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TREATMENT TECHNOLOGIES FOR CHROMIUM HEXAVALENT

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A survey and analysis have been made of existing technologies in reduction of toxic Cr(VI) penetrated into water and soil with wastes of the aluminium plant to practically harmless Cr(III). Most of these technologies do not free the drinking water and soil from Cr(VI). In addition they are expensive. The aim of the work is to reveal the most efficient reducing technology for Cr(VI). Such technology turned to be one based on the chemical method (nanotechnology).

Keywords: *chromium, soil, groundwater, remediation, bioremediation, phytoremediation, membrane filtration, reduction.*

Chromium is a silver-grey metal that has a beautiful shine when polished. It is commonly seen as reflective ″chrome″ coatings on items like car bumpers and the metal is an ingredient in stainless steel. People also need tiny amounts in their food to help control amount of sugar in their blood. There are more than ninety elements in nature. All matter is made from the elements-either pure, in mixtures, or as chemical compounds. Cr(VI) is the most oxidized, mobile, reactive, and toxic form of chromium, and it would be the only existing form if all chromium were to be in thermodynamic equilibrium with the atmosphere. Small concentrations can be the result of oxidation of natural Cr(III), but larger concentrations usually are the result either of pollution with Cr(VI) or the oxidation of Cr(III).

Physical and chemical properties of chromium

Chromium is metallic element with oxidation states ranging from chromium (–2) to chromium (+6) with the trivalent and hexavalent states being the most predominate. The Chemical Abstracts Service (CAS) Registry numbers for trivalent and hexavalent chromium are 16065-83-3 and 18540-29-9, respectively elemental chromium, chromium(0) does not occur naturally. Although there is a divalent state (chromous) it is relatively unstable under environmental conditions and is readily oxidized to the trivalent (chromic) state. Chromium compounds are more stable in the trivalent state under environmental conditions and occur in nature in ores, such as ferrochromite ($FeCr_2O_4$). The hexavalent is the second most stable state; however, it only occurs naturally in rare minerals such as crocoites ($PbCrO_4$). Hexavalent chromium compounds primarily arise from anthropogenic sources. The solubility of chromium compounds varies, depending primarly on the oxidation state. Trivalent chromium compounds, with the exception of acetate, hexahydrate of chloride, and nitrate salts, are generally insoluble in water. The alkaline metal salts (e.g., calcium, stronsium) of chromic acid are slightly soluble in water. The zinc and lead salts of chromic acid are practically insoluble in cold water. Some hexavalent compounds, such as chromium(VI) oxide (or chromic acid), and the ammonium and alkaline metal salts (e.g., sodium and potassium) of chromic acid are readily soluble in water. The hexavalent chromium compounds are reduced to the trivalent form in the presence of oxidizable organic matter. However, in natural water where there is a low concentration of reducing materials, hexavalent chromium compounds are more stable. In human, chromium(III) is an essential nutrient that may play a role in glucose, fat, and protein metabolism possibly by potentiating the action of insulin. However, there is some emerging controversy whether chromium(III) is essential and more work has been suggested to elucidate its mechanism of action (Table). Chromium picolinate, a trivalent form of chromium complexed with picolinic acid, is used as a dietary supplement, because it is claimed to speed metabolism and may have antidiabetic effects. However, researchers claim no demonstrated effects of chromium(III) on diabetes or insulin resistance. Currently, the mechanism of transport and absorption of chromium picolinate has not been determinated, although spectroscopic analysis has shown that chromium picolinate is a very stable complex in the body and its absorption properties may be due to its ability to cross membranes.

Physical and chemical properties of chromium

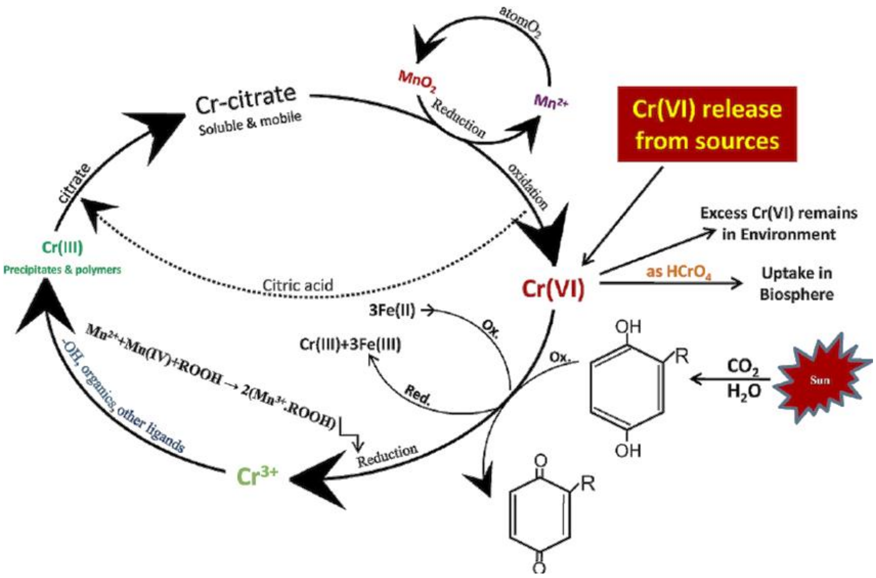
Property	Chromium	Chromic acid, Cr(VI)
Molecular weight	51.996	118 g/mol
Color	Steel-grey	Dark purple-red
Physical state	Solid	Solid
Melting point	11907^0C	196^0C
Boiling point	2671^0C	Decompose before boiling
Density at 20^0 C	7.19 g/sm^3	1.201 g/sm^3
Solubility in water at 20^0 C	Insoluble	169 g/100 ml
Vapor pressure	At 1800^0C 267 Pa	No data

Toxicology of Chromium

Cr is considered an essential nutrient for health. However, for instants, Cr in oxidation state +6 is considered harmful even in small intake quantity (dose) whereas Cr in oxidation state +3 is considered essential for good health in moderate intake. The health effects or nutriational benefits of Cr in other oxidation states are unknown although there are regulatory limits for the metal, Cr(0) and Cr(II) along with those for Cr(III) and Cr(VI). For example, the maximum concentration level (MCL) for total Cr in drinking water is 100 mg/l, the California MLC is 50 mg/l, and the National Institute for Occupational Health and Safety (NIOSH) recommends an exposure limit for Cr(VI) of 1 mg/m^3 and an exposure limit for Cr(0), Cr(II), and Cr(III) of 500 mg/m^3 for a 10 hour workday, 40 hours week. Human activity further contributes to Cr in the environment (air, surface water, groundwater, soil). The greatest anthropogenic sources of Cr(VI) emissions are: 1) chromium plating, 2) chemical manufacturing of chromium, and 3) evaporative cooling towers. While combustion of coal and oil also release large quantities of chromium (1700 metric tons per year), only approximately 0.2% of 16 this is Cr(VI). Approximately 35% of Cr released from all anthropogenic sources is Cr(VI). However, the ratio of Cr(III)/Cr(VI) in the natural environment varies considerably, from perhaps 0.3 to 1.5, depending on oxidation/reduction and acid/base conditions. Chromium metal or elemental chromium, Cr(0), rarely occurs naturally, and Cr(II) is unstable in the environment, readily oxidizing to Cr(III). Only small quantities of Cr(II) are used in industry. Thus, most exposures to Cr in the environment will be to Cr(III) and not to Cr(IV), the toxic constituent of total Cr. Occupational exposure to Cr(VI) is the most likely potential for adverse health effects.

In recent years, contamination of environment by Cr, especially hexavalent Cr, has become a major area of concern. Chromium is used on a large scale in many different industries, including metallurgical, electroplating, production of paints and pigments, tanning, wood preservation, Cr chemicals production, and pulp and paper production. Often wastes from such industries (e.g., sludge, fly ash, slag, etc.) are used as a fill material at numerous locations to reclaim marshlands, for tank dikes, and for backfill *t* sites following demolition. At many such sites, leaching and seepage of Cr(VI) from the soils into the groundwater poses a considerable health hazard.

The fate of chromium in soil is greatly dependent upon the speciation of chromium, which is a function of redox potential and the pH of the soil. In most soils, chromium will be present predominantly in the chromium(III) state. This form has very low solubility and low reactivity resulting in low mobility in the environment and low toxicity in living organisms. Under oxidizing conditions, chromium(VI) may be present in soil as CrO_4^{2-} and $HCrO_4^-$. In this form, chromium is relatively soluble, mobile, and toxic to living organisms. In deeper soil where anaerobic conditions exist, chromium(VI) will be reduced to chromium(III) by S^{2-} and Fe^{2+} present in soil. The reduction of chromium(VI) to chromium(III) is possible in aerobic soils that contain appropriate organic energy sources to carry out the redox reaction, with the reduction of chromium(VI) to chromium(III) facilitated by low pH. Chromium is one of the most important heavy metals present in the environment. Chromium is widely detected in surface water and groundwater at sites associated with industrial and military activities [1]. The properties of Cr are highly dependent on the molecular structure of the Cr compound, particularly on the oxidation state of the Cr. Cr is an element that exists



primarily in two different states, Cr(VI) and Cr(III). Cr(VI) anions, including chromate $(CrO_4)^{2-}$ and dichromate $(Cr_2O_7)^{2-}$, are highly soluble in aquatic systems and are severe contaminants to environment due to their carcinogenic, mutagenic, teratogenic features in biological systems. Hexavalent chromium is widely used in industries such as leather tanning, electroplating or pigment production. By contrast, Cr(III) species are relatively stable and have low solubility and mobility in soils and aquifers [2], and is one of the micronutrient elements in human bodies.

Cr(III) generally forms highly insoluble minerals, frequently in combination with iron, therefore, it is the less hazardous chemical species, and in fact it is an essential micro-nutrient involved in sugar, fat and protein metabolism. Cr(VI) in contrast is highly oxidant, water-soluble, and thus a very mobile reactive species that is hazardous to living beings. In addition, Cr(III) can be easily absorbed onto the surface of clay minerals in precipitates or complexes with positive charges. Due to high water-solubility and toxicity, Cr(VI)-containing wastes are considered as severe pollutants. Therefore, the development of technologies to prevent further chromium discharge and remediate Cr(VI) contamination are of great importance.

In recent years, a great deal of research efforts has gone to find better strategies to treat chromium contamination. Some of the most common remediation strategies utilize oxidation-reduction reactions, converting Cr(VI) to Cr(III). An electron donor that commonly drives this reaction is Fe(II) which either artificially supplied or present from the natural weathering of iron oxides. Elemental Fe [(Fe(0)], Mn(II), S^{2-}, CH_4 (methane), and reduced organics such as humic acids, fulvic acids, and amino acids can also be used as electron donors [1]. The mechanism of this reaction is still a topic of research. In [1] found that the oxidation rate of Cr(III) by MnO_2 increased proportionately with the surface area to volume ratio and with decreasing pH. The reduction of Cr(VI) to Cr(III) may influence the redox and pH of the subsurface.

Sorption processes for Cr can also be used in treatment strategies. The kinetics of Cr(III) sorption is rapid in clays, sands, and soil containing Fe and manganese oxides. For example in one laboratory study, about 90% of Cr(III) added to clay minerals and iron oxides was adsorbed within 24 h [1]. Cr behaves like a positively charged ion (such as Cr^{3+}) when adsorbing onto surfaces. As pH increases, surfaces are deprotonated, increasing as pH increases. If soil has a high organic content, sorption is also enhanced, as more sites are present for sorption to occur.

Equilibration between solid and dissolved forms of Cr is a third physical-chemical interaction that used in treatment processes.

Precipitation of Cr(III) occurs as $Cr(OH)_3$ solid (s), $FeCr_2O_4$(s), Fe_xCr_y(OH) (s) [3]. Precipitation/dissolution is a function of pH, complextion by organic matter, and the presence of other ions. As pH increases, OH^- concentration increases and more Cr precipitates.

The conventional physico-chemical remediation methodologies for soils contaminated with Cr(VI) require high energy and plenty of chemical reagent when applied to large scale what's more, these methods will be inefficient when the Cr(VI) is in low concentration and it could not remove chromium completely [4]. Therefore, these methods do not economically feasible. Consequently, the economical and environmental friendly remediation of Cr(VI) contaminated sites is in urgent need. Bioremediation is one of the promising methods to clean up the contaminated sites. To facilitate the in situ remediation of Cr(VI)-contaminated soil extensive efforts have been made to optimize the influencing factors, including the dosage, pH, etc. [5, 6]. To date, however, researchers have mainly focused their attention on the removal of aqueous-bound Cr(VI) rather than soil-bound Cr(VI), which may be absorbed by plants and subsequently spreads into the human food chain. Moreover, the mechanisms for the removal of Cr(VI) from contaminated soil proposed by different researchers are often contradictory. Cao and Zhang [7] reported that Cr(VI) was primarily reduced to Cr(III) by nano zero valent iron (nZVI) and then precipitated as hydroxides on the soil surface, although they had insufficient evidence for that assumption [8]. Chrysochoou and Johnston [9] suggested that sorption and co-precipitation may be the mechanisms for the removal of Cr(VI) by nZVI.

The strategy of bioremediation is to detoxify Cr(VI) in the soil to less soluble trivalent form via the normal function of the microbial metabolism. Microorganisms including bacteria, fungi, algae and yeast uptake metal either through bioaccumulation or through biosorption. Recently, attention has been paid on the bioremediation of contaminated soil using bacteria. Many Cr(VI) reduction microbes have been isolated and characterized from either aerobic or anaerobic conditions [10–14]. Cheng and Li [15] isolated eight isolates from soil samples of iron mineral area, one of which, the MDS05 showed great promise for use in Cr(VI) detoxification under a wide range of environmental conditions. Lee et al. [16] enriched the bacteria in the chromium contaminated sediment, and found that this bacteria reduced 34% of dissolved Cr(VI) in the sediment. Martins et al. [17] discovered that the uranium(VI) removing communities also have the ability to remove chromium(VI), and be the first to propose the members of Enterobacteriaceae and Rhodocyclaceae families that could remove chromium and uranium.

Though many studies reported on bioremediation of Cr(VI) contaminated soil, most of them require the addition of exogenous microbes or the microbes isolated from the contaminated soil but enriched and cultivated before applying in the actual bioprocess [18–20], which would bring about the ecological unbalance. More and more researchers on soil remediation started to focus on indigenous microorganisms. Colin et al. [11] summarized the indigenous microbial that has effect on the chromium contaminated medium and tried to explain the mechanisms. Jastin et al. [21] reported that they isolated three kinds of indigenous bacteria from the water of chromium mining sites at Sukinda Valley, which showed a considerable enhancement in Cr(VI) bioreduction rate, and successfully provided a choice for chromium mine sites remediation. Chai et al. [22] reported in 2009 that they isolated and identified an indigenous bacteria from soils contaminated by chromium-containing slag and found that once culture medium was added into the contaminated soil, the concentration of the water soluble Cr(VI), exchangeable Cr(VI) and carbonate-bonded Cr(VI) decreased. Most of the researches were focused on the discovering, isolation and identification of the specific indigenous bacteria, few has the actual application to the contaminated sites. The indigenous bacteria discovered by Chai et al. [22] have been applied in the remediation of Cr(VI) contaminated sites in west of Hunan Province, China. And it is the first time to report that we conducted a bench-scale study and confirmed the technological parameters of the indigenous bacteria discovered by Chai et al. [22] before starting the pilot scale and the field scale remediation.

Microorganisms often carry out enzymatic redox reactions as part of their metobalic processes. Cr(VI) can also be reduced nonmetabolically by reactions that occur on bacterial surfaces. Bacteria can enzymatically reduce Cr(VI) by both aerobic and anaerobic pathways. However, other nonbiological Cr reduction pathways compete with the biological pathways. Under anaerobic conditions, biological reduction is slow so abiotic reduction by Fe(II) or hydrogen sulfide is expected to dominate. Microbial reduction of toxic hexavalent chromium has practical importance, because biological strategies provide green technology that is cost-effective. Microbial reduction only becomes kinetically important in aerobic environments [2]. Oxygen concentrations in the systems are the primary factor influencing reduction rate, followed by pH and geochemical conditions.

Bioreduction of Cr(VI) can occur directly as a result of microbial metabolism (enzymatic) or indirectly, mediated by a bacterial metabolite such as H_2S. A number of chromium-resistant microorganisms have been reported, including Pseudomonas, Microbacterium, Desulfovibrio, Enterobacter spp, Escherichia coli, Shewanella alga, Bacillus spp, and several other. However, most of them have been isolated from tannery sludge, industrial sewage, evaporation ponds, or discharge water, or were purchased from cultural collections.

Many microbes were reported to reduce Cr(VI) under aerobic and anaerobic conditions. Bio-reduction of Cr(VI) can be directly achieved as a result of microbial metabolism or indirectly achieved by a bacterial metabolite such as H_2S [13]. Various bacteria were reported to remedy Cr(VI) contamination in soils. For instance, Jeyasingh and Philip [6] isolated a bacterial strain from a highly contaminated site and found the strain could reduce 5.6 mg/g Cr(VI) within 20 days in soil reactors. Desjardin et al. [23], found that Cr(VI) in soils was reduced by Streptomyces thermocarboxydus isolated from the contaminated soil. Bader et al. [24], studied Cr(VI) reduction in soil by microbial community under aerobic conditions and found that Cr(VI) was reduced by as much as 33% within 21 days. Virtually, most of the previous researches on biological reduction of Cr(VI) were conducted in batch reactors using pure cultures. The strains from contaminated sites were enriched and used as exogenous inoculums to remedy Cr(VI) contamination in the autoclaved soils. However, exogenous strains will inevitably lead to ecology risk in soil environmental due to the competition between exogenous strains and indigenous microorganisms. Since Cr(VI)-reducing microbial populations may widely distribute in soils, we can effectively utilize indigenous microorganisms to remedy contaminated soils. Furthermore, most of researches focus on the removal of water soluble Cr(VI). The information on the reduction of other Cr(VI) forms in soils is scanty.

While many examples of bacterial Cr(VI) reduction have been reported, virtually all were conducted at near-neutral pH values. To our knowledge, few reports of bacterial Cr(VI) reduction under alkaline conditions have been published [25]. Cr(VI) reduction under high pH conditions is important for certain bioremediation efforts because Cr(VI) contamination has been reported in high pH soils in association with improper tannery waste disposal. Chromite ore processing residue (COPR) is another major source of high pH Cr contamination [18]. Since Cr(VI) reduction products are least soluble at pH=9, alkaliphilic Cr(VI) reducing bacteria could potentially be useful in the remediation of these types of Cr contaminated sites.

Phytoremediation is a multifaceted approach towards Cr remediation. Plants contain the Cr by converting it to the less mobile Cr(III) (phytostabilization) and simultaneously reduce its toxicity. In addition, phytoremediation can be a removal technology, if Cr is sequestered in plant tissue and the plants are harvested (phytoextraction and rhizofiltration). For simplicity, all three mechanisms of phytoremediation are classified primarily as toxicity reduction methods and are discussed here. All three techniques are currently in the lab-scale or pilot-scale of development. Phytoaccumulation, one of the most common forms of Cr(VI) phytoremediation, consists of the uptake of the Cr from the soil to the plant roots and ultimately into the above ground parts of the plants. Some plants can accumulate very large amounts of a specific metal, such as Cr. The plant, Leptospermum scoparium was found to contain soluble Cr in the leaf tissue as the trioxalatochromium(III) ion $Cr(Cr_2O_4)_3^{3-}$. The function of the chromium-organic acid complex was to reduce the toxicity of the Cr.

Phytostabilization is perhaps the least advanced technology of the three been currently in development. This method is sometimes viewed as a temporary measure until phytoexrtaction is further developed. Plant and other biological secretions can stabilize Cr in the root zone. These can change pH or complex the Cr as Cr(III). In addition, plant roots minimize erosion and migration of contamination or large polluted areas, when conventional chemical-physical methods are most expensive. Phytostabilization can be combined with best management practices such as phosphorus amendments, lime, or organic matter to enhance immobilization and avoid leaching.

Several varieties of grasses are comercially available for phytostabilization of copper (Cu), and acid or calcareous lead (Pb) and zinc (Zn), but none for Cr. Trees and other high-biomass crops can be used for phytostabilization, since harvest is not performed. Phytostabilization using poplar trees is currently a topic of research. Metal accumulating plants are undesirable for phytostabilization, owing to the risk of generating hazardous plant waste and/or passing Cr along in the food chain.

More research has been conducted on phytoextarction and rhizofiltration of Cr. Cr reductases have not yet been identified in plants. Some research suggests that Cr is taken up as organic material/Cr complexses. Complexation with organics was identified as facilitating Cr availability to plants in lab-scale experiments. The sulfate transport system is apparently involved as it is for bacteria. In most experiments, Cr(VI) id preferentially taken up over Cr(III). Roots take up 10 to 100 times more Cr than shoots and other tissues. Much research has been done on the toxic effects of Cr(VI) on plants. Cr(III) is relatively nontoxic. The reason that Cr(VI) is toxic is that it generates free OH radicals as it is broken down to Cr(III). The energetic $\dot{O}H$ radicals can mutate DNA and lead to other toxic effects. Cr(VI) causes plant growth reduction owing to root damage.

Rhizofiltration refers to the uptake of Cr from wastewater by plants roots. Terrestrial plants with long fibrous roots and high surface areas are typically used because sorption onto the surface of roots provides an additional uptake mechanism. However, in some studies, only live roots were able to remove metals from solution. Selected aquatic plants have the ability to tolerate Cr. Water hyacinth (Eichhornia crassipes) can accumulate Cr as Cr(III) in high concentrations (6 mg/g dry mass) was observed in the plant's roots when it was growing in only 10 ppm Cr(VI). Herniaria hirusta was also found to be a Cr accumulator. Sulphur-loving plants such as cauliflower, kale and cabbage showed huge concentrations of Cr accumulation (160 to 135 mg/kg in roots, 1.6 to 2.0 mg/kg in shoots) with Brassica spp. accumulating the most.

Membrane Filtration

Semipermeable membrane filters are used in water treatment to filter soluble compound anions and cations from water, including $HCrO_4^-$ and CrO_4^{2-}. The flux water through the membrane is proportional to the pressure that is applied. The flux of solute (Cr) can be related to the flux of water, the concentration of Cr and other empirically derived membrane parameters. Membrane filtration systems are categorized by pore size. From largest to smallest pore size, these include microfiltration, ultrafilrtation (UF), nanofiltration (NF) and reverse osmosis (RO). Although RO membranes can achieve the highest effluent water purity, they must operate at higher pressure. For this reason, nanofiltration has attracted increasing attention.

Hafiane et al. (2000) [8] tested a thin film charged surface (TFCS) nanofiltration membrane for Cr(VI) removal and found that results were promising. Owing to the negative surface charge of the membrane, Cr and other anions are repelled by the membrane surface. As ionic strength of the water increases; however, this effect is shielded, and Cr removal decreases. As expected, Cr removal improves with increasing pH (membrane surfaces are deprotonated, increasing electrostatic repulsion, and Cr charge increasing as CrO_4^- forms). The rejection rate of Cr(VI) (equivalent to the removal rate) can be expressed as the following:

$$\text{Rejection rate} = \sigma(1-F)/(1-\sigma F),$$

where rejection rate is dimensionless (no unit) σ is the reflection coefficient and corresponds to the maximum rejection at an infinite volume flux, and *F* is defined by the following:

$$F = \exp(1-\sigma)\, J_V/P$$

or

$$F = e^{(1-\sigma)J_V/P},$$

here J_V is the flux of water through the membrane, with units of volume per membrane area per time, and P is an empirical parameter, known as the solute permeability, also with units of volume per membrane area per time. Hafiane et al. [8] determinate the empirical σ and *P* parameters for different ionic strength and pH values, allowing Cr rejection efficiency to be predicted once ionic strength and pH are known.

Cr(VI) ions are too small to be removed by microfiltration or ultrafiltration membranes, unless pretreatment is performed to complex the Cr(VI) by larger molecules. Hexadecylpyridine chloride has been used in the past, followed by ultrafiltration through membrane with 17.5% of greater polymer content. Approximetly 98% of the Cr(VI) was removed with this system [26]. Microfiltration has been used for removing Cr(VI) precipitates from industrial wastewaters.

Most of the physical and chemical approaches are generally costly and have the disadvantages of high energy input and secondary pollution. Although bioremediation is an economical and environmentally friendly strategy, it still has some limitations, e.g. plant uptake is a long time remediation [27] few microorganisms could survive high level of Cr(VI). When Cr(VI) concentration in soil exceeded 200 mg/kg, the ability of microorganisms to reduce Cr(VI) is significantly weakened. As an reduction-oxidation system, microbial fuel cells (MFCs) are recently becoming popular in treating wastewater, including Cr(VI) contaminated wastewater [28]. Electrochemical active microbes degrade organic compounds and transfer electrons to anode. The electrons then flow through a conductor to the cathode where Cr(VI) acts as an acceptor and is reduced to Cr(III) [4, 28]. Therefore, the treatment process does not need energy input, rather it produces electrical power. In addition, the benefits of using MFCs involve many aspects: cleaniness, safety, sustainability and easity in operating. To date, MFCs were mostly studied in wastewater treatment, whereas its feasibility in remediating heavy metal-contaminated soil has not been studied. Soil is a more complex medium compared with water. In soil, many variables can affect the behavior of metal ions and MFC operation. For example, soil pH and adsorption can affect the ion activity [4]. Soil contains NO_3^-, Fe(III), SO_4^{2-} and humic substances which can act as electron acceptors or shuttles and then affect current generation. As a result, the remediation of Cr(VI)-contaminated soil using MFCs may depend largely on soil properties. In addition, changing external loading is a general method to adjust current and thus control the reaction rate on electrodes. However, whether the high current is connected with effective soil remediation is hardly known.

The conventional methods to remove Cr(VI) from wastewater are chemical redox, followed by precipitation, ion exchange, adsorption, solvent ectraction, membrane separation, concentration, evaporation, reverse osmosis, bisorption, and emulsion petraction technology. Ion exchange and reverse osmosis are not economically attractive because of their high operating costs. Among the above mentioned methods, adsorption is highly efficient and economical, and therefore, it is a promising technique for the removal of Cr(VI) from wastewater and soil. Various adsorbents have been used to remove Cr(VI) from wastewater. They include activated carbons, coconut husk carbon, MnO_2 coated sand, basic yttrium carbonate, activated alumina, carbon from fly ash, granular titanium dioxide, hybrid polymeric adsorbent, etc. Among these adsorbents, activated carbon has been studied extensively.

Much of the research has focused on the remediation of Cr(VI) and many treatment processes have been developed. For example, the remediation of Cr(VI) by physicochemical adsorption has long been investigated [29] but its operational cost is high. Moreover, Cr(VI) is often just transferred, but not removed. Bioremediation by strains of bacteria is a cost-effective alternative to reduce Cr(VI) to Cr(III), but a variety of bactericidal toxicants (e. g. hydrocarbon) at many waste sites may limit their growth and effectiveness [30]. Chemical reduction is also known to transform Cr(VI) to Cr(III) rapidly and effectively. Many reducing agents have been reported, these include H_2S, Fe^{2+} Fe^0 etc. [30]. Cr(VI) reduction by Fe^0 [31] appears to be one of the most promising technologies. Powell et al. suggested that the mechanism of Cr(VI) reduction by Fe^0 is a cyclic, multiplestep electrochemical corrosion process and confirmed that aluminosilicate minerals could enhance the rate of Cr(VI) reduction. [31] evaluated the effect of the different type of iron metal, the Fe^0 area concentration and the pH value on the removal efficiency of Cr(VI) reduction by Fe^0. Fe^0 nanoparticles, due to their extremely high surface areas, can enhance the reduction efficiencies remarkably. Typically, Fe^0 nanoparticles are prepared by reducing Fe(II) or Fe(III) in an aqueous solution using a strong reducing agent (e.g., $NaBH_4$). However, because of their high surface area and high reactivity, Fe^0 nanoparticles prepared by this approach tend to react rapidly with their surrounding media (e.g., dissolved oxygen, or water) or agglomerate rapidly, resulting in the formation of much larger particles and rapid loss in reactivity [22]. As a result, new processes are being investigated to prepare stable Fe^0 nanoparticles using stabilizers such as cetylpyridinium chloride (CPC) [15], starch [22], hydrophilic carbon, poly (acrylic acid), as well as other surfactants and polymers [32]. Recently, carboxymethyl cellulose (CMC) was used as a stabilizing agent for preparing bimetallic nanoparticles in aqueous media. A range of Fe(0) and Fe(II)-bearing materials can promote the reduction and precipitation of Cr(VI). The net reactions of Cr (VI) reduction with Fe^0 and co-precipitation of Cr(III) and Fe(III) can be written as below [32]:

$$CrO_4^{2-} + Fe^0 + 8H^+ \rightarrow Fe^{3+} + Cr^{3+} + 4H_2O,$$

$$(1-x)Fe^{3+} + (x)Cr^{3+} + 2H_2O \rightarrow Fe_{(1-x)}Cr_xOOH\downarrow + 3H^+.$$

To prepare physically more stable and chemically more reactive Fe^0-based nanoparticles, Mallouk et al. [33] employed carbon nanoparticles and poly(acrylic acid) (PAA) as supports for iron and bimetallic nanoparticles [34]. These supports prevented iron particles from agglomerating and thereby prolonged the reactivity of the particles. Generally, polymers such as CMC, guar gum, chitosan, and PAA provide steric stabilization that exhibit a larger repulsion force than electrostatic repulsion [19], hence they can help to stabilize Fe^0 nanoparticles [32] and superparamagnetic ferrofluid via carboxylate binding. CMC is a commercial, environmentally friendly material and has already been applied for stabilizing Fe^0 nanoparticles [22].

Traditionally, Cr(VI) is removed from water through reduction of Cr(VI) to Cr(III) using a reducing agent. As a reductive material, zero-valent iron is extensively used for removing all kinds of contaminants including Cr(VI). However, it is concluded that metallic iron shows a kinetic limitation with a low reaction rate because of limited available surface. The reactivity of Fe^0 has been significantly improved by the development of smaller sized Fe^0, i.e., nanoscale zero-valent iron particles (nZVI) due to large specific surface area and more active sites [35]. Although the use of nZVI as reactive medium in the field of in situ subsurface environment remediation has recently been intensely investigated for removal of trichloroethylene (TCE), polychlorinated biphenyl (PCB), benzoic acid and As(III), there are still serious technical challenges associated with its application. Due to forces being either much too weak to hold Fe^0 particles together or too strong to disperse them, nZVI was found to lack stability in water [22]. Further, as agglomerated ZVI particles are often in the micron scale, they are essentially not transportable and transferable in soils. Thus, they cannot be used for in situ applications. Several methods have been proposed to solve this problem and one approach is to use a support which prevents the iron from agglomeration and therefore presents a higher specific surface area of iron to the solution. The use of resin [35] and carbon as a support for nZVI were extensively studied by other researchers. However, a good support should be cheap, widely available and able to disperse the metals forming a feasible particle size. At the same time, the support must be suitable to stimulate the reaction on its surface. Silica fume is generated during silicon metal production as very fine dust of silica from a blast furnace and historically considered a waste product. It can be successfully used to improve the resistance of concrete against chloride penetration. However, no studies have been reported on silica fume in environmental remediation. The silica fume is chosen as a support because it is cheap and easy to obtain, and because it provides a high surface area upon which nZVI particles can be dispersed. Furthermore, silica surface had been shown to strongly bind Fe(III) and Cr(III) via surface complexation [2] which may be important for Cr(VI) removal.

In particular, a number of studies have demonstrated that zero valent iron [Fe(0)] is an effective reductant for Cr(VI) [36, 37]. For example, [36] reported that iron fillings and cast iron effectively removed Cr(VI), with its removal efficiency varying with the surface area and composition of iron. They also observed that the presence of aluminosilicate aquifer materials significantly enhanced the removal of Cr(VI) by iron, and attributed the enhancement to the material's ability to generate protons. Protons are generated by dissolution of aluminosilicate minerals (e.g. montmorillonite and kaolinite) along with silica, and by subsequent reaction of silica with iron oxides [36]. The primary effect of the generated protons in a Fe(0) treatment system is to maintain solution pH and thus reduce surface passivation of iron. A similar buffering effect was also reported for quartz grains in Fe(0)–Cr(VI) reaction [38]. Spectroscopic analyses of Fe(0) surfaces after reaction with Cr(VI) suggested that the removal pathway involves initial reduction of Cr(VI) to Cr(III), followed by adsorption of Cr(III) onto the surfaces, or by precipitation of Cr(III)/Fe(III) hydroxides [39, 40]. The surfaces for Cr(III) adsorption may include a range of secondary minerals including goethite, lepodocrocite, maghemite and hematite, most of which are derived from reactions between inorganic constituents in water and Fe(0). The type of the secondary minerals, primarily dependent on the solution chemistry of water being treated. For example, [40] recently obtained 8-year monitoring results of a permeable reactive barrier (PRB) placed in sulfate-rich groundwater in Elizabeth City, NC, and reported that the majority of chromium removal occurred in regions where the secondary mineral formation was most significant and the removed chromium was associated with iron sulfide minerals. Authors [38] reported that Cr(III) precipitated on the surface of Fe(0) in the form of Cr(III)-goethite mixtures in a calcite-saturated water. The removal of Cr(III) via precipitation is consistent with the fact that the Cr(III)/Fe(III) hydroxides, $Cr_xFe_{1-x}(OH)_3$, has lower solubility than cromichydroxides. The use of resin [35] and carbon as a support for nZVI were extensively studied by other researchers. A good support should be cheap, widely available and able to disperse the metals forming a feasible particle size. At the same time, the support must be suitable to stimulate the reaction on its surface. Zeolite has higher cation exchange capacity (CEC), thus enabling it to be used as a substrate to remove heavy metal cations including Cr(III) under column and fixed bed tests [41]. Although the sorption capacity of Cr(III) on zeolite was as high as 4% [19], the unmodified zeolite showed no affinity for anions. Under pH 4–12, raw zeolite could not remove more than 20% of the input Cr(VI).

Despite nZVI being used to remediate both organic and inorganic contaminants in groundwater for over decade, there are still technical challenges associated with its application. The poor transport properties of nZVI in porous media such as soil and groundwater aquifers made nZVI relatively ineffective for in situ remediation. In addition, controlling the aggregation of nZVI, targeting them to contaminant source zones in the subsurface, and optimizing their reactivity and stability are some of the remaining technical challenges. Furthermore, the application of nZVI and their agglomerates in systems is inevitable because of the extremely high pressure drops, lack of durability and mechanical strength in conventional systems. To address these issues, technologies have attempted to develop porous supporting materials such as ArsenXnp system, which is a hybrid sorbent consisting of nanoparticles of hydrous ion iron oxide distributed through porous polymeric beads. Resin-supported nZVI particles were used to remove Cr(VI) and Pb(II) from aqueous solutions where apparent rates of removal for Cr(VI) and Pb(II) were enchanced by 5 and 18 fold, respectively. Chitosan-stabilized Fe^0 nanoparticles have recently been used for the reduction of Cr(VI) in water, where it was suggested that nitrogen and oxygen atoms on the chitosan bound to iron increased the stability of Fe^0 nanoparticles and Cr(VI) reduction rates were 3 times higher than when using Fe^0 nanoparticles alone. Black carbon and hexadecyltrimethylammonium (HDTMA) modified montmorillonite supported nZVI was evaluated for Cr (VI) remediation. The specific surface area (SSA) of black carbon and HDTMA modified montmorillonite supported nZVI was 130 and 38.1 m^2/g respectively both materials show high removal efficiencies compared unsupported nZVI [34, 42]. These reports revealed that the introduction of various support materials could enhance the reactivity of nZVI.

Another limitation is the high cost associated with nZVI remediation. Since contaminants are typically distributed over very large volumes of groundwater, effectively treating them requires a large stoichiometric excess of iron. Bentonite, as a low-cost and efficient adsorbent, has a great potential in application for removing heavy metals from wastewaters because of its abundance, chemical and mechanical stability, high adsorption capability and unique structural properties. Removal of metal ions using bentonite is based on ion exchange and adsorption mechanisms because of bentonite's relatively high cation exchange capacity (CEC) and specific surface area.

Many studies were conducted to reduce Cr(VI) to Cr(III) via in situ chemical reduction, or using zero valent iron Fe(0) as the materials for permeable reactive barriers (PRBs) to intercept and reduce Cr(VI) into Cr(III). The presence of Fe(II) or Fe(II)-bearing minerals in soils could also limit the Cr(VI) transport as demonstrated by a field study [26]. In addition, Cr(VI) could be reduced by green rust which is made of ferrous–ferric iron oxides. The reduction rate was affected by Fe(II) concentration and the types of anions with chloride showing the fastest rate in comparison to carbonate and sulfate. Furthermore, combination of Fe(0) and Fe_3O_4 resulted in a much higher Cr(VI) reduction rate in comparison to Fe(0)/α-Fe_2O_3, Fe(0)/γ-Fe_2O_3 and Fe(0)/FeOOH. In municipal landfill leachate under a reducing condition (Redox potential of −310 mV) in the presence of bacteria, Fe(III) and Fe(II) were the crucial components for Cr(VI) Reduction via an electron shuttle process where Fe(III) was microbially reduced to Fe(II) which then chemically reduced Cr(VI) to Cr(III). Besides in situ reduction, sorptive removal of chromate from water was also experienced extensive studies. Ferric iron oxides and hydroxides had strong affinity for Cr(VI) and arsenic. Cr(VI) adsorption capacity was 2.3 and 2.0 mg/g on hematite and goethite, respectively. The presence of high concentrations of phosphate greatly reduced Cr(VI) adsorption by Fe(III). Higher partial pressure of CO_2 shifted Cr(VI) adsorption edge on goethite drastically to the low pH side. At lower partial pressure of CO_2, the inner sphere Cr(VI) surface complex dominated the adsorption behavior, while the outer-sphere complex was prevalent at a CO_2 partial pressure of 40 matm. In addition to iron and aluminum (oxy) hydroxides, other materials used to remove Cr(VI) include maize tassel and weathered basalt andesite products. Zeolite has higher cation exchange capacity (CEC), thus enabling it to be used as a substrate to remove heavy metal cations including Cr(III) under column and fixed bed tests. Although the sorption capacity of Cr (III) on zeolite was as high as 4%, the unmodified zeolite showed no affinity for anions [43]. Under pH 4–12, raw zeolite could not remove more than 20% of the input Cr(VI).

Due to its advanced hydraulic properties, zeolite was subject to extensive studies on its modification. The advantage of using zeolite as the substrate for surface modification lies on the following two aspects: its large surface area and high CEC to facilitate contaminant removal and its good hydraulic conductivities to serve as packing materials for fluid bed or PRB application. Fe(II)-modified zeolite showed good removal potential for both Pb and Cr(VI) [15]. The kinetics of Cr(VI) adsorption on a zeolite NaX followed the first order reversible reaction with an optimum solution pH of 4 [44]. In addition to modification by ferrous iron, zeolite can also be modified by aluminum to enhance the adsorption of arsenate from water. Modification of zeolite by cationic surfactants resulted in significant Cr(VI) retardation. Modification with even heavy metals such as Ag^+, Hg^{2+}, and Pb^{2+} could also increase the Cr(VI) uptake by zeolite dramatically [43].

One of the most promising methods is reduction using iron-based materials such as zero-valent iron and dissolved Fe(II) and solids containing Fe(II).

Interest has increased over the past few years in using zero-valent iron Fe(0) and its respective nano-scale form to reduce chromium(VI) contamination. Zero-valent iron (ZVI) is a readily available and low-cost reducing agent that is also used extensively to remove a number of other kinds of contaminants, such as chlorinated compounds, pesticides and heavy metals e.g. As(V) Although the efficiency of ZVI and especially nano-scale ZVI (nZVI) in reducing the concentrations of Cr(VI) and other pollutants is well documented, only a few works have focused on its ecotoxicity for indigenous organisms in the soil.

Transition metal ions, such as Mn(II), can greatly catalyze the reduction of Cr(VI) by organic acids. The enhancement of reducing Cr(VI) by citric acid in the presence of Mn(II) is attributed to the ring structure formation between Mn(II) and citric acid, which increases the activity of –OH and thus results in the formation of a Cr(VI)–citric acid–Mn(II) complex. Two reaction stages were observed in this kind of reaction: a slowly inducing reaction in the initial stage and a rapidly accelerating reaction in the late stage. However, the catalysis of Mn(II) is markedly suppressed when EDTA is introduced to the reaction system since it is presumed that EDTA forms a complex with Mn(II) and thus Mn(II) is deactivated. In recent years, many efforts have been focused on the photocatalytic impact of Fe(III) on the reduction of Cr(VI) by organic acids. It has been shown that Fe(III) catalyzes photochemical reduction of Cr(VI) by oxalic acid and citric acid, and the reduction of Cr(VI) in the presence of these two organic acids and Fe(III) is extremely fast, with more than 95% initial Cr(VI) reduced to Cr(III) in 20–40 min. It is hypothesized that the fast reaction between Cr(VI) and the two organic acids in the presence of Fe(III) is mainly due to the photoreaction products generated when solution is exposed to sunlight, such as Fe(II), $O_2^{\bullet}-$, or $CO_2^{\bullet}-$, which catalyze the reduction of Cr(VI). The rate of Cr(VI) photoreduction in sunlight natural waters is related to the amount of Fe(III) present and the nature of the dissolved organic matter substrate [45]. Based on their difference in Fe(III) photocatalytic reduction, low-molecular-weight organic acids can be categoryzed into two groups: 1) low Fe (III) photoreductivity such as acetate and succinate, and 2) high Fe(III) photoreductivity such as citrate and tartarate. As a result, light and Fe(III)-induced Cr(III) oxidation occurs in the presence of acetate or succinate, but not in the presence of citrate or tartarate because the formed Cr(VI) is rapidly reduced by organic radicals produced from photolysis of Fe(III) complexes with these acids.

Unfortunately, nZVI has poor stability and tends to agglomerate easily reducing the ability to reduce contaminants. Loading another metal, such as Cu, Ni, or Pd, on the surface of nano zerovalent iron could enhance its performance and accelerate the reduction rate. Bimetallic particles can retard oxidation of nZVI and is favor for speeding up the reduction rate. The reactivity of bimetallic particles is higher than that of nZVI. It has been used to degrade organic pollutant and heavy metal. In recent years, bimetallic material has been researched for removing Cr(VI). Kadu et al. [46] used Fe–Ni bimetallic nanocomposites to reduce Cr(VI). The study showed that Cr(VI) was reduced completely in 10 min and first order reaction kinetics could be used to describe the reaction process. Hu et al. [5] used copper coated on the nZVI surface to form copper–iron bimetallic particles. The bimetallic particles reduced hexavalent chromium in near natural groundwater, with a significant rise in the Cr(VI) removal rate. The study showed that nZVI required higher copper levels to remove Cr(VI), compared with other oxidative contaminants.

Photocatalytic reduction of Cr(VI) in the presence of TiO_2 and organic compounds has also been extensively investigated. A rapid removal of Cr(VI) by organic compounds with different numbers of carboxylic groups was observed in a TiO_2 suspension, and the rate of Cr(VI) reduction increased with the number of carboxylic groups. Wang et al. [4] showed that an acidic medium was favorable for Cr(VI) photocatalytic reduction which mainly occurred on the surface of TiO_2, and pointed that the presence of Fe(III) enhanced the photocatalytic reduction of Cr(VI) by organic acids since an additional reaction between Fe(II) and Cr(VI) was observed in the UV/TiO_2 reduction process. Therefore, photochemical production of Fe(II) from both solid Fe(III) phases and dissolved Fe(III) in the presence of organic acids can easily occur [10].

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ALTIVALENTLİ XROMUN TƏMİZLƏNMƏ TEXNOLOGİYALARI

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Alüminium zavodunun tullantıları ilə suya və torpağa düşən zəhərli Cr(VI)-nın Cr(III)-ə çevrilməsi üçün mövcud texnologiyaların icmalı və analizi verilmişdir. Bu texnologiyaların əksəriyyəti suyu və torpağı Cr(VI)-dan tam təmizləməyə imkan vermir, həm də onlar baha başa gəlir. Işin məqsədi Cr(VI) üçün effektiv bərpa texnologiyasını aşkar etməkdir. Kimyəvi üsullara əsaslanmış texnologiya (nanotexnologiya) məqsədə uygun olmuşdur.

Açar sözlər: *xrom, torpaq, qrunt suları, membranla filtrləmə, bərpa*.

ТЕХНОЛОГИИ ОЧИСТКИ ШЕСТИВАЛЕНТНОГО ХРОМА

Г.Р.Аллахвердиева, А.М.Магеррамов, Лука Ди Палма, М.А.Рамазанов, Ф.В.Гаджиева

Проведены обзор и анализ существующих технологий по восстановлению токсичного Cr(VI), попадающего в воду и почву с отходами алюминиевого завода, до практически безвредного Cr(III). Многие из этих технологий не освобождают полностью воду и почву от Cr(VI). Кроме того, они дороги. Цель работы – выявить наиболее эффективную восстановительную технологию для Cr(VI). Таковой оказалась технология, основанная на химическом методе (нанотехнология).

Ключевые слова: *хром, почва, грунтовые воды, мембранная фильтрация, восстановление.*