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CHEMICAL REMEDIATION TECHNOLOGIES

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Abstract. Environmental pollution remains one of the most serious world problems. Great efforts are made to limit the release of harmful compounds into the environment, and a variety of methods for remediation of soil, surface water, and groundwater have been developed over the years. Chemical remediation technologies are of great interest since they can remove and degrade pollutants in contaminated sites. This paper focuses on several chemical remediation technologies, such as precipitation, flocculation, adsorption and ion exchange, chemical oxidation, soil washing and flushing, and electrokinetic remediation. Remediation technologies are almost always combined one with another, although they can be used separately. Choosing an appropriate technology will depend on the type of the pollutants and site conditions, and it should be done in such a manner so that the most cost-effective and efficient technology is chosen. Even though some of the technologies are used full-scale, research should be focused on enhancing the existing, and developing new remediation technologies.

Key words: adsorption, ion exchange, electrokinetic remediation, chemical oxidation, soil remediation, water remediation

1. INTRODUCTION

Rapid industrialization and urbanization after the Second World War have led to considerable pollution of soil, surface water, and groundwater resources, which has been one of the main environmental problems ever since (Ong and Kolz, 2007; Thomé et al., 2018). Contaminated sites can be potentially harmful to living organisms, humans, and the environment. These sites are often contaminated with various toxic substances and carcinogens, such as petroleum hydrocarbons, pesticides, heavy metals, dyes, and others (Yeung, 2010). Thus, a variety of remediation technologies have been developed for

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treating industrial wastewaters, groundwaters, soils, and sediments, including *ex-situ* and *in situ* methods.

Remediation technologies are often divided into three categories: physical, chemical, and biological methods. They are also often categorized as technologies that either contain, remove, or degrade contaminants (Fig. 1). The choice of the method will depend on the characteristics of the contaminated site, the cost of the process, and time constraints (Riser-Roberts, 1998). These methods can be used separately or in conjunction with one another. The currently available remediation techniques are contaminant- and site-specific so, it should be emphasized that not one technology, or a certain combination of them, could be universally used for the treatment of contaminated sites (Khan et al., 2004).





2. CHEMICAL REMEDIATION TECHNOLOGIES

Chemical remediation technologies are used for the removal or immobilization of pollutants, particularly persistent organic compounds (Ong and Kolz, 2007). They include technologies such as precipitation, chemical oxidation and reduction, stabilization and solidification (S/S), adsorption, ion exchange, and electrochemical processes (Khan et al., 2004).

2.1. Precipitation

Precipitation is commonly used for treating wastewaters and groundwaters containing heavy metals (Ong and Kolz, 2007). Metal ions dissolved in the water react with added chemicals, forming insoluble compounds. The formed precipitate can then be removed by different separation techniques. The main parameters that affect the precipitation process are pH and concentration. Heavy metals tend to form insoluble hydroxides in alkaline solutions. They can also be precipitated as sulfides, carbonates, and sulfates by adding suitable precipitating agents. It should be noted that this process

can be reversed if environmental conditions change (such as pH). Also, high concentrations of present salts and organic complex formers influence the solubility of formed precipitates (Honeyman and Santschi, 1988).

In some cases, remediation is carried out with *in situ* precipitation of certain salts or oxides that causes the co-precipitation and adsorption of contaminants. Wang and co-workers (2020a) used *in situ* hydrous ferric oxide (HFO) for remediation of subsurface iodine contamination. They injected an acidic ferric solution into the sediments, which displayed self-pH buffering because of the dissolution of the present minerals. This lead to the precipitation of HFO under neutral pH. The precipitated HFO significantly slowed down the transport of iodate in the sediments due to the co-precipitation, as well as the adsorption process. The injection of IO_3^- (100 µgdm⁻³) at the same time as the ferric iron solution (pH 1.5) resulted in the co-precipitation of 23-47% of iodate (Wang et al., 2020a).

Pi and co-workers (2016) used the *in situ* precipitation of Fe(II) sulfides for the removal of arsenic-contaminated groundwater. They periodically injected FeSO₄ into the site for 25 days, where the precipitation of sulfides was biogenically enhanced (reduction of sulfates). The removal rate was 73%. They concluded that the immobilization mechanisms are adsorption and co-precipitation (Pi et al., 2016).

2.2. Flocculation

The most used method for the removal of suspended particles from water is flocculation. This method requires the use of flocculants (flocking or clarifying agents). Flocculants accelerate the agglomeration of colloidal particles, which are usually not subject to gravity and cannot be filtered (Salehizadeh et al., 2018).

Colloidal particles in nature are often negatively charged. The charge that they carry on their surface leads to the stabilization of the suspension, which is determined by interactions between the particles (Tripathy and De, 2006). In a stable dispersed system, attractive (van der Waals) and repulsive (electrostatic) forces between single particles are in equilibrium. By disturbing the equilibrium, the suspension becomes unstable. This process is called destabilization, and the processes of destabilization are coagulation and flocculation (Hughes, 1990; Gregory, 1993). These two terms are often used as synonyms even though they are different processes. Coagulation refers to the destabilization of colloidal systems by adding certain electrolytes, *i.e.* chemicals with charges opposite to those of suspended solids. The addition of these chemicals decreases the double electrical layer, making van der Waals forces of attraction the dominant forces, which results in the formation of the flocks. The precipitation of formed agglomerates is usually slow so small amounts of organic polymers are added to enhance the process and form larger flocks (Aydin et al., 2012). This process is called flocculation. Coagulation and flocculation often occur in successive steps by adding inorganic coagulants and organic flocculants. The more economical version only uses charged polymer flocculants which neutralize colloid particles' charge and aggregate them.

2.3. Flocculants

Flocculation reagents can be divided into two large categories: inorganic and organic. Inorganic flocculants are often based on aluminum and iron salts. Aluminum and iron ions neutralize the suspended particles and form hydroxides that can enhance microflocks formation. Inorganic flocculants often alter the pH of the water but are commonly used

because of their low price, availability, and effectiveness (Bharti, 2019). Aluminum compounds that are used for the removal of suspended solids are dry and liquid alum. Iron salts that are used are ferric sulfate, ferric chloride, and ferrous sulfate. Iron compounds cost less but are corrosive and may result in high iron concentrations in water after the treatment (Tripathy and De, 2006).

Organic flocculants include polymeric materials, that can be natural or synthetic. Natural polymers are mostly nonionic (less than 1% charge within the monomeric unit), while synthetic polymers can be nonionic, cationic, or anionic. Natural polymers such as starch, guar gum, chitin, and cellulose are non-toxic, but their efficiency is low. They are also biodegradable, which can be a problem during their storage. On the other hand, synthetic polymers are highly efficient, but they are often non-biodegradable, toxic, and expensive (Bratby, 1980; Gregory, 1983). Cationic polymers can be based on polyacrylamide, polyamines, polyimines, and polyvinylpyridines. Their unique properties are a result of positive charges distributed along the polymer backbone. Anionic polymers are most commonly based on poly(ethylene oxide). Organic flocculants form larger and stronger flocs and do not require pH adjustment after the treatment (Tripathy and De, 2006).

2.4. Adsorption and ion exchange

Adsorption is a widely applied remediation technology that is useful for removing inorganic pollutants (such as heavy metals and non-metallic ions) and organic pollutants (such as pesticides and various hydrocarbons). It is often described as a surface phenomenon in which the accumulation of pollutants occurs at the interface of two phases (Rashed, 2013). When a solution that contains pollutants (adsorbate) comes into contact with a highly porous solid (adsorbent), intermolecular forces of attraction cause the deposition of the pollutants on the solid surface.

According to the type of bond being formed, adsorption mechanisms can be classified into three types (IAEA, 2002; Ong and Kolz, 2007):

- Physical adsorption: This type of adsorption is independent of the electronic properties of the molecules involved. It is the result of intermolecular forces between the adsorbate and the adsorbent.
- Chemical adsorption: Chemisorption involves the formation of a chemical bond between the adsorbate and the adsorbent. Desorption of the adsorbate can often result in a different compound.
- Electrostatic adsorption (ion exchange): This type of adsorption involves Coulombic attractive forces that result in ion-ion interactions and is often classified as ion exchange. Ion exchange is defined as a process where readily exchangeable ions in the solid phase are replaced by mobile ions from an external solution that is in contact with the solid phase.

Adsorbents can be classified into two groups: natural and synthetic adsorbents. Natural adsorbents include clay minerals, charcoal, ores, etc. They are relatively cheap, abundant in nature, and have the potential for the enhancement of their adsorption capability. Synthetic adsorbents are usually made from various types of wastes (agricultural, household, industrial) or polymer materials (Ong and Kolz, 2007).

Activated carbon (AC) is often used as an adsorbent for the removal of organic and inorganic pollutants. Both powdered activated carbon (PAC) and granular activated carbon

(GAC) are used. They are often made from coconut shells, lignite, wood, and peat (Tadda et al., 2016).

Carbonaceous adsorbents (CA) have been used for the successful removal of polycyclic aromatic hydrocarbons from sediments (PAHs). They reduce the PAHs bioavailability and bioaccumulation. Jakob with his co-workers (2012) showed that the bioaccumulation of PAHs reduces by 50% when treated with AC. It should be noted that CAs can cause some side effects, such as changing the sediment characteristics, habitat quality (which can be harmful to sediment organisms), etc. (Burgess et al., 2009).

Amstaetter and co-workers (2012) used anthracite-based and coconut shell-based PAC for the removal of PAHs, and achieved removal efficiency of over 95%. Oleszczuk et al. (2012) used AC and biochar for the removal of PAHs. They mixed 0.5 to 10% of AC and biochar with sewage sludge and removed 56-95% of contaminants by AC and 0-57% by biochar.

Ion exchange materials can also be natural or synthetic, organic or inorganic. Today, organic synthetic ion exchange materials are widely used. They are usually cross-linked polymer matrices that have certain functional groups. Those functional groups can be strongly acidic, strongly alkaline, weakly acidic, and weakly alkaline. For example, exchangers that contain sulfo groups are strongly acidic, while those that contain tetraammonium groups are categorized as strongly alkaline. It should be noted that ion exchange materials can also act as adsorbents (IAEA, 2002).

2.5. Chemical Oxidation

Chemical oxidation is used for the degradation of various organic contaminants such as aromatic compounds, chlorinated hydrocarbons, and inorganic contaminants, such as cyanides (Ong and Kolz, 2007). It was predominantly used for ex-situ treatment of groundwaters, until the 1990s, when an *in situ* method of remediation of organically contaminated sites was developed. This development occurred because it was found that many organic pollutants were susceptible to complete or partial chemical degradation (Siegrist et al., 2000). Today, in situ chemical oxidation is a well-established technology in which chemical oxidants are added to contaminated sites to degrade organic contaminants. Organic contaminants are either transformed into carbon dioxide and water, or to less harmful compounds. There are a few available oxidants that could be used, but hydrogen peroxide/Fenton's reagent, permanganate, persulfate and ozone are the main reagents. They are favored because of their availability, non-toxicity, their oxidizing power, and low cost. The reaction chemistry of each of these oxidants can be different, so the selection depends on the nature and type of the contaminant, and the characteristics of the contaminated site. In recent years, chemical oxidation has been used in combination with ultraviolet (UV) light, ultrasound (US), inorganic catalysts, enzymes, or a combination of oxidants. These processes are known as advanced oxidation processes (AOPs) (Ong and Kolz, 2007).

2.5.1. Hydrogen peroxide/Fenton's reagent

Hydrogen peroxide, although a strong oxidant, is not exactly useful for remediation. The rate of direct reaction with organic contaminants is too low. Thus, hydrogen peroxide is activated:

$$H_2O_2 + Fe^{2+} \rightleftharpoons Fe^{3+} + HO^{\bullet} + HO^{\bullet}$$

This reaction is known as Fenton's reaction. The generated hydroxyl radical is a shortlived, reactive oxidant that degrades most organic contaminants rather quickly. In practice, when treating soil or groundwater, 2-12% solutions of hydrogen peroxide are used in the presence of various catalysts. This modified system is often called catalyzed hydrogen peroxide propagation (CHP). When these concentrations of hydrogen peroxide are used, other reactive species are also generated, which is shown by the next sequence of reactions:

$$\begin{aligned} H_2O_2 + HO^{\bullet} &\rightarrow HO_2^{\bullet} + H_2O \\ HO_2^{\bullet} &\leftrightarrows O_2^{\bullet} + H^+ \ (pK_a=4.8) \\ HO_2^{\bullet} + Fe^{2+} &\rightarrow HO_2^{-} + Fe^{3+} \\ RH + HO^{\bullet} &\rightarrow R^{\bullet} + H_2O \\ R^{\bullet} + H_2O_2 &\rightarrow ROH + HO^{\bullet} \\ R^{\bullet} + O_2 &\rightarrow ROO^{\bullet} \\ H_2O_2 &\leftrightarrows H^+ + HO_2^{\bullet-} \end{aligned}$$

Reactive species that are generated are perhydroxyl radicals (HO₂[•]), superoxide radical anions (O₂^{••}), hydroperoxide anions (HO₂⁻), and organic radicals (R[•]) (Bennedsen, 2014). Fenton's reaction is ineffective under moderate and strongly alkaline conditions. It is most effective under acidic conditions (Siegrist et al., 2000).

2.5.2. Ozone

Since ozone is a gas, it is different compared to other oxidants used for remediation. Ozone has been used for water treatment for more than 100 years (Langlais et al., 1991). Ozone is injected into soil and groundwater along with air, or it can be injected in the form of ozonated water, but its use is limited by its stability in the subsurface. The decomposition of ozone is affected by the pH of the environment and the concentration of ozone. Inorganic and organic substances that are present in the subsurface can promote the decomposition of ozone (Bennedsen, 2014). It can oxidize contaminants either through the formation of hydroxyl radicals or directly. Hydroxyl radicals can be generated in the reaction with hydrogen peroxide:

$$2O_3 + 3H_2O_2 \rightarrow 2HO^{\bullet} + 4O_2 + 2H_2$$

Contaminants that can be degraded by ozone include aromatic compounds, polycyclic aromatic compounds, pesticides, and aliphatic hydrocarbons (Siegrist et al., 2000).

2.5.3. Permanganate

Permanganate is a chemical oxidant that is commonly used in the form of potassium (KMnO₄) or sodium permanganate (NaMnO₄). Potassium permanganate is usually supplied as a solid, the solution prepared on-site and injected in concentrations up to 4%. Sodium permanganate is supplied as a 40% solution and it is usually diluted on site. Permanganate has been used as a selective oxidant for the treatment of chloroalkenes. Oxidation reactions at contaminated sites can be complex because of the multiple valence states of Mn and its mineral forms (Bennedsen, 2014). Side reactions involve the direct

transfer of electrons, unlike other oxidation processes used for remediation, which involve radical formation. Some of the reactions that take place at contaminated sites are (Siegrist et al., 2000):

$$MnO_{4^{-}} + 8H^{+} + 5e^{-} \leftrightarrows Mn^{2+} + 4H_2O (pH < 3.5)$$

$$MnO_{4^{-}} + 2H_2O + 3e^{-} \leftrightharpoons MnO_2 + 4OH^{-} (3.5 < pH < 12)$$

$$MnO_{4^{-}} + e^{-} \leftrightharpoons MnO_{4^{2-}} + 4H_2O (pH > 12)$$

The second reaction, the reduction of permanganate ions in water, is the dominant reaction in environmental conditions, which involves the precipitation of MnO_2 . The precipitation of manganese oxide is a limiting factor because it can affect mass transport and transfer. On the other hand, permanganate is stable and can persist in the subsurface for longer periods, which can result in a good distribution of the oxidant.

2.5.4. Persulfate

Persulfate ions are strong oxidizing agents that are also used for *in situ* chemical oxidation. Much like hydrogen peroxide, direct reactions are too slow to be effective, so persulphate needs to be activated. The activation of persulfate anions involves the generation of free sulfate radicals (SO_4 [•]), which can be done by heat, metals, UV light, by strong alkaline conditions, or in the presence of various compounds (hydrogen peroxide, ketones, primary alcohols, etc.). Once activated, the sulfate radical initiates a sequence of reactions that involve the formation of other radicals and oxidants (Anipsitakis and Dionysiou, 2004), some being:

$$SO_4^{\bullet^-} + H_2O \rightarrow HO^{\bullet} + H^+ + SO_4^{2-}$$
$$SO_4^{\bullet^-} + RH \rightarrow R^{\bullet} + H^+ + SO_4^{2-}$$
$$R^{\bullet} + S_2O_8^{2-} \rightarrow SO_4^{\bullet^-} + SO_4^{2-} + R$$

2.5.5. Advanced oxidation processes

Combinations of ozone, and/or hydrogen peroxide along with UV irradiation are often used for the enhancement of hydroxyl radical formation. In $UV/O_3/H_2O_2$ systems, it is speculated that hydrogen peroxide initiates the decomposition of O_3 that results in the formation of hydroxyl radicals (Aieta et al., 1988):

$$H_2O_2 \rightarrow HO_2^- + H^+$$

$$HO_2^- + O_3 \rightarrow O_3^- + HO_2^-$$

$$HO_2^- \rightarrow H^+ + O_2^-$$

$$O_2^- + O_3 \rightarrow O_3^- + O_2$$

$$O_3^- + H^+ \rightarrow HO_3$$

$$HO_2 \rightarrow HO^- + O_2$$

Ultrasound has also been used for enhancing the oxidation of hazardous organic compounds. Its use is based on the "acoustic cavitation" effect. The mechanical vibration

of sound waves induces the formation and collapse of bubbles. The successive compression and expansion of bubbles become a quasi-adiabatic process. The temperatures inside a bubble can go as high as 5000 °C (Suslick, 1986), while the pressure increases to 1000 atm (Mason and Lorimer, 1989). The implosion of the bubbles creates high local temperatures and pressures, which leads to the dissociation of water vapor and oxygen, forming hydrogen, hydroxyl- and hydroperoxyl-radicals. These radicals can oxidize organic compounds present in the solution. Sometimes, hydrogen peroxide or ozone are added to enhance the process (Yasui, 2010).

AOPs are most commonly used for remediation of soil and groundwater, with persulfate-based processes being on top. These processes usually give great results with the advantage of degrading organic contaminants into non-toxic or biodegradable products. The activation of persulfate can be done by heating the solution, with UV light, ultrasound, or chemically (in the presence of metal ions). These means of activation induce the decomposition of persulfate which generates sulfate and hydroxyl radicals. Heat activation is the most used method since it is the easiest one to implement.

Gu and co-workers (2011) investigated the effect of temperature on the oxidation of 1,1,1-trichloroethane (TCA) in groundwater by persulfate. The removal efficiency of TCA increased with the temperature. At 20 °C the removal efficiency was 7.6%, at 30 °C it was 31.6%, while at 40 and 50 °C the achieved removal efficiency of TCA was 100%.

Ji et al. (2015) used heat-activated persulfate for the removal of atrazine (ATZ) from water. They noticed the increase of initial persulphate concentration and temperature enhance the degradation efficiency. Full removal of ATZ can be obtained after 2 h of treatment with the persulphate concentration of 1 mM and 60 °C.

Yang with his co-workers (2020) compared Fenton and activated persulfate oxidation for removing petroleum-hydrocarbon from contaminated groundwater. They used benzene and toluene to contaminate groundwater and experimented with three different concentrations of H_2O_2 and $Na_2S_2O_8$. The oxidants were activated with the ferrous iron solution. The results of the experiments showed that the Fenton process would be a more efficient approach (Yang et al., 2020). On the other hand, when Dominguez and co-workers (2021) compared these two technologies for the remediation of soil contaminated with lindane (γ -HCH) and other isomers, the experiments showed that the Fenton process wouldn't be an appropriate choice. The consumption of hydrogen-peroxide was too high due to the high carbonate content in the soil (Dominguez et al., 2021). These results confirm the fact that the choice of the remediation technique will depend on the characteristics of the site and the nature of the pollutants.

Diaw et al. (2020) used the electro-Fenton process for the removal of monolinuron from water. This process is based on the Fenton process, but the H_2O_2 is generated *in situ* by reducing the dissolved O_2 in the water. 98% removal was achieved after 8h on boron-doped diamond anode at 500 mA.

2.6. Soil washing and soil flushing

Soil washing is an *ex-situ* process that is based on chemical and physical extraction. It is used to remove a broad range of pollutants from soil (Kuhlman and Greenfield, 2006). This technology uses appropriate washing fluids, that are most often aqueous solutions with additives, such as acids, bases, and surfactants (Jankaite and Vasarevičius, 2005). It can be difficult to formulate the washing solution since mixed waste is often complex.

The soil washing process includes the excavation of the soil, the screening process, the separation of fine-grained and coarse-grained fractions, and the treatment of these fractions (soil washing). After the process is finished, the excavated soil is returned to its original site, and the extracting solution is further treated. The technology has been successful in removing organic, inorganic, and radioactive pollutants. The biggest advantage of this technology is that it employs a closed system and permits full control of conditions (pH, temperature) under which the soil is treated. However, contaminants tend to sorb onto silt, clay, or organic matter, so this technology is not as effective for soils with a high percentage of these materials. Also, since the treatment of the washing solution is needed, it can be expensive (Yeung, 2010). Soil washing is often referred to as a solvent extraction technology when organic solvents are employed. It should be noted that organic washing solutions should be handled with care as they can be inflammable and volatile. The amount of the residual solvent left in the soil could be potentially a problem, because of the residual toxicity (Silva et al., 2005).

Wang with co-workers (2020b) experimented with different washing solutions for the removal of heavy metals. They used six different washing solutions: H_3PO_4 , K_2CO_3 , CH₃COOK, KH₂PO₄, HNO₃, and KNO₃, and different concentrations of each solution (0.01%, 0.1%, 0.3%, 1%, and 3%). The experiments indicated that the best washing solution is nitric acid. At the concentration of 3%, nitric acid is more efficient than other washing solutions in removing Cu, Cd, Pb, and Zn. However, it wasn't as efficient in removing As. Considering the effect on the soil and the cost of the process, they concluded that 1% HNO₃ is the best among other washing solutions, at the temperature of 35 °C. With the solid-liquid ratio of 1:10, and the washing time of 90 min, the removal efficiency of Cd was 75.7%, while the removal efficiency of Pb was 60.6%. (Wang et al., 2020b).

Soil washing is often used with other technologies. Liu and co-workers (2020) used soil washing followed by electrooxidation (EO) and electro-Fenton (EF) processes for the remediation of synthetic soil contaminated with diesel. The extraction of diesel was enhanced with surfactant Tween 80. The time of extraction was 180 min and different amounts (5, 7.5, and 10 g) of surfactant were used for the preparation of the washing solution. The extraction efficiency increased with the concentration of the surfactant, reaching 87.9% for the highest concentration of Tween 80. The washing effluent was further treated with EO and EF, and the highest removal efficiency was achieved with the EF process (87.2%) (Liu et al., 2020).

Soil washing can also be performed *in situ* (soil flushing), where the flushing solution is used to leach contaminants from the soil. The flushing solution can be water, or a carefully formulated solution with additives that solubilize the contaminants, chemically react with them, or form emulsions (Martel et al., 2002). This solution can be injected directly into the soil, or by using sprinklers, horizontal or vertical drains, surface trenches, or flooding. The water that contains the contaminants is collected after the process is finished and is often treated onsite and reused. Soil flushing is effective for removing both organic and inorganic contaminants (Lee et al., 2004). It is a relatively simple process, but it can be slow because of the geologic heterogeneities.

Pei and co-workers (2017) used different surfactant flushing solutions for the remediation of dichlorobenzene-contaminated soil. They investigated the removal of *o*-dichlorobenzene and *p*-dichlorobenzene using saponin, alkyl polyglycoside, and Tween 80 flushing solutions (in deionized water). The highest removal efficiencies were achieved with saponin solution, with 76.34% for *o*-dichlorobenzene and 80.43% for *p*-dichlorobenzene (Pei et al., 2017).

Senevirathna et al. (2021) provided a study that proposed a complete treatment of soil contaminated with perfluorooctane sulfonate (PFOS), in which one of the operation units was soil flushing. They compared three flushing solutions, methanol, ethanol, and propanol, in the concentration range from 50 to 75%. Methanol and ethanol were both more efficient than propanol. Since methanol is more toxic, 50% ethanol was chosen as the most suitable washing solution, achieving a removal efficiency of more than 98% (with five-bed volumes) (Senevirathna et al., 2021).

Soil flushing has also been coupled with other technologies. For example, it was coupled with phytoremediation for remediating soil contaminated with arsenic. Yan et al. (2017) used *Pteris vittata* L. (P.v.) and flushing with potassium dihydrogen phosphate. They concluded that the P.v./flushing combination was more effective, removing 54.04% of arsenic, compared to 47.16% in the flushing treatment (Yan et al., 2017).

2.7. Electrochemical remediation

Electrochemical processes can be used for remediation in a manner similar to chemical reduction or chemical oxidation, except they include the use of electrical current (Ong and Kolz, 2007). The low-intensity electrical current is used to either mobilize or break down both organic and inorganic contaminants. Electrochemical processes are mostly used for treating contaminated low permeability soils and have been described as the most promising for remediating fine-grain soils (Asadollahfardi et al., 2015).

2.7.1. Mechanism and enhancement of the process

Electrochemical remediation, or electrokinetic decontamination, includes placing a contaminated sample between two electrodes and applying direct current. This induces some transportation mechanisms such as electroosmosis, electromigration (that often results in electrolysis), and electrophoresis (Fig. 2) (Dada et al., 2015). Electroosmosis is a process in which the fluid phase in the soil is transported due to the applied electrical field (Lynch et al., 2007). The transportation of the fluid is almost always from the anode to the cathode, because the soil particle surfaces are predominantly negatively charged. Electromigration involves the movement of ions under the influence of the electrical field. Cations migrate towards the cathode, while anions migrate towards the anode (Reddy et al., 2004). Contaminants that are in the aqueous phase or that are desorbed from the soil are transported towards the respective electrodes (depending on the charge). where they are either deposited on the electrodes or extracted to a recovery system. This mechanism includes the transport of H⁺ and OH⁻ ions produced by the electrolysis of water. The production of H⁺ and OH⁻ ions affects the process since they induce the formation of a pH gradient (Asadollahfardi et al., 2015). Electrophoresis involves the movement of charged particles and colloids that are suspended in the pore fluid. These particles are repelled from one another but are electrostatically attracted to one of the electrodes. Electromigration and electroosmosis are far more important mechanisms than electrophoresis in terms of max flux (Shenbagavalli and Mahimairaja, 2010).



Fig. 2 Mechanisms involved in electrokinetic remediation

The effectiveness of this process, as well as the transport and extractability of contaminants, depend on the soil type that's being treated, the concentration and type of contaminants, pH of the treated soil, buffer capacity and zeta potential of the soil, operating parameters and characteristics of the soil particle surfaces (Yeung, 2010). With the formation of hydrogen and hydroxyl ions and their migration, a rapid transition from low to high pH occurs, which could result in the deposition of minerals. The deposition front that forms can reduce the permeability of the soil. The sorption-desorption, precipitation-dissolution and oxidation-reduction behaviors of the pollutants are pH-dependent, and significantly affect the remediation efficiency (electrokinetic remediation of contaminated habitats). One of the ways of enhancing this method and controlling the pH is adding chelating agents to the cathode and anode compartments (Reddy et al., 2004; Villen-Guzman et al., 2014). This type of decontamination is referred to as enhanced electrokinetic remediation. Chelating agents can make complexes with heavy metals and make them more soluble. Also, they can be beneficial for treating some combinations of pollutants within a reasonable remediation time. Electrokinetic decontamination can also be enhanced by manipulating the redox state of the soil for mobilization of heavy metals (Reddy and Cameselle, 2009).

An improvement of the electrokinetic process is the Electrochemical Remediation Technologies (ECRTs) process. This process uses a proprietary AC/DC converter to produce a low-voltage, low-amperage electrical field that induces the mineralization of organic pollutants and the removal of metals. ECRTs are effective within months instead

of years. Also, in this technology, metals deposit on both electrodes, contrary to the electrokinetic process where the metals deposit only on one electrode (Niroumand et al., 2012).

Baskaran, Dhivakar, and Gunasegaran (2020) have experimented with different anolyte and catholyte solutions in the remediation of copper polluted soil. They conducted six experiments. In all of the experiments, graphite electrodes were used. In the first experiment, they used tap water as both anolyte and catholyte which resulted in poor removal efficiency of 29.33%. In the second experiment, they added 0.1 moldm⁻³ ammonium acetate as an anolyte, which resulted in a slightly better efficiency of 35.10%. In the third experiment, the obtained removal efficiency of 51.72%. The anolyte was 0.1 moldm⁻³ ammonium acetate and the catholyte was 0.1 moldm⁻³ acetic acid. In the last three experiments, the electrokinetic remediation process was supplied with adsorption zones near the catholyte. They used activated charcoal, steel slag, and sawdust as adsorbents. The maximum achieved removal efficiency was 63.95%, with sawdust used as an adsorbent (Baskaran et al., 2020).

Kim and co-workers (2012) used electrokinetic remediation for treating paddy and dry soil. The experiment duration was 8 weeks, and the target contaminant was arsenic. The purging solutions used in this experiment were NaOH and EDTA, and the achieved removal efficiencies were 78.6% and 78.8%, respectively (Kim et al., 2012).

Zhao with his co-workers (2016) worked on the remediation of copper polluted kaolin. They coupled electrokinetic remediation with activated carbon permeable reactive barrier with pH control of the catholyte (citric acid and sodium citrate). The duration of the remediation was 4 days, and the achieved copper removal efficiency was 96.6% (Zhao et al., 2016).

3. CONCLUSION

Although there are various remediation technologies available for treating contaminated sites, choosing the appropriate technology is a challenge. There are site-specific or contaminant-specific technologies, and a combination of technologies is often used. The applicability of the chosen technology will depend on site conditions, the nature and the type of contaminants, the source of the pollution, remediation objectives, effectiveness, and time. All of the mentioned technologies have certain advantages and disadvantages. If more than one technology seems like an appropriate choice, it should be evaluated and explored, so the most cost-effective and efficient process or a combination of processes can be chosen. New and improved remediation technologies are being developed, and the research should be focused on making them more affordable and effective.

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HEMIJSKE REMEDIJACIONE TEHNOLOGIJE

Zagađenje životne sredine predstavlja jedan od najvećih problema u svetu. Veliki napori se ulažu za ograničavanje ispuštanja polutanata u životnu sredinu i razvijen je veliki broj metoda koje se koriste za remedijaciju životne sredine. Hemijske remedijacione tehnologije su od velikog interesa s obzirom na to da uklanjaju i razgrađuju molekule polutanata. Ovaj rad se fokusira na nekoliko hemijskih remedijacionih tehnologija, kao što su precipitacija, flokulacija, adsorpcija i jonska izmena, hemijska oksidacija, ispiranje tla i elektrokinetička remedijacija. Remedijacione tehnologije, iako se mogu primenjivati zasebno, gotovo se uvek kombinuju. Izbor odgovarajuće tehnologije zavisi od prirode polutanata, kao i karakteristika zagađenog terena i treba se izvršiti tako da se odabere ekonomski najisplativija i najefikasnija tehnologija. Iako se neke od ovih tehnologija uspešno primenjuju, fokus istraživanja treba da bude na unapređenju postojećih, kao i razvoju novih, remedijacionih tehnologija.

Ključne reči: adsorpcija, elektrokinetička remedijacija, hemijska oksidacija, jonska izmena, remedijacija vode, remedijacija zemljišta