Bio-Chemical Separations and Purification of Heavy Metal from Industrial Waste Water: A Review on Adsorption and Precipitations

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Abstract: The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. In small quantities, certain heavy metals are nutritionally essential for a healthy life. Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial and residential settings. To address this situation, this study presents a review on how the reduction of heavy metal form our surrounding can be achieved in particular by adsorption and precipitation methods including the type of adsorbent, characteristics of adsorbent and effectiveness in treatment. It has been found that these methods are quite effective in removing harmful heavy metals from wastewater. These methods generally use natural low cost materials like activated carbon, sawdust chitin and azadirachta indica (neem). These materials can be used effectively in developing countries like Ethiopia as they are quite inexpensive.

Keywords: Adsorption; precipitation, activated carbon, chitin, neem.

1. Introduction

Nowadays, environmental pollution is a global problem; it has been an active area of research and scientists are struggling for a solution. The sources of environmental contaminants include geological weathering, mining effluents, industrial effluents, and uses of chemicals like fertilizers (Atkinson et al., 2008). Generally industrial or municipal wastes, containing different chemicals, are disposed to water bodies such as lakes, oceans and rivers as water is considered as a universal solvent. The chemical contamination of drinking water leads to health problems primarily through chronic exposure, as it may persist for years before detection (Bosnic et al., 2000). In many countries, the major chemical pollutants of surface water come from industrial and municipal sewages as many cities lack sufficient waste treatment facilities (ESID, 2003). Sometimes the corrosion of the urban water supply system also contributes heavy metal contamination of water (Toprak, 1994; Fabiani et al., 1996; Andualem, 2005). The preservation and maintenance of natural water resources is a burning issue. The quality of water resources is deteriorating day by day due to continuous discharge of municipal and industrial effluents to water systems. On the other hand, the demand for safe water is increasing continuously due to the increase in population, living standard and industrialization.

The discharges from many industrial wastes contain various organic and inorganic contaminants including higher level of toxic heavy metals like Pb, Cd, Zn and Cu. Among the various water bodies river water is the most exposed one for pollution due to the direct discharge of municipal and industrial effluents to many rivers. Groundwater in the vicinity of drain systems can be polluted by toxic metals contamination from industrial, domestic, mining and others waste discharges (ESID, 2003).The incorporation of toxic metal ions in human organs through drinking water and various food chains may cause serious health problems.

Since metals are biologically no degradable they tend to accumulate in various vital organs; therefore, even exposure to trace concentration of various metal ions can lead to long term toxic effect (UNEP 2010) . Toxic concentration of trace metals, like zinc, lead, cadmium, copper and others, interfere with the normal metabolic process of fish and other species life in marine environment. These metals can be passed onto humans who consume them and pose adverse effects on the human metabolic process. National and international regulations on food quality have lowered the maximum permissible levels of toxic metals in human food; hence an increasingly important aspect of food quality should be to control the concentration of trace metals in food (Deng et al 2006). The health and welfare of people, which is intimately connected with the quality of water for drinking and for common household purposes, should control the level of heavy metals in different water supplies (Monser and Adhoum, 2002). These days, there is a great interest to the investigation of toxic heavy metals in environmental samples especially in industrial wastes, as they do have potential for contamination of surface and groundwater supplies (Agarwal et al., 2006).

Among the various metal ions Pb, Cd and Hg are toxic at all concentration levels and have no known functions in animal bodies. The metal ions of Cu, Zn, Co and Fe are required for physiological and cellular activities, but toxic above a certain level (Bosnic et al., 2000; Toprak, 1994; UNEP 2010; Deng et al 2006). Toxic metals as they are non-degradable and bio-accumulative, cause tissue degradation in nature (Monser and Adhoum, 2002; Agarwal et al., 2006). Mercury (Hg) both elemental and organic mercury are highly toxic to the central nervous system and kidney, especially in children. Brain damage can also be observed in developing fetus if the mother is exposed. It is a highly toxic metal; it has no known beneficial effects in humans (Machel and Gregorious, 1948). This paper presents a review of various adsorption and precipitation processes to remove heavy metals from wastewater. At the beginning, treatment studies by adsorption are discussed, followed by precipitation. A number of case studies are also presented.

2. Treatment by adsorption

Adsorption is a process in which a single or a group of ions/compounds get accumulated on the surface of another solid or liquid. The substance on which the adsorption takes place is known as adsorbent and the substance which gets adsorbed is called adsorbate. Due to ease of operation, the adsorption techniques have been used widely to treat metal ion containing wastewater. Several contender technologies exist to eliminate heavy metals from industrial wastewater, including reduction followed by adsorption on miscellaneous adsorbents, supercritical fluid extraction , ion exchange, ion flotation, electrocoagulation, high-gradient magnetic separation and enhanced ultrafilteration (Murphy and Erkey, 1997). Most methods seem to be almost equally effective. However, further consideration of suitability places a large portion of them outside of industrial scale applications due to the high capital investment and operational costs involved. Specifically speaking, the most effective and versatile technique for heavy metal removal, even at very low concentrations, is adsorption. However, the high price of adsorbents (usually activated carbon) is regarded as the major obstacle for industrial application. From an economic point of view, it is not feasible to utilize activated carbon for industrial wastewater treatment. To that end, the focus of heavy metal adsorption studies has been changed towards natural materials that are available in vast amounts, as well as certain waste products from industrial and agricultural operations (Monser and Adhoum, 2010). Among other processes for removal of Cr (VI) from industrial wastewater, biosorption process is an economically feasible alternative. The major advantages of biosorption over other conventional treatment methods are: (i) low cost and easy availability of adsorbent; (ii) utilization of industrial, biological and domestic wastes as adsorbent; (iii) low operational cost and high efficiency of metal removal from dilute solution; (iv) ease of operation compared to other processes and regeneration and recycling of the biosorbent; (v) ability to remove complex form of metals that is generally not possible by other conventional methods.

Based on the extent of attraction between the adsorbent and adsorbate, the adsorption process can be classified into two types: physical adsorption and Vander Waal's adsorption and Chemisorption. Adsorption, which can result from the Vnder Waal's force of interaction, is known as physical adsorption or VanderWall's adsorption. In this type of adsorption, the process heat is of the order of 20-40 kJ/mol. Physical adsorption process is reversible and established rapidly. Physical adsorption can be of two types, i.e., monolayer adsorption and multi-layer adsorption. In chemisorption, the chemical interaction/electrostatic force of attraction occur between the adsorbent surface and adsorbate molecules. In this process, the heat of adsorption usually varies from 40 to 400kJ/mol. It is associated with appreciably high activation energy and therefore termed as activated adsorption. It is relatively a slow process (Sundar, 2010). Physical adsorption is a reversible process that occurs at a temperature lower or close to the critical temperature of an adsorbed substance. On the other hand chemisorption, in general, is an irreversible process because of strong electrostatic force of interaction between the adsorbent and adsorbate molecules. Physical adsorption is very effective, particularly at a temperature close to the critical temperature of a given fluid. Chemisorptions occur usually at temperatures much higher than the critical temperature and by contrast to physical adsorption, is a specific process, which can only take place on some solid surface for a given fluid. Contrary to physical adsorption, chemisorption leads to monolayer adsorption. Under favorable conditions, both the processes

can occur simultaneously or alternately. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system; this process is exothermic in nature (Samuel et al., 1954).

Most of the adsorbents in industrial processes have complex porous structures that consist of pores of different sizes and shapes. The total porosity is usually classified into three groups: micropores (diameter, $d < 2$ nm), mesopores ($2 < d < 50$ nm) and macropores ($d > 50$ nm). The significance of pore size in the adsorption process is well known. Because the size of micro pores are comparable to those of adsorbate molecules, all atoms or molecules of the adsorbent can interact with the adsorbate species. This is the fundamental difference between adsorption in micro, meso and macro pores. Consequently, the adsorption in micro pore is essentially a pore filling process in which the pore volume is the main controlling factor.

In case of mesopores whose walls are formed by a large number of adsorbent atoms or molecules, the boundary of the inter-phase has a distinct physical meaning. That means the adsorbent surface area has a physical meaning. The adsorption forces do not occur throughout the void volume in macropores, but at a close distance from their walls. Therefore, the mono and multilayer adsorption take place successively on the surface of mesopores and their final fill proceeds according to the mechanism of capillary adsorbent condensation. The basic parameters characterizing mesopores include specific surface area, pore volume and pore size or pore-volume distribution. The mechanism of adsorption on the surface of macro pores does not differ from that of the flat surfaces. The specific surface area of macro-porous solid is very small; that is why adsorption on this surface is usually neglected. The capillary adsorbate condensation does not occur in macro pores (Dubinin and Stoeckli, 1980). Various forms of chemical adsorbents and materials of biological origin or biosorbent have been shown to be effective metal removers from the industrial wastewater.

2.1 Biosorption of heavy metals

Based upon the metal binding capacities of various biological materials, biosorption can separate heavy metals from wastewater. Lately, biosorption has emerged as a cost-effective and efficient alternative for application to low strength wastewaters. Biosorption, a term used to describe the removal of heavy metals using a passive binding process with nonliving microorganisms including bacteria, fungi, and yeasts, and other biomass types that are capable of efficiently collecting heavy metals (Vilar et al., 2007; Pavasant, 2007; Parvathi and Nagendran, 2007). Obviously, some of the advantages biosorption have over conventional treatment methods include low cost, high efficiency for dilute solutions, a minimal amount of chemical and/or biological sludge, no additional nutrients required and the possibility of biosorbent regeneration and metal recovery (Vilar, et al., 2007). The sorption of heavy metals onto these biomaterials is attributed to their constituents, which are mainly proteins, carbohydrates and phenolic compounds, since they contain functional groups such as carboxylates, hydroxyls and amines, which are able to attach to the metal ions (Pavasant, 2007). Heavy metal accumulation in aquatic organisms, which is an active process involving metabolic activity within living organisms, has been studied by several researchers since 1978 (Wong,1978; Volesky, 1978; Volesky and Holan, 1995; Volesky, 2003; Gutnick and Bach, 2000; Ahluwalia and Goyal, 2007). At present, the biosorption field has been enriched by a vast amount of studies published in different journals. Although in the beginning most researchers focused their efforts upon heavy metal accumulation and concentration within living organisms, upon noticing that dead biomass possesses high metal-sorbing potential, their interest shifted to biosorption. This is mainly due to the abundant availability, adsorption capacity and economic value of agricultural, plant tissue and industrial wastes, which has made them the main subject for biosorption research during the last decade (Shukla, 2006).

Several reviews are available that discuss the use of biosorbent for the treatment of water and wastewater containing heavy metals. The most encountered mechanism is the ion exchange mechanism. Recognition of ion exchange between protons and heavy metals, contribution of surface functional groups in ion exchange processes and ion exchange isotherm development are presented. Reliable sorption equilibria and kinetic data are of substantial value for adsorption separation system design. A majority of biosorption studies have been devoted to this end. Furthermore, a combination of basic equilibrium sorption data, sorbate behavior in solution, sorbate uptake mechanisms, mass transfer characteristics and fluid dynamic characteristics is required for the design of adsorption systems (Volesky, 2003).

Other researchers also provide several reviews that are worthy of mention. For instance, structural modifications of bacteria through alteration of their polysaccharide backbone or side chains or through sugar modification for biosorption purposes have been performed by many research groups. The discussion focus on mainly, cation binding to specific bacterial biopolymers, binding of cations by biopolymers, molecular approaches to biopolymer modification and preparations, and also potential application for metal sequestration. This review presents useful information on polymer engineering applications within the biosorption area. The remark drawn is that the benefits associated with enhanced specificity and cation-binding capacity should be examined to judge the economic competitiveness of polymer engineering for industrial

applications (Gutnick and Bach, 2000). Furthermore, studies about the applications of microbial and plant derived biomass to sequester metal ions from solutions were presented. Some conventional techniques utilized to remove heavy metals from industrial effluents, as well as the advantages and disadvantages of biosorption processes and an outline of the use of different surface and structural characterization methods, such as SEM (scanning electron microscope), and X ray diffraction method (EDAX), to determine biosorption mechanisms, were mentioned (Ahluwalia, and Goyal, 2007).

Sawdust, being cheap and easily available, is used widely either as such or in treated form to remove metal ions from wastewater. Sorption studies were also carried out mostly in batch scale and various adsorption parameters affecting the overall process were studied (Shukla et al., 2002). The role of saw dust for wastewater treatment has been given emphasis by some researchers. The adsorption mechanism, influencing factors and favorable conditions for different sawdust materials were discussed (Shukla et al., 2002; Bailey et al., 1999). A statistical review on the biosorption of Cd (II), Cr(IV), Ni(II), Pb(II) and Zn(II) using different classes of algae was provided. The focus was mainly on the biochemistry of biosorption, which revolved around a detailed description of the macromolecular conformation of the alginate biopolymers, metal binding mechanisms and the role of cellular structure, storage polysaccharides and cell wall and extracellular polysaccharides on metal sequestration (Romera et al., 2006; Davis et al., 2003). The state-of-the-art review in the field of heavy metal biosorption employing *Saccharomyces cerevisiae* was also compiled. The result showed that yeast-utilized biosorption depends largely on pH, the initial metal ion to biomass concentration ratio, culture conditions, the presence of various ligands and competitive metal ions in solution, and, to a more limited extent, temperature (Wang and Chen, 2006).

2.2 Use of activated carbon

The well known adsorbent which is in application in industrial scales is the activated carbon, which can remove metal ions from wastewater. The activated carbon is made from various raw materials having high carbonaceous materials, including wood, saw dust, coconut shell etc. They can be activated by thermal decomposition in a high-temperature oxidation or lower temperature chemical dehydration reaction. The activated carbon is being used widely to treat wastewater to remove organic or inorganic pollutants because of their large specific surface area, high adsorption capacity and special surface chemical properties. These physical and chemical properties of the activated carbon depend on pore size, pore distribution and number of surface oxygen groups. The pore size and pore volume can be controlled during the activation process such as activation time, activation agent and temperature. The surface oxygen can also be changed by using suitable oxidizing agents and thermal treatment in order to get the surface functional groups such as carboxyl, phenolic and lactonic group attached to carbon. These groups can improve the adsorption capacity and selectivity on a certain adsorbate in the gaseous or liquid phase (Yunhai et al., 2008; Schneider et al., 2007; Lodeiro et al., 2006).

2.3 Roles of living organisms

Waste microorganisms usually in the form of dead cells are also used as an alternative adsorbent for the treatment of heavy metal containing wastewater. In this process biological materials accumulate heavy metals from wastewater by either metabolically mediated or purely physico-chemical pathways of uptake. The microorganisms can take up metal ion in numerous pathways. The uptake of heavy metal ions can take place by entrapment in the cellular structure and subsequent sorption on to the binding sites present in the cellular structure (Pavasant, 2007). Mucor hiemalis was also reported to remove Cr(VI) from solutions. The detailed studies were made with regards to its kinetics and mechanism of adsorption. The competitive biosorption of Fe(III) and Cr(VI) on *C. vulgaris* from binary mixtures was investigated in a single stage batch reactor by varying the solid/liquid ratio at an initial pH of 2.0. The batch adsorption was assumed to be a single stage equilibrium operation (Volesky, 1978).

A number of fresh water macrophytes like a*eromonas caviae* was reported to treat Cr(VI) contaminated wastewater. The adsorption studies were carried out in a stirred reactor. Equilibrium and kinetic experiments were carried out for various parameters like bulk concentration, biomass load, temperature and ionic background. The isotherm followed monolayer Langmuir model. The adsorption process followed chemical sorption. The Cr(VI) reducing capacity was enhanced by modifying the amino and carboxyl group (Volesky, 2003).

2.4 Roles of agricultural and cellulosic materials

Agricultural by-products are mostly composed of lignin and cellulose, as well as other polar functional group-containing compounds, which include alcohols, aldehydes, ketones, carboxylates phenols and ethers. These groups are able to bind heavy metals through replacement of

hydrogen ions with metal ions in solution or by donation of an electron pair from these groups to form complexes with metal ions in solution (Ahluwalia and Goyal, 2007).

Adsorption studies were also carried out using various agricultural crop wastes. In these studies, adsorption analyses were carried out using different reactor types. Various adsorption parameters were studied to evaluate their effects on Cr(VI) removal efficiency. Among the adsorption parameters, pH was observed to be an important factor in determining the adsorption efficiency. Adsorption kinetics was observed to be reasonably faster and followed dual rate, i.e. initial faster rate followed by slower one. The initial faster and latter slower rates might be due to surface and intra particle diffusion processes, respectively (Lodeiro et al, 2006).

An adsorption study was made on *Tamarindus indica* on the capability of Cr(VI) removal by Agarwal et al., (2006). It was concluded that the use of tamarind seed as an alternative adsorbent is more economical and worthwhile than other conventional methods. The removal of Cr(VI) ions by tamarind seed is significantly reduced with a pH increase, slightly decreased with ionic strength enhancement and enhanced with rising temperature. It is suggested that chemisorption is the most plausible mechanism involved (Agarwal et al., 2006).

Azadirachta indica (neem) is a typical tree in the mahogany family of *Meliciae*. Products derived from neem have proven to possess therapeutic value such as anthelmintic, antifungal, antidiabetic, antibacterial, antiviral, anti-infertility and sedative activities. Several researchers have investigated the prospects of neem leaf as an alternative adsorbent for Cr(VI), Cd(II) and Pb(II). Azadirachta indica (Neem Leaf Powder) was utilized to extract chromium (VI) from solution. The adsorption was carried out in a batch process using different concentrations of metal ions in aqueous solution in parallel with variation in the adsorbent amount, pH, agitation time and temperature. The suitability criteria of the adsorbent were checked by the Langmuir and Freundlich isotherms, and also by various equilibrium kinetic data. On the basis of the Langmuir model, an adsorption capacity of neem leaf powder for Cr(VI) of 0.0028 mmol/g was obtained. A relatively low amount of *Azadirachta indica* (Neem Leaf Powder) (1.6 g/ dm^3) could remove as much as 87% of Cr(VI) from a dilute solution (0.137 mmol/l) during a 300 min period at 300K. The optimum pH range in the study was 4.5–7.5. By modifying the physical structure and surface chemistry of the neem leaf via an activation process, the adsorption capacity could be significantly enhanced (Babu and Gupta, 2008; Sharma and Bhattacharyya, 2004).

Chitin, the waste polymer from fishery industry, was reported to be a good adsorbent for Cr(VI). It is white, hard inelastic material containing nitrogenous polysaccharides derived from the outer skeleton of insects, crabs, shrimps and other marine animals. Chitin is the second most abundant natural polymer i.e. polysaccharide and its estimated annual production is almost equal to cellulose. Chitin is converted to chitosan by alkaline hydrolysis using 50% (W/W) aqueous NaOH solution. Chitosan has many applications due to the presence of reactive $-NH_2$ group and -OH groups. Due to the presence of these functional groups, chitosan is a good chelator and forms complexes with almost all heavy metal ions. Further, due to its cationic nature, it adsorbs various anionic species. The solubility of chitosan in aqueous acids is a limiting factor for many such applications. It is therefore necessary to crosslink chitosan to render it insoluble in acid media. Chitosan is generally cross-linked using chemical reagents such as glutraldehyde and epichlorohydrin (Schneider et al. 2007).

It was revealed that a major rice bran fraction contains 12%-13% oil and highly un-saponifiable components. In view of its abundant availability and ease of retrieval as an unused by-product, the possibility of using this material as an alternative adsorbent for heavy metal removal from synthetic wastewater was conceived. The study also explored the influence of parameters such as pH, temperature, and particle size and adsorption time on sorption capacity. The results underscore the importance of pH on heavy metal sorption capacity, while to a certain extent; the capacity also relies upon sorbent size (Grimm et al., 2008). With the aim of increasing biosorption capacity, modifications of the biosorbent surface have been carried out. For instance, thiolation of coconut fiber, alteration of the surface properties of pine bark using the Fenton reagent, alteration of the surface of olive pomace by phosphoric acid and hydrogen peroxide (Igwe et al., 2008; Argun and Dursun, 2008).

2.5 Chemical adsorbents

Apart from biomaterials, a number of chemical adsorbents were used to treat Cr(VI) contaminated water by Ghosh and Goswami (2005). Stannous hydroxide was reported to have good Cr(VI) adsorptive capacity. Various adsorption parameters were studied to evaluate their effect. The adsorption process followed first order kinetics (Ghosh and Goswami, 2005). Hydrotalcite was also used to treat Cr(VI) contaminated water. Hydrotalcite, $Mg_6Al_2(OH)_{16}$ $CO_3.4H_2O$ (HT), is a double layered mixed metal hydroxide. Due to positive charge of HT, it is a potential adsorbent for various anions. Cr(VI) adsorption studies were carried out by using manganese nodule leach residue. Since the leached residue has a high surface area, it is a potential adsorbent. Its adsorption behavior was studied as a function of contact time, pH, temperature, concentrations of adsorbate and adsorbent dose. The adsorption process was endothermic in nature (Lazaridis, 2003). Metallurgical wastes like

red mud was also reported to be a good adsorbent for Cr(VI). Activated red mud was prepared by acid dissolution followed by ammonia precipitation and drying at 110 ^{o}C. The process was optimized by varying the adsorption parameters (Pradhan et al., 1999). Various other chemical adsorbents were used to treat Cr(VI) contaminated water such as clay, zeolites , feldspar , hydrated zirconium oxide, hydrous titanium oxide and ion exchange resins (Marchiorett, et al., 2009).

Apart from process development in small scale, adsorption studies were also carried out in different reactors, which helped in scaling up the laboratory/bench scale data to pilot or industrial scale. The main requirement of a large scale sorption process is that the sorbent should be used in a suitable reactor configuration such as packed or fluidized bed or stirred tank reactor. Such large scale adsorption in reactors requires suitable adsorbent in granulated or pellet form. The size, density and shape of the particles should prevent clogging or large pressure drops across the adsorbent bed (in case of packed bed column) and at the same time, should permit optimum flow. Continuous adsorption of metal ions from solution can be accomplished by employing different types of reactor configurations. The reactors commonly employed for wastewater treatment include packed bed, fluidized bed, expanded bed, stirred tank reactor and moving column reactor etc. (Marchioretto et al., 2009).

3. Precipitation methods to remove heavy metals

Precipitation is the formation of a solid in a solution during a chemical reaction or by diffusion in a solid. When the reaction occurs in a liquid, the solid formed is called the precipitate, and the liquid remaining above the solid is called the supernatant. Natural methods of precipitation include settling or sedimentation, where a solid form over a period of time due to ambient forces likes gravity or centrifugation. During chemical reactions, precipitation may also occur particularly if an insoluble substance is introduced into a solution and the density happens to be greater (otherwise the precipitate would float or form a suspension). With soluble substances, precipitation is accelerated once the solution becomes supersaturated. An important stage of the precipitation process is the onset of nucleation. The creation of a hypothetical solid particle includes the formation of an interface, which requires some energy based on the relative surface energy of the solid and the solution. If this energy is not available, and no suitable nucleation surface is available, supersaturation occurs (Veeken, et al., 2012).

When the precipitate has low solubility products, supersaturation is favored and consequently the nucleation rate increases, as the particle sizes decrease. The particle size of precipitates depends on the competition between nucleation and crystal growth. When the nucleation rate dominates the crystal growth rate, colloidal particles (<0.05 mm) will result. If the initial concentration of the reactant is high, consequently increasing the concentration of the precipitate, which has a low solubility, the resulting high supersaturation leads to high rates of a primary nucleation. In fact, after filtration, the liquid was a bit turbid and this is an indication of the high nucleation rate. Common reagents used include alkalis, such as lime, magnesia, NaOH, NaHCO$_3$, Na$_2$CO$_3$. Heavy metals like Cr, Cu, and Zn do not precipitate at pH below 7, permitting some possibility for separation from ferric iron and aluminum which precipitate at pH below 6.5.

The association of heavy metal ions with a ferric or aluminum hydroxide precipitate is controlled by adsorption or co-precipitation. Co-precipitation implies the simultaneous removal of a metal ion during the formation of the primary metal precipitates. In addition to common alkalis, sulfides such as Na$_2$S, H$_2$S, NaHS, or FeS can also be used to precipitate metals and have been applied frequently for metal removal from waste effluents to achieve discharge standard limitations.

The lower solubility of metal sulfides in the acid region below pH 7 permits reduction of metal solubility to values that are orders of magnitude lower than are attainable by hydroxide precipitation (Marchioretto et al., 2009). Hydroxide precipitation is the most frequently applied treatment technology for removing heavy metals from industrial wastewaters and polluted ground waters. Disadvantages of hydroxide precipitation include the relatively high residual effluent metal concentrations (0.5 - 2 mg/ L), the interference of chelating compounds, and unsuitability of metal sludge reuse in case more metals are present. A well-known alternative is sulfide precipitation. Sulfide precipitation is superior to hydroxide precipitation for removal of heavy metals from wastewaters as it results in lower effluent concentrations (< 0.01 mg/ L) and less interference from chelating agents. However, sulfide precipitation is not widely applied in practice because the dosing of sulfide cannot adequately be controlled, and excess sulfide in the effluent is toxic and corrosive. Moreover, precipitation by sulfide results in colloidal metal sulfide precipitates that are poorly separable from the water phase by sedimentation or filtration (Veeken et al., 2012).

Nowadays, a combination of hydroxide and sulfide precipitation for optimal metals removal is being considered. A common configuration is a two-stage process in which hydroxide precipitation is followed by sulfide precipitation with each stage followed by a separate solids removal step. This could produce the high quality effluent similar to that obtained with the sulfide precipitation process. Moreover, it will reduce the consumption of sulfide reagents, which are usually more expensive than hydroxide reagents, and will result in a smaller amount of sludge compared to the hydroxide precipitation process alone. The drawbacks of the chemical precipitation process are related to the amount of

chemicals, final amount of wastes, difficulty to separate precipitate and liquid, and of course the costs of chemicals, waste disposal and equipment (Marchioretto, et al., 2009).

4. Case studies

Novel Technology for Biosorption and Recovery Hexavalent Chromium in Wastewater by Bio-Functional Magnetic Beads: Li et al. (2008) presented a study to develop an applied technique for the removal and recovery of heavy metal in wastewater. It was novel that the Cr(VI) could be adsorbed and recovered by bio-functional magnetic beads. Furthermore, the magnetic separation technology would make their separation more convenient. The beads were constituted by the powder of *Rhizopus cohnii* and Fe_3O_4 particles coated with alginate and polyvinyl alcohol (PVA). The parameters effecting Cr(VI) removal were obtained at the optimum pH of 1.0 and optimum temperature of 28 °C. The biosorption took place mainly in form of Cr(VI) and *R. cohnii* biomass played a key role in Cr(VI) adsorption. The group of –NH– played an important role in the Cr(VI) adsorption. Consequently, the beads exhibited the superior performances in Cr(VI) cleanup, separation and recovery and the perspective potential in application (Li et al., 2008).

Effects of Rhamnolipids on Chromium-Contaminated Kaolinite: Hexavalent chromium Cr(VI) is a common environmental pollutant that is treated by its reduction to the trivalent form Cr(III). The latter can be re-oxidized to the toxic form, Cr(VI), under specific conditions. A study was conducted by Hafez et al. (2007) on the removal of Cr(III) to eliminate the hazards imposed by its presence in soil as there has been some evidence that organic compounds can decrease its sorption. The effect of addition of negatively-charged biosurfactants (rhamnolipids) on chromium contaminated kaolinite was studied. Results showed that the rhamnolipids have the capability of extracting 25% portion of the stable form of chromium, Cr(III), from the kaolinite, under optimal conditions. The removal of hexavalent chromium was also enhanced compared to water by a factor of 2 using a solution of rhamnolipids. Results from the sequential extraction procedure showed that rhamnolipids remove Cr(III) mainly from the carbonate and oxide/hydroxide portions of the kaolinite. The rhamnolipids had also the capability of reducing close to 100% of the extracted Cr(VI) to Cr(III) over a period of 24 days. This study indicated that rhamnolipids could be beneficial for the removal or long-term conversion of chromium Cr(VI) to Cr(III) (Hafez et al., 2007).

Modified Activated Carbon for the Removal of Copper, Zinc, Chromium and Cyanide from Wastewater: Modified activated carbon is carbonaceous adsorbents which have tetrabutyl ammonium iodide (TBAI) and sodium diethyl dithiocarbamate (SDDC) immobilised at their surface. Monser and Adhoum (2002) investigated the adsorption of toxic ions, copper, zinc, chromium and cyanide on these adsorbents that have undergone surface modification with tetrabutyl ammonium (TBA) and SDDC in wastewater applications. The modification technique enhance the removal capacity of carbon and therefore decreases cost-effective removal of Cu(II), Zn(II), Cr(VI) and CN– from electroplating unit wastewater. Two separate fixed bed modified activated carbon columns were used; TBA-carbon column for cyanide removal and SDDC-carbon column for multi-species metal ions (Cu, Zn, Cr) removal. Wastewater from electroplating unit containing 37 mg/ l Cu, 27 mg/ l Zn, 9.5 mg/ l Cr and 40 mg/ l CN– was treated through the modified columns. A total CN– removal was achieved when using the TBA-carbon column with a removal capacity of 29.2 mg/g carbon. The TBA-carbon adsorbent was found to have an effective removal capacity of approximately five times that of plain carbon. Using SDDC-carbon column, Cu, Zn and Cr metal ions were eliminated with a removal capacity of 38, 9.9 and 6.84 mg/g, respectively. The SDDC-carbon column has an effective removal capacity for Cu (four times), Zn (four times) and Cr (two times) greater than plain carbon (Monser and Adhoum, 2002).

Removal of Chromium (VI) from Wastewater by Combined Electrocoagulation–Electroflotation without a Filter: A combined electrocoagulation and electroflotation process was designed by Gao et al. (2005) to reduce Cr6+ to Cr^{3+} first and then to remove the total Cr from wastewater to a value below 0.5 mg/l. Acidic condition was employed in the reduction of Cr^{6+} and neutral conditions were found to be beneficial for the coagulation of the precipitates of $Cr(OH)_3$ and $Fe(OH)_3$. The formation of $Fe(OH)_3$ was ensured by sparging compressed air in the coagulation unit through a draft tube. The air not only oxidizes Fe^{2+} produced electrically, but also helps to mix the water for a better coagulation of the particles. The two-stage electroflotation arrangement can separate the solids from the wastewater to a value of less than 3 mg/L with total Cr less than 0.5 mg/L. The residence time required is about 1.2 h. The optimal conditions for the treatment are: charge loading of about 2.5 Faradays/m^3 water, pH value in the coagulation unit is 5–8. The power consumption is less than 1 kwh/m^3 water at the conductivity of 1.5 mS/cm (milli simens per cemetimeter). When aluminum ions are either added or produced in situ in the coagulation unit, the treated wastewater can be discharged without any filtration. (Gao et al., 2005).

Trivalent Chromium Removal from Wastewater Using Low Cost Activated Carbon Derived from Agricultural Waste Material and Activated Carbon Fabric Cloth: A low cost activated carbon (ATFAC) was prepared by Mohan et al. (2006) from coconut shell fibers (an agricultural waste), characterized and utilized for Cr(III) removal from water/wastewater. A commercially available activated carbon fabric cloth (ACF) was also studied for comparative evaluation. All the equilibrium and kinetic studies were conducted at different temperatures, particle size, pH, and adsorbent doses in batch mode. The Langmuir and Freundlich isotherm models were applied. The Langmuir model best fit the equilibrium isotherm data. The maximum adsorption capacities of ATFAC and ACF at 25 °C are 12.2 and 39.56 mg/g, respectively. Cr(III) adsorption increased with an increase in temperature (10 °C: ATFAC 10.97 mg/g, ACF 36.05 mg/g; 40 °C: ATFAC 16.10 mg/g, ACF 40.29 mg/g). The kinetic studies were conducted to delineate the effect of temperature, initial adsorbate concentration, particle size of the adsorbent, and solid to liquid ratio. The adsorption of Cr(III) follows the pseudo-second-order rate kinetics. From kinetic studies various rate and thermodynamic parameters such as effective diffusion coefficient, activation energy and entropy of activation were evaluated (Mohan et al., 2006).

Removal of Lead and Chromium from Wastewater Using Bagasse Fly Ash - A Sugar Industry Waste: An inexpensive and effective adsorbent was developed by Gupta and Ali (2004) from bagasse fly ash, obtained from a sugar industry, for the dynamic uptake of lead and chromium. Lead and chromium are sorbed by the developed adsorbent up to 96–98%. The removal of these two metal ions up to 95–96% was achieved by column experiments at a flow rate of 0.5 ml/ min. The adsorption was found to be exothermic in nature. The adsorbent was successfully tried for the removal of lead and chromium from wastewater in the laboratory scale. The developed system for the removal of two ions was found to be useful, economic, rapid, and reproducible (Gupta and Ali, (2004).

4. Conclusion

Presence of heavy metals in the environment is of great concern as these affect human health negatively. Wastewater contains many harmful heavy metals, which can be bio-accumulated and enter into the food chain. This paper presents a review on the removal of heavy metals from wastewater by adsorption and precipitation methods. It has been found that these methods are quite effective in removing harmful heavy metals from wastewater. These methods generally use natural low cost materials like activated carbon, sawdust chitin and azadirachta indica (neem). These materials can be used effectively in developing countries like Ethiopia as they are inexpensive. Further research is recommended to enhance the knowledge of heavy metal treatment by cheaper materials and means to achieve a sustainable environment.

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