IRON BASED IMMOBILIZATION FOR METAL CONTAMINATED SOILS

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ABSTRACT

Remediation of contaminated soils is an important task which aims to reduce the impact of toxic metalloids such as Cd, Cu and As on public health. In-situ immobilization via the addition of soil amendments such as iron-based materials reduces the mobility and transport of these toxic metalloids in the environment. A wide range of iron-based materials have been used for metal immobilization in contaminated soils including iron oxides, zerovalent iron, nano-zerovalent iron (nZVI), iron salts, green synthesized iron oxide nanoparticle (GION) or phytogenic iron oxides nanoparticles (PION), Fe-Al layered double hydroxide and CMC (carboxymethylcellulose) based iron. The reactivity and surface area of zerovalent iron is increased at the nanoscale when utilized as nZVI thereby increasing its effectiveness as demonstrated by previous studies. The efficiency of nZVI in remediation of contaminated soils is limited by the strong tendency of its particles to agglomerate. In order to overcome this limitation and facilitate the delivery and mobility of nZVI in soils, nZVI is immobilized onto a carrier such as resin, potato starch, zeolite, or mesoporous silica or by increasing colloidal stability with the addition of other soil amendments. Even though, there is g rowing concern over the environmental impact of nanoparticles, the use of plant extracts to synthesize iron nanoparticles is environmentally friendly and economical.

Keywords: Remediation; iron; cadmium; arsenic; copper

1. INTRODUCTION

Anthropogenic activities such as fertilization, waste disposal, industrialization and mining have led to elevated concentrations of toxic metals such as arsenic (As), chromium (Cr), copper (Cu) and cadmium (Cd) in the environment. There are thousands of contaminated sites in the USA classified "Superfund sites" which exist due to hazardous waste from manufacturing facilities, processing plants, landfills and mining sites (EPA, 2018). "A Superfund site is any land in the

United States that has been contaminated by hazardous waste and identified by the EPA as a candidate for cleanup because it poses a risk to human health and/or the environment and are placed on the National Priorities List (NPL)" (NIH, 2018). Most of the Superfund sites are contaminated with heavy metals with about 306 sites contaminated with chromium, 235 with As and 224 with Cd (EPA, 1996; Nejad et al., 2018). The type of metal contamination is dependent on the type of industrial operation performed at each site (EPA, 1996).

Arsenic exists mostly as the inorganic forms such as arsenite (As III) and arsenate (As V) with arsenite being the most toxic inorganic form of arsenic in the soil (Peters et al., 1996). The US EPA lowered its limit for As in drinking water from 50 to 10 ppb while the European Union (EU) lowered it from 10 to 5 ppb to protect public health from the lethal effects of As (Giacomino et al., 2010). Chromium exists mostly as the Cr (III) and Cr (IV) forms with Cr (III) being the most stable and most predominant in the soil (Namiesnick and Rabajczyk, 2012). Cr (VI) is the most toxic to biological systems in the soils with strong oxidizing properties (Namiesnick and Rabajczyk, 2012). Cr (VI) is more mobile than Cr (III) in the soil especially in the presence of organic matter which acts a reducing agent and favors the retention of Cr (III) (Galdames et al., 2017). Cd which exists as the +2 ion is one of the most mobile and potentially bioavailable soil elements (Markovic et al., 2019) while Cu exists as the +1 or +2 ion in the soil solution. The mobilization of Cd occurs mainly in oxic, acidic conditions while its sorption is enhanced by the presence of high amounts of hydrous oxides, clay minerals, and organic matter (Kubier et al., 2019).

These three metals, As, Cr and Cd classified as carcinogens are a threat to public health and their release into the environment must be regulated and contained (National Toxicology Program, 2000; Guan et al., 2019; Lin et al., 2019). The mobility of metals in soils have been drastically limited by the addition of readily available and economical amendments such as industrial wastes, iron rich materials and mineral based amendments (Li et al., 2019). It is widely known that iron-rich compounds are effective in immobilizing heavy metals in contaminated soils without risk of secondary contamination (Nejad et al., 2018).

A wide range of iron-based materials have been used for metal immobilization in contaminated soils including iron oxides, zerovalent iron, nano-zerovalent iron (nZVI), supported NVI, iron sulfide, green synthesized iron oxide nanoparticle (GION) or phytogenic iron oxides, Fe-Al layered double hydroxide and CMC (carboxymethylcellulose) based iron (Zhang et al., 2014; Frick et al., 2019; Mitzia et al., 2020; Fresno et al., 2016; Su et al., 2019; He et al., 2018). Iron oxides are generally used in contaminated sites because they are regarded as scavengers of trace metals in soils due to their high reactivity and large surface area (Zhang et al., 2014; Nejad et al., 2018).

The reactivity and surface area of zerovalent iron is increased at the nanoscale when utilized as nZVI thereby increasing its effectiveness as demonstrated by previous studies (Stefaniuk et al., 2016; Wang et al., 2014). However, there may be a need to support nZVI with materials such as biochar, activated carbon, silica as a sorbent in the soil to reduce agglomeration of nZVI (Trakal et al., 2019; Dong et al., 2017). The addition of carboxymethyl cellulose (CMC), a surfactant can also eliminate the inhibition to reactivity of nZVI and can accelerate contaminant removal (Dong and Lo, 2013; Hou et al., 2019). Iron oxide nanoparticles may also be synthesized using plant extracts and advantages of these plant based nZVI are their simplicity of preparation, environmental friendliness and cost effectiveness (Lin et al., 2018). These "green synthesized iron oxide nanoparticles (GION) are also richer in carbon-oxygen functional groups, which provide far more active adsorption sites for both anions and cations than traditionally prepared nanoparticles" (Su et al., 2019). This paper is an overview of research work conducted on iron-based immobilization of metal(loid)s in contaminated soils.

2. METAL(LOID) CONTAMINATED SOILS

Globally, As contaminated soils exist due to human activities such as mining, industrial and agricultural activities (Rahman et al., 2019). Arsenic contamination is widespread globally due to the irrigation of agricultural soil with arsenic contaminated groundwater (Garcia-Manyes et al., 2002). Historically, As has been used in a variety of agricultural chemicals such as wood preservative, insecticides, herbicides, algaecides, and growth stimulants (Fillol et al., 2010). The extensive use of the wood preservative chemical known as chromated copper arsenate (CCA), made up of a mixture of Cr and Cu salts (CrO_3 and CuO) and arsenic acid (H_3AsO_4) since the 1940s has led to sites contaminated with Cr, Cu and As (Frick et al., 2019).

In the early 1900s, excessive application of lead arsenate pesticides in apple orchards led to the accumulation of arsenic and lead in the soil (Newton et al., 2006). The use of As containing pesticides at cattle dip vats have also led to elevated As levels in the soil, for example, As concentrations up to 14, 000 mg kg^{-1} have been reported in New South Wales in eastern Australia in a region where the investigation level is 20 mg kg^{-1} (Rahman et al., 2019). Arsenic contaminated soils have also been reported in golf courses where arsenic containing herbicides were used (Cai et al., 2002). Naturally, As also exists in the soil from the weathering of parent materials in the soil (Giacomino et al., 2010) because it occurs naturally in many kinds of rock, especially ores that contain copper, lead, iron, nickel, and other metals (Fillol et al., 2010). Arsenic is present in natural environments as minerals such as realgar (As_4S_4), orpiment (As_2S_3), arsenopyrite (FeAsS), arsenolite (As_2O_3), and scorodite ($FeAsO_4.2H_2O$) (Kim et al., 2014).

Chemical processes that determine the mobility, bioavailability and toxicity of As include sorption processes in the soil (Rahman et al., 2019). Processes such as sorption/desorption,

precipitation, redox reactions may occur on mineral surfaces which may influence the solid-state speciation of As in the soil (Kim and Batchelor, 2009). Arsenate is often present in oxic conditions while arsenite is often found in flooded conditions where reducing conditions are dominant (Newton et al., 2006). Arsenate is often sorbed into organic matter, clays, and iron and manganese oxides and oxyhydroxides (Newton et al., 2006). It has been reported that Fe and Al oxy-hydroxides have a higher affinity for As than clays which have more negatively charged surfaces resulting in low As adsorption capacity of clays (Rahman et al., 2019).

Rahman et al. (2019) explained that results of previous studies utilizing X-ray adsorption fine structure spectroscopy and Fourier transform infrared spectroscopy suggest that both arsenate and arsenite form mono- or bidentate inner sphere surface complexes with iron-oxyhydroxides via a ligand exchange mechanism. Iron minerals such as hydrous ferric oxide, goethite, hematite and pyrite are some of the primary minerals controlling arsenic mobility in the soil and are important sinks for As (Kim et al., 2014).
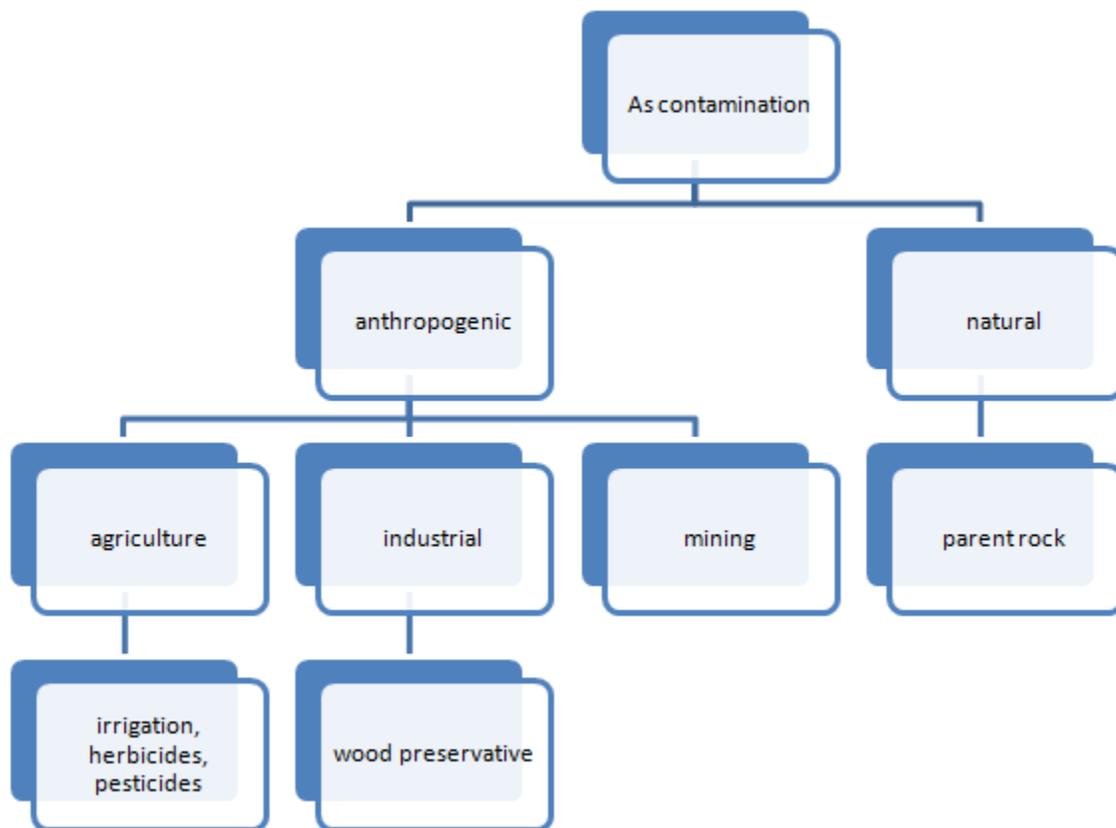

Fig 1: Sources of As contamination

Copper contamination of soils is associated with smelting, metallurgy, mining and application of biocides (Garrido et al., 2012; Palanivel et al., 2020). The soils surrounding a smelter are not only contaminated with heavy metals such as copper, they are also acidic. They contain up to 680 mg Cu/kg soil (Ginocchio, 2000; Ginocchio et al., 2004) with Cu present as chalcocyanite ($CuSO_4$), a highly soluble compound in smelter dust (Neaman et al., 2009). Addition of smelter dust to soils results in their acidification because of formation of sulfuric acid which gives it an extremely acid pH (around 2–3) in solution (Ginocchio et al., 2006). Soil acidification could eventually cause considerably increase in Cu dissolution in contaminated soils (Sauvé et al., 2000).

Copper contamination is often reported in agricultural soils because of the use of fertilizers and pesticides to improve crop production (Gonzaga et al., 2020). It has been reported that copper-based fungicides are the major source of Cu contamination in many organic-based farms and vineyards (Meier et al., 2017; Andreazza et al., 2010). In Brazil, soils used for the cultivation of grapes generally have a long history of copper (Cu) based fungicide applications which leads to an accumulation of Cu at levels that can cause toxicity in plants that co-inhabit the vineyards (Girotto et al., 2016). The use of copper containing dietary supplements in pig farming also leads to copper contamination of soils when pig manure is applied to soils (Cornu et al., 2017).
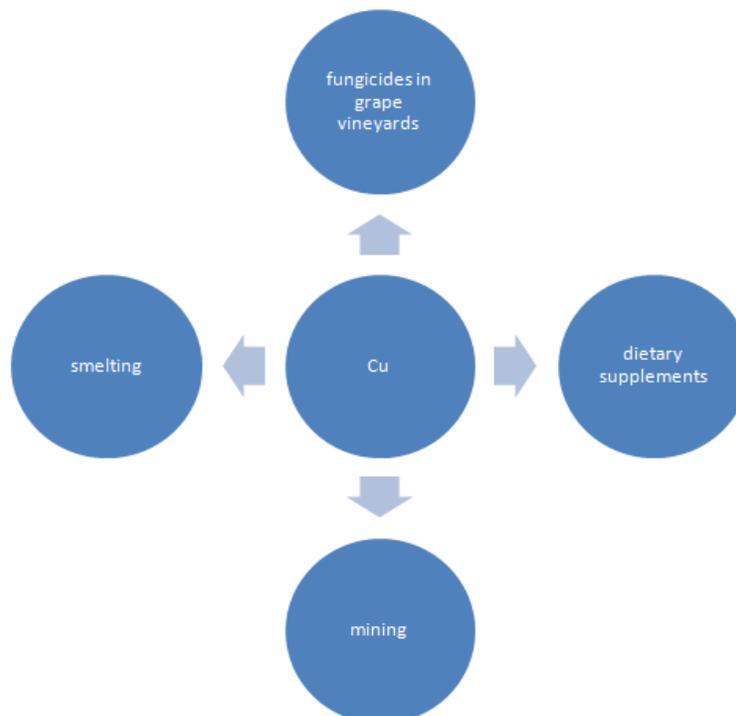

Fig. 2: Sources of Copper contamination in the soil

In uncontaminated soils, Cu is naturally found in trace amounts in soil at concentrations ranging from 13 to 24 mg kg^{-1} (Kabata-Pendias 2001). The highest soil Cu concentrations are found in the topsoil (0–30 cm) of copper-mined tailing areas (Shutcha et al. 2015; Cornu et al., 2017) which contain copper in several thousand mg kg^{-1} of soil and timber treatment sites. Copper is one of the components of the wood preservative, chromated copper arsenate (CCA), which is one of the common sources of copper contamination in the soil (Frick et al., 2019). Copper concentrations in a copper sulfide mine in Italy ranged from 160-13347 mg kg^{-1} in waste rock disposal and surrounding soils (Marescotti et al., 2008, 2010, 2013). This high concentration was attributed to the presence of Cu-bearing pyrite, chalchopyrite, Fe-oxides and Fe-oxyhydroxides formed as a consequence of sulfide oxidation processes (Zotti et al., 2014). The main processes governing the mobility of Cu are the adsorption and desorption of Cu on these minerals in the soil (Hooda et al., 2010). The mobility of Cu is high in these sulfidic waste rock dumps which are characterized by low pH, low clay mineral and organic matter content with high permeability (Kabata-Pendias and Mukherjee, 2007).

Even though Cd is a trace element whose total concentrations in agricultural soil ranges between 0.4 and 0.5 mg kg^{-1} (Bjelkova et al., 2011), it's one of the most mobile and potentially bioavailable toxic elements in the soil environment (Khan et al., 2017). Heavy application of organic fertilizers on a long-term basis, industrial sewage irrigation and atmospheric Cd deposition from coal combustion from nearby industries has led to Cd accumulation and contamination in the soil in greenhouse vegetable production (Zhang et al., 2017; Yang et al., 2020).

Another source of Cd in agricultural soils are phosphatic fertilizers (Wu et al., 2016) and wastewater irrigation (Sun et al., 2012). Cd contamination can also occur as a result of mining and smelting of metalliferous ores (Cui et al., 2016). In Thailand, abandoned Zn mines are facing issues with Cd contaminated soils because Cd ores occur as minor components of Zn deposits (Inkham et al., 2019).
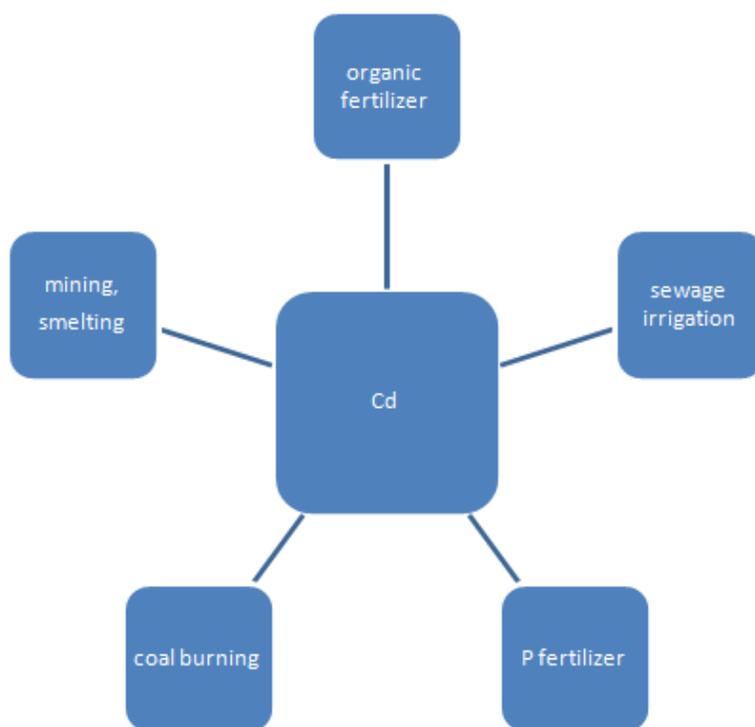
Fig 3: Cd sources in the environment

Cd contamination in the paddy soil of a village in Thailand ranged from 0.1 to 284 mg kg^{-1} which was much higher than the Cd content limit of 3 mg kg^{-1} for agricultural lands in Thailand (Simmons et al., 2005). Other sources of Cd pollution in soils are domestic and sewage sludge including pulp and paper mill waste, printing industry, cement production, wear of automobile tires, lubricants and metallurgical activities (Kabata-Pendias and Mukherjee, 2007; Borah et al., 2018).

Cr is released into the environment through human activities such as chromate production, electroplating and leather tanning (Su et al., 2016). Other sources of Cr contamination are wood preservation, uncontrolled treatment of Chromite ore processing residue and Cr-containing wastewater from chromium producing or consuming industries and alloy production (Saha and Orvig, 2010). Illegal discharge of illegal wastes and uncontrolled disposal has led to chromium contamination of groundwater (Su et al., 2016). There is extensive chromium contamination in China due to development of industrialization in the region (Su et al., 2016).
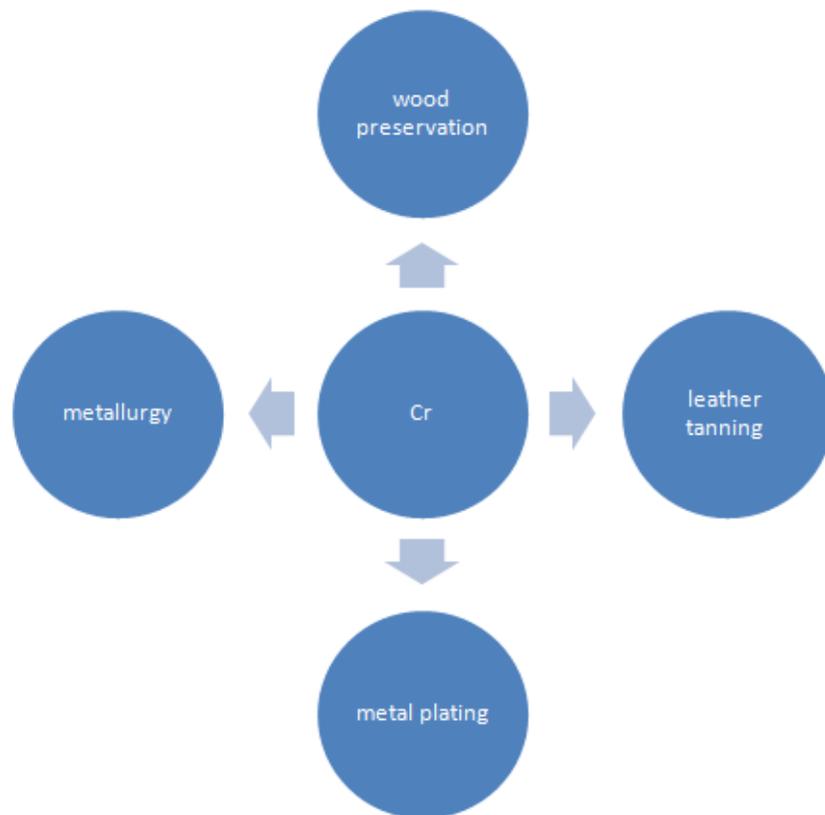
Fig 4: Some sources of chromium in the environment

3. IRON BASED TECHNOLOGIES FOR METAL IMMOBILIZATION

Compared with other soil amendments such as aluminum and manganese oxides and kaolinite, iron-based amendments such as zerovalent iron powder, ferrihydrite and ferric chloride were the most effective at reducing As in leachates in a soil column leaching study (Doherty et al., 2017). In this study, zerovalent iron powder and ferrihydrite were the most effective for the reduction of As in leachate reducing As concentrations by more than 80% (Doherty et al., 2017).

3.1 Iron oxides

Iron oxides occur naturally in the soil and are important scavengers for As and other metals and has been reported to immobilize As in short and long term experiments (Fresno et al., 2016). In a study, iron oxides with three different degrees of crystallization were used for the immobilization of Cd in contaminated sediments because well crystallized iron oxide have higher stabilities under reducing and acidic conditions (Yin et al., 2016; Li et al., 2019). Results of the study showed that crystalline iron oxides were able to reduce the mobile fraction and increase the stable fraction of Cd in contaminated sediment after treatment for 56 days (Li et al., 2019).

Nano-sized particles of three iron oxides showed high capacity to remove Cd with adsorption capacities that ranged from 2.8 to 7.4 mg Cd/g substrate via mechanisms such as ion exchange, hydrolysis, electrostatic attractions, chemical binding or specific interactions (Zhang et al., 2016).

The synthesis of iron oxides from plant leaf extracts is more environmentally friendly than traditional methods which involve toxic chemicals and solvents and result in detrimental residues when applied to soils (Wang et al., 2014). Weng et al. (2016) showed that iron oxide synthesized from eucalyptus leaf extracts effectively removed Cu from wastewater. Similarly, phytogenic iron oxide nanoparticles (PION) synthesized from leaf extracts of *Excoecaria cochinchinensis* effectively removed Cd from aqueous solution (Lin et al., 2018).

The application of phytogenic iron oxide nanoparticles synthesized from leaf extracts of *Excoecaria cochinchinensis* also effectively immobilized Cd under both oxic and anoxic conditions in the soil via mechanisms such as formation of insoluble hydroxides at elevated pH; ligand complexation and co-precipitation (Lin et al., 2019). Green iron oxide nanoparticles synthesized from the leaf extracts of *Euphorbia cochinchinensis* decreased mobile As fractions after 120 days of incubation and transformed As to more stable fractions (Su et al., 2019).

3.2 Zerovalent iron

Zerovalent iron (ZVI) has been used for the in-situ immobilization of As in contaminated soils (Miretzky and Cirelli, 2010; Nielsen et al., 2011). Upon addition to the soil, zerovalent iron is rapidly transformed into reactive iron (hydro) oxides which can adsorb both cations and anions due to their high surface area and large number of reactive terminal adsorptive groups (Komarek et al., 2013). Application of zerovalent iron and compost to a copper contaminated soil increased the content of iron hydr(oxides) which also increased the copper binding to iron hydr(oxides) in treated soil (Kumpiene et al., 2011).

Another study investigated the long-term effect of zerovalent iron on dissolved copper and arsenic in contaminated soils and results showed that the ZVI remained reactive for 6 to 15 years after application while the dissolved concentrations of Cu and As decreased in the treated soil (Tiberg et al., 2016). At the end of the study, there was a shift in copper speciation from organic matter complexes in the untreated soil to surface complexes with iron (hydr)oxides in the ZVI-treated soil (Tiberg et al., 2016).
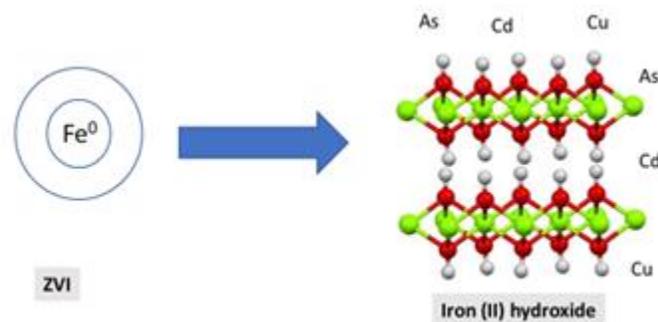
Fig 5: Transformation of zerovalent iron (ZVI) in soil after application.

The use of zerovalent Fe as a precursor of iron oxides has been shown to result in a decrease in As mobility and zero-valent iron nanoparticles (nZVI) have recently been used in metal immobilization due to their high surface area and high reactivity (Machado et al., 2013). Iron nanoparticles behave like reducing agents by donating their electrons to pollutants which are reduced as they accept the electrons thereby making pollutants more stable, less mobile and less toxic in the soil (Galdames et al., 2017). However, there is concern about the uncertainty of the long-term fate, transformation and ecotoxicity of nZVI in contaminated sites as they could potentially contaminate the food chain or spread other non-target pollutants in the soil (Masciangioli and Zhang, 2003).

The application of nZVI for in-situ immobilization of a soil contaminated with both As and Cr led to a decrease in the concentration of As in the soil and a decrease of concentration of Cr in leachates of tested soils (Galdames et al., 2017). The efficiency of nZVI and ngeothite to immobilize As in a polluted soil was tested in a recent study. At a dose of 2 %, nZVI reduced As in mobile fractions by about 89.5 % while ngeothite reduced As concentrations by about 82.5 % at the lowest dose of 0.2 % (Baragano et al., 2020).

The efficiency of nZVI in remediation of contaminated soils is limited by the strong tendency of its particles to agglomerate (Zhang et al., 2011; Xie et al., 2016). In order to overcome this limitation and facilitate the delivery and mobility of nZVI in soils, nZVI is immobilized onto a carrier such as resin, potato starch, zeolite, or mesoporous silica (Qiu et al., 2011, Fu et al., 2013, Kim et al., 2013) or by increasing colloidal stability with the addition of other soil amendments (Dong and Lo, 2013).

Iron phosphate nanoparticles stabilized by sodium carboxymethyl cellulose and supported by biochar was used to immobilize Cd in contaminated soil in a past study (Qiao et al., 2017). The treatment decreased the mobility of Cd by about 81.3 % after 28 days and reduced the bio-accessibility of Cd by about 80 % (Qiao et al., 2017). In a recent study, synthetic iron sulfide

nanoparticles (FeS NPs) stabilized with carboxymethyl cellulose (CMC) were used to remediate Cr (VI) contaminated groundwater and saturated soil. The treatment reduced Cr (VI) concentrations in leachates from contaminated soil from 4.58 mg L^{-1} to 46.8 – 80.7 μg L^{-1} (Wang et al., 2019).

Biochar supported carboxymethyl cellulose (CMC)-stabilized nanoscale iron sulfide (FeS) composite was used for immobilization of chromium Cr(VI) in contaminated soil and results showed that the treatment reduced leachable Cr and extractable Cr 94.7 % and 95.6 % respectively (Lyu et al., 2018).

Microscale iron sulfide stabilized by CMC was used for the immobilization of Cr (VI) in contaminated soil. The treatment reduced Cr(VI) and decreased leachate concentrations in the Toxicity Characteristics Leaching Procedure (TCLP), decreased bioaccessibility of Cr and converted the exchangeable Cr fraction to the Fe-Mn oxides bound fraction (Li et al., 2017). Compared with iron sulfate, stabilized microscale iron sulfide had a higher Cr removal and higher immobilization efficiency (Li et al., 2017).

Biochar supported zerovalent iron nanoparticles was used for the immobilization of Cr (VI) in chromium contaminated soil. Results showed an immobilization efficiency of 100 % and 91.94 % for Cr (VI) and Cr total respectively with Cr almost completely converted to Fe-Mn oxides and organic matter bound fractions (Su et al., 2016). Frick et al. (2019) showed that a combination of biochar and zerovalent iron effectively reduced water-extractable concentrations of Cr, Cu and As in CCA contaminated soil and reduced the toxic effects on the soil microbial community in the soil.

3.3 Iron salts

Iron salts such as sulfates have been recommended for metal immobilization because they immobilize contaminants such as arsenic more efficiently than iron oxides by inducing chemical reactions such as precipitation (Komarek et al., 2013; Cutler et al., 2014). A recent study evaluated the effect of iron sulfate in combination with organic amendments such as paper mill sludge, olive mill waste compost and olive tree pruning biochar on the immobilization of As and Cu in contaminated soils. They reported that iron sulfate with compost was the most suitable treatment that reduced both As and Cu availability and enhanced plant growth (Fresno et al., 2016). However, another iron salt was reported to be more effective than iron sulfate on a microscale.

Another iron salt, iron hydroxyl phosphate was used in the simultaneous immobilization of Cd, As and Pb in contaminated soil (Yuan et al., 2017). Application of iron hydroxyl phosphate resulted in an increase of Cd, As and Pb in residual fractions and a decrease in exchangeable

fractions as shown by sequential extractions (Yuan et al., 2017). This shows a decrease in mobility and bioavailability of these toxic elements in the soil after application of iron hydroxyl phosphate. Fe (II) and Al (III) layered double hydroxide completely immobilized Cr (VI) in contaminated soil probably via adsorption and reduction (He et al., 2018).

3.4 Iron-rich Industrial By Products

Some iron-rich industrial by-products such as red mud, iron oxide coated cement, water treatment sludges, and steel shot have been used for the immobilization of metals in contaminated soils because of their cost effectiveness and potential to reduce mobility of metals and metalloids (Rodriguez-Jorda et al., 2010). Red mud and aluminum rich water treatment residue were used for the immobilization of As and Cu under two different redox conditions. Both amendments reduced plant uptake of As and Cu under aerobic conditions even though the efficiency of the treatments was influenced by soil conditions and source of contamination (Silvetti et al., 2014).

Soil amendments such as red mud, limestone and furnace slag were added individually and in two amendment combinations to mining soil contaminated with As, Cd, Pb, and Zn. A combination of red mud and limestone was the most effective at reducing extractable As and heavy metal concentrations while 2 % red mud was most effective at reducing exchangeable fractions and decreasing labile metal fractions (Lee et al., 2011).

Red gypsum, an industrial by product from the production of titanium dioxide was tested as one of the amendments in a study on the immobilization of arsenic in contaminated soil. Red gypsum was one of the amendments that was effective in reducing the extractability of arsenic and considerably large amounts of arsenic was associated with the iron mineral (maghemite) in the red gypsum (Rodriguez-Jorda et al., 2010).

A by-product of titanium dioxide containing ferrous sulfate and phosphates was used to prepare polyhydric hydroxyl ferric phosphate (PHFP) which was then used for the immobilization of Cd in the soil. PHFP removed 33 % extractable Cd and reduced water-soluble Cd concentrations by 56 % (Yuan et al., 2017). A metal sorbent, FIXALL, consisting mainly of ferrihydrite and gypsum was synthesized from ferrous sulfate, a by product of titanium ore refinement and used for the simultaneous removal of As and Pb from soil and solution (Kameda et al., 2017). FIXALL decreased the concentration of water-soluble As and Pb simultaneously and continuously for 754 days (Kameda et al., 2017). The mechanism for As removal was by surface adsorption on ferrihydrite (Kameda et al., 2017). Ferrihydrite was the most effective amendment in reducing As bioavailability when the following amendments were added to arsenic contaminated soil; sepiolite, red mud, iron grit, phosphogypsum, ferrihydrite, iron phosphate, and layered double oxides (LDO) (Sun et al., 2015).

Industrial by-products from steel making processes (slag materials) removed As from leachates from an abandoned mine via adsorption of arsenate ions on the active sites of the Fe and Al oxides and hydroxides of the by-products (Ayala and Fernandez, 2020). The by-products were effective in simultaneously removing pollutants such as As, Hg, Pb, Cu, Ni, Zn, and Cd (Ayala and Fernandez, 2020). Steel abrasive and oxygen scarfing granulate, two iron rich industrial by products decreased arsenic concentration in pore water of CCA contaminated soils but their effectiveness reduced with increasing organic matter content (Lidelow et al., 2007).

Addition of Fe-Mn wastes produced by the water treatment plant in increasing doses substantially reduced As extractability in highly contaminated soils (Lewinska et al., 2018). In another study with Fe-Mn binary oxide wastes from water treatment plants, arsenite (As III) was oxidized to arsenate (As V) by the Mn oxide component while the arsenate is sorbed to the Fe oxide (McCann et al., 2018). The bioaccessibility of arsenic was significantly reduced by the binary waste addition (McCann et al., 2018).

4. FUTURE DIRECTIONS

Review of current literature showed that a lot of work has been done on iron-based technologies in remediation of aqueous solutions but there is paucity of published data on the use of these materials for the remediation of As, Cu and Cd in contaminated soils. There was however a lot more work done on Cr immobilization using iron-based materials in the soil especially zerovalent iron nanoparticles in chromium contaminated soils. The use of plant extracts to synthesize iron oxides nanoparticles is fast gaining attention but similar studies should be conducted with zerovalent iron nanoparticles. There have been studies using green synthesized zerovalent iron nanoparticles to remediate soils polluted with organic substances such as ibuprofen but very few or no studies with metal contaminated soils.

5. CONCLUSION

Iron based technologies have been shown to be efficient in the immobilization of As, Cu, Cr and Cd contaminated soils. A higher percentage of studies on iron-based immobilization are on nanoscale iron rich materials such as zerovalent iron or iron oxide nanoparticles. However, there is concern about the impact of nanomaterials on the environment as they could potentially contaminate the food chain or spread other non-target pollutants in the soil. Some studies have shown that this is not always the case. The use of phytogenic or green iron oxide nanoparticles synthesized from leaf extracts is a more environmentally friendly alternative in the use of these iron-based technologies. A lot of work has been done with iron rich industrial by products because they are cheap and readily available amendments that have been proved effective in metal contaminated soils.

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