrokinetic technologies to perform further study to remediate the heavy metal contaminated soils, sediments, mining dumps, industrial sludge and ground water. Based on previous studies on laboratory/pilot-plant/field-scale investigations, it is recommended that, the integrated or coupled electrokinetic technologies and enhanced electrochemical technologies will be effective to improve the removal efficiency of heavy metals to a maximum level from the contaminated soils, sediments, industrial and mining waste. Moreover, solar panels are suggested to drive the electrokinetic technologies with solar electricity in order to reduce the power consumption and the cost of the electrokinetic process.

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