CHAPTER 1

Introduction
INTRODUCTION

Water is an important and essential component of living being, which is increasingly polluted from day to day. Water pollution requires ongoing evaluation and revision of water resource policy at all levels (international down to individual aquifers and wells). It was observed that the use of deleterious quality of water caused for various diseases or even deaths throughout the globe (Daniel, 2006). In addition to the acute problems of water pollution in developing countries or even industrialized countries continue to struggle with the strategies to adopt in the remediation policies for decontamination of polluted water bodies.

Water is typically referred to as polluted when it is impaired by anthropogenic contaminants and either does not support a human use, such as drinking water, and/or undergoes a marked shift in its ability to support its constituent biotic communities. Natural phenomena such as volcanoes, algae blooms, storms, and earthquakes also cause major changes in water quality and the ecological status of aquatic environment. The reclaimed water often contained with the contaminants of emerging concerns (CECs) that includes pharmaceuticals, household chemicals, personal care products, disinfectants, insecticides, heavy metal toxic ions etc., which poses a serious concern to maintain the water quality standards (Laws et al., 2011; Ternes et al., 1998; Kolpin et al., 2004; Wells et al., 2009).

Many chemicals undergo reactive decay or chemical change especially over long periods of time in groundwater reservoirs. A noteworthy class of such chemicals is the chlorinated hydrocarbons such as trichloroethylene (used in electronic industries for metal degreasing) and tetrachloroethylene used in the dry cleaning industry (note latest advances in liquid carbon dioxide in dry cleaning that avoids use of chemicals). Both of these chemicals
which are known to be potential carcinogens, undergo only partial decomposition, leading to new hazardous chemicals (including dichloroethylene and vinyl chloride).

Groundwater pollution is much more difficult to abate than surface water pollution since groundwater moves greater distances through unseen aquifers. Micro or meso-porous aquifers such as clays partially purify the water from bacteria by simple filtration (adsorption and absorption), dilution, and, in some cases, chemical reactions and biological activity: however, in some cases, the pollutants merely transform to soil contaminants. Groundwater that moves through cracks and caverns is not filtered and can be transported as easily as surface water. In fact, this can be aggravated by the human tendency to use natural sink holes as dumps in areas of Karst topography.

There is variety of secondary effects stemming not from the original pollutant, but a derivative condition. An example is silt-bearing surface runoff, which can inhibit the penetration of sunlight through the water column, hampering photosynthesis in aquatic plants.

The contamination of surface/ground waters by heavy metal toxic ions is a serious environmental and public concern because of the fact that these ions are virtually non-biodegradable and tend to accumulate within the bio-system, causing various biological disorders (Martin, 1985). Increasing use of toxic metals in various industrial process leads to the contamination of our aquatic environment. Besides the toxic and harmful effects to the aquatic life the extended perseverance of these pollutants in the biological systems and accumulating in the biosphere through the food chain results in the environmental and occupational hazards (Martins, 2004; Rout et al., 2009). Contamination of water bodies with heavy metals arises mainly from the aqueous waste streams of industries viz., metal plating, mining operations, tanneries, etc. Toxic metals such as mercury, cadmium, arsenic, copper
and many other species tend to accumulate with the sediments from which they may be released by various processes of remobilization which further can move up to the biologic chain, thereby reaching human beings where they produce chronic and acute ailments (Förstner et al., 1981). Leachates emanating from old mines often contain higher concentrations of dissolved metals like iron, manganese, aluminium, zinc, etc. and sulphate which could even contain high acidity (Bamsforth et al., 2006; Manzano et al., 1999; Younger, 2002). Heavy metals form compounds in the body that can be carcinogenic and mutagenic even at very low levels (Ruiz-Manriques et al., 1998). Inorganic micro-pollutants are of considerable concern since these are non-biodegradable, highly toxic and perhaps cause for carcinogenic effect (Cimino et al., 1990; Madoni et al., 1996). The increased level of industrialization/urbanization is known to be an additional source of contamination of fresh water. Although, several heavy metals are reported to be essential at trace level concentration however, an increased level of intake caused for adverse effects towards the living beings. Heavy metals such as cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), arsenic (As) etc. often present in industrial waste/effluent waters which is a potential hazard to the aquatic ecosystem and poses human health risk.

1.1. TOXICITY OF HEAVY METALS

1.1.1. Chromium

Chromium is usually found in industrial effluent. The most common sources of chromium includes with steelworks, chromium electroplating, leather tanning, chemical manufacturing and textile industries etc. (Sankararamakrishnan et al., 2006; Stasinakis et al., 2003; Raji and Anirudhan, 1998; Balasubramanian and Pugalenthi, 1999; Liang et al., 2003; Gopi Krishna et al., 2004; Adria-Cerezo et al., 2000; Deng and Bai, 2004). Chromium(VI) is
poisonous to most living organisms but has many applications including in wood preservation (Lakatos et al., 2002; Chwastowska et al., 2005; Sankararamakrishnan et al., 2006). Humans are exposed to excessive amount of Cr(VI) through food, drinking water, and inhaling air that may contain chromium particles. The average daily intake from air, water, and food is estimated to be 0.01 – 0.03 µg, 2.0 µg/L and 60.0 µg, respectively (Donais et al., 1999). Cr(VI) is known to be toxic to both plants and animals, as a strong oxidizing agent and potential carcinogen (Costa and Klein, 2006). Cr(VI) is considered by the IARC (International Agency for Research on Cancer) as a potential carcinogenic agent that modifies the DNA transcription process causing important chromosomal aberrations (IARC, 1982). The NIOSH (National Institute for Occupational Safety and Health) recommends that the levels of Cr(VI) in water should be reduced to 10^{-3} mg/m^3 (Muir, 1977). The discharge of Cr(VI) to surface water is regulated to below 0.05 mg/L by the US EPA (Baral, 2002). The inhalation of chromium compounds has been associated with the development of cancer in workers in the chromate industry. The relative risk for developing lung cancer was calculated to be as much as 30 times that of controls (Hayes, 1982; Leonard and Lauwerys, 1980; Langard, 1983). There is also evidence for an increased risk of developing nasal, pharyngeal and gastrointestinal carcinomas (Hamilton and Wetterhahn, 1988). Quantitative epidemiological data were obtained by Mancuso and Hueper, (1951), they observed an increase in deaths (18.2 %; P < 0.01) from respiratory cancer among chromate workers compared with 1.2 % deaths with controls. In a follow-up study, conducted when more than 50 % of the workers were died, the observed incidents for lung cancer deaths were increased to approximately 60% (Mancuso, 1975). The workers were exposed to total chromium of 1-8 mg/m^3/year. Mancuso (1975) observed a dose response for total chromium exposure and
attributed to the lung cancer deaths on exposure to insoluble Cr(III), soluble Cr(VI) and total chromium.

1.1.2. Arsenic

Arsenic is generally found as a contaminant in soil and water systems due to various anthropogenic sources, geologic variance, the arsenic mine drenching, the dissolution of ground rock along with the human activities such as mining, metallurgy, leather process, dyeing industry, use of pesticide and insecticide etc. (Chakravarty et al., 2002; Smedley et al., 2002; Bhumbla et al., 1994; Kim et al., 2002).

Arsenic occurrence in the environment, its toxicity, health hazards, and the techniques used for speciation analysis is well reviewed elsewhere (Penrose, 1974; Bodek et al., 1998; Jain and Ali, 2000; Matschullat, 2000; Bissen and Frimmel, 2003). Long-term drinking water exposure caused for skin, lung, bladder, and kidney cancers as well as pigmentation changes, skin thickening (hyperkeratosis) neurological disorders, muscular weakness, loss of appetite, nausea etc. (Jain and Ali, 2000; Kiping, 1997; WHO, 1981; Mandal and Suzuki, 2002). This differs from acute poisoning, which typically caused for vomiting, oesophageal and abdominal pain, and bloody “rice water” diarrhea (Jain and Ali, 2000; Kiping, 1997; WHO, 1981; Desesso et al., 1998; Duker et al., 2005; Ng et al., 2003). Arsenic in natural waters is a worldwide problem. Arsenic pollution reported in various countries including USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan and India (Burkel & Stoll, 1999; Cebrian et al., 1983; Dhar et al., 1997; Karim, 2000). The largest population at risk among the 21 countries with known groundwater arsenic contamination is in Bangladesh, followed by West Bengal in India (Das et al., 1995; Jain and Ali, 2000; Chatterjee et al., 1995)
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Arsenic is classified as a Group A carcinogen by the United States Environmental Protection Agency (USEPA). The toxic effects ranged from acute lethality to chronic effects, such as cancer and diseases of the vascular system (Borum et al., 1994; Saha et al., 1999). It was reported that serious health problems, such as cancers, skin alteration, etc., was linked to arsenic ingestion even at a low concentration (20–50 mg/l) (O’Connor, 2002). Extensive epidemiological studies showed that chronic ingestion of high levels of inorganic arsenic caused skin cancer (National Research Council, 1999). It was found that Arsenic exposure also caused cancers of the nasal cavity, trachea, bronchus, lung, liver, bladder, colon, kidney, prostate, brain, the lymphatic and hematopoietic tissues as well as the nervous system (Chen and Lin, 1994; Naqvi et al., 1994; Remembrance, 2003). Recent report by the United States National Academy of Science and United States National Research Council revealed that even at 3µg/L of arsenic, the risk of bladder and lung cancer was between four and seven deaths per 10,000 people. At 10 µg/L, the risk was increased to between 12 and 23 deaths per 10,000 people (NRC, 2001). In addition, arsenic can cause high blood pressure and diabetes. The US EPA announced its ruling in October 2001 to lower the maximum contaminant level (MCL) from 50 µg/L to 10 µg/L (An et al., 2005; EPA, 2000). China has adopted a new standard of arsenic in drinking water which was promulgated by National Standard Committee and Sanitation Ministry, lowered the arsenic level from 50 µg/L to 10 µg/L. The World Health Organization (WHO) also recommended lowering the As -drinking water standard to 10 µg/L (WHO, 2001). The improved drinking water standard posed new challenges to water treatment technique.

1.1.3. Cadmium

Cadmium (Cd) is a toxic element whose presence in the environment, mainly due to the industrial processes and phosphate fertilizers through which it is transferred to the food
Cadmium enters into surface water with the discharge of industrial effluents/wastes from metal plating, smelting, paint pigments, batteries, fertilizers, metallurgical alloying, mining, ceramics and other industrial operations (Davis et al., 2000; Iqbal and Edyvean, 2005) or by leaching of soil, to which sewage sludge is added. It is biologically very reactive and therefore gives rise to both acute and chronic poisoning. Nariagu (1983) emphasized the effects of cadmium on aquatic organisms. It became popularized in late 1940’s in Japanese villages causing a condition known as the “itai-itai” or ouch-ouch bone degenerative disease (Aoshima, 2003; Kasuya, 2000; Hutton, 1983). Cadmium toxicity was observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects (Hajialigol et al., 2006). It was reported that cadmium found to be carcinogenic and caused for lung fibrosis and dyspnea (Sud et al., 2008). Chronic exposure to elevated levels of cadmium caused for bone degeneration, liver damage etc. (Iqbal et al., 2007). Acute exposure to cadmium fumes may cause flu like symptoms including chills, fever, and muscle ache sometimes referred to as "the cadmium blues". More severe exposures can cause tracheal bronchitis, pneumonitis and pulmonary edema. Symptoms of inflammation may start hours after the exposure and include cough, dryness and irritation of the nose and throat, headache, dizziness, weakness, fever, chills, and chest pain. Cigarettes are also a source of cadmium exposure. Although there is generally less cadmium in tobacco than in food, but lungs absorb cadmium more efficiently than the stomach (Jarup, 1998). Workers exposed to cadmium-containing fumes were reported to develop acute respiratory distress syndromes (ARDS) (Barbee and Prince, 1999). Intake of cadmium-contaminated food caused acute gastro-intestinal effects, such as vomiting and diarrhoea (Nordberg, 2004). The IARC (International Agency for Research on Cancer) decided to classify cadmium as one of human carcinogen group I. Latest data
however, supported the assumption that only an uptake of cadmium via the respiratory system has carcinogenic potential (Jin et al., 2002).

1.1.4. Copper

The primary sources of copper includes with the effluents aroused from printed circuit boards, metal surface treatments and mining operations. Copper in small amount known to be an essential element of humans and living organism where it is an important catalyst for heme synthesis and iron absorption. However, higher concentrations of copper in the biological systems possessed with several toxic effects (Benaissa and Elouchdi, 2007). Copper can cause severe mucosal irritation and corrosion, widespread capillary damage central nervous system irritation, stomach and intestinal distress, liver and kidney damage, and anemia (Gardea-Torresdey et al., 1996; Ajmal et al., 1998). The human body has a natural mechanism for maintaining the proper level of copper. However, children fewer than one year old do not show such mechanism therefore is more vulnerable to the toxic effects of copper. People with Wilson’s disease also showed a problem with maintaining the proper balance and taking care to limit the exposure of copper. Concentration of copper in drinking water with level of 5 to 8 mg/L make the water undrinkable (HDR Engineering Inc, 2001). Maximum Contaminated Level (MCL) for copper is 1.3 mg Cu/L based on taste and to a lesser extent on limited toxicity data (Donald et al., 1999).

1.1.5. Lead

Lead is one of potential toxic heavy metals and once absorbed into the body showed several biological disorder (Friberg et al., 1979). Lead contamination of the environment is primarily due to anthropogenic activities making it the most ubiquitous toxic metal in the environment (Environmental health criteria 165 1995, Amdur et al., 1991). Research on lead (Pb) becomes an important topic of research for environmental and medical scientists for the
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reasons: (1) It has no known biological use and (2) It is toxic to most living beings. Lead readily bio accumulates in the human-rich surface layer of the soils due to its complexation with organic matter. It is the least mobile heavy metal in soils under reducing or non-acidic conditions. Furthermore, it is one of the most common trace metal contaminants in urban soils due to atmospheric deposition from industries and automobile emission. The sources of lead in the environment is mainly because of waste streams of battery manufacturing, acid metal plating and finishing, ammunition, tetraethyl lead manufacturing, ceramic and glass industries printing, painting, dyeing, and other industries (An et al., 2001; Li et al., 2002). Lead has been well recognized for its negative effect on the environment where it accumulates readily in living systems. Lead is non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain and can be readily absorbed into the human body (Wong et al., 2003). The presence of lead in drinking water even at low concentration level may cause diseases such as anemia, encephalopathy, hepatitis and nephritic syndrome (Lo et al., 1999). Severe exposure to lead was associated with sterility, abortion, stillbirths and neo-natal deaths (Goel et al., 2005). When Lead is ingested, there is rapid uptake into red blood cells forming PbB, then into soft tissues (kidney, bone marrow, liver and brain) and followed by a slow redistribution to mineralizing tissues (bones and teeth) (Nriagu, 1988; Environmental health criteria 165, 1995; Lum Max et al., 1994). Current Environmental Protection Agency (EPA) guidelines indicated that the maximum limit of lead in drinking water is 0.05 mg/L, but a level of 0.02 mg/L is proposed which is under review (Groffman et al., 1992). According to the Indian Standard Institution, the tolerance limit for discharge of lead into drinking water is 0.05 mg/L and in land surface water is 0.1 mg/L (I.S.I., 1982).
1.2. REMOVAL TECHNIQUES OF HEAVY METALS

The removal of heavy metal toxic ions from wastewaters has received an increased attention in recent decade for global awareness of the underlying detriment of heavy metals in the environment. The tighter national and international regulations on water pollution and the discharge of heavy metals make it necessary to develop efficient and cost effective technologies for their effective and efficient removal. Various treatment technologies were developed for the removal of heavy metals from water. The commonly used technologies for removing metallic impurities from effluents include chemical precipitation, lime coagulation, ion exchange (Gode et al., 2005; Chakravarti et al., 1995; Qdais et al., 2004), electro dialysis, reverse osmosis membrane filtration (Low et al., 1999; Lacour et al., 2001; Juang et al., 2000), electro winning (Gode et al., 2006), solvent extraction, adsorption (Gode et al., 2006; Leinonen et al., 2000; Yu et al., 2003), complexation/sequestration, electro-chemical operation and biological treatment etc. (Kiffis, 1987; Namasivayam, 1995). Chemical precipitation was traditionally employed to remove heavy metal toxic ions from aqueous solutions. However, metal removal via coagulation/flocculation is, in many cases, insufficient to meet strict regulatory requirements (Lee and Davis, 2001). Iron oxide-coated sand was used to remove the toxic metal ions (Thirunavukkarasu et al., 2003). The applications of traditional treatment techniques thus need enormous cost and continuous input of chemicals, which become impracticable and unconventional and also caused for further environmental damage (Tiwari et al., 2007b).

Among several methods available, ion exchange is an attractive process as its application is relatively simple and safe. Ion exchange is the exchange of ions between a liquid phase and a porous solid phase, which may be synthetic or natural (Wartelle and Marshall, 2006; Korngold et al., 2003). Ion-exchangers play a prominent role for the removal
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/speciation of several cationic/anionic species in waste waters and if the adsorbent is chosen so carefully and the solution chemistry adjusted accordingly, it can provide an effective waste treatment even at wide range of solution pH (Benjamin and Leckie, 1982; Davis and Leckie, 1978; Elliot and Huang, 1980; Mishra et al., 2004). The low-cost exchangers like zeolite etc. is used, the method is reported to be cost – effective (Inglezakis et al., 2004; Inglezakis et al., 2005; Yebra-Biurrun et al., 1995; Dabrowski et al., 2004). Synthetic ion exchangers are often used in elimination of heavy metal pollutants (Patterson et al., 1975; Schwuger and Smolka, 1976; Schore, 1972; Higgins, 1973). During treatment, ion exchange involves the reversible exchange of ions between a solution and a solid phase that are in direct contact (Dean, 1985).

The biosorption process which is an innovative technology using living or dead biomasses to remove toxic heavy metals from aqueous solutions offers potential advantages such as low operating cost, minimization of chemical or biological sludge, relatively high efficiency of heavy metal removal from diluted solutions, regeneration of biosorbents, possibility of metal recovery and environment friendly (Ahluwalia and Goyal, 2007).

Several natural and synthetic hydrous solids have been investigated as adsorbents of heavy metals. Among these, metal oxides (Benjamin and Leckie, 1981; Elliott and Huang, 1984; Davis and Bhatnagar, 1995) and activated carbon (Tan and Teo, 1987; Corapcioglu and Huang, 1987; Seco et al., 1997) are the most extensively employed. However, the high cost of these materials limit their large-scale use for the removal of metals. Hence, the interest lies for more effective, economic and eco-friendly techniques to be developed for the fine-tuning of effluent/waste water treatment (Chiron et al., 2003; Kadirvelu and Namasivayam, 2003). Therefore, numerous approaches are intended for the development of cheap metal trapping materials, such as fly ash (Sen and De, 1987), peat (Gosset et al., 1986), activated sludge
(Fristoe and Nelson, 1983; Tien and Huang, 1987), waste slurry (Srivastava et al., 1989) and biosorbents (Huang et al., 1990 &1991).

It is reported that the adsorption phenomena can remove metals over a wide pH range and lower concentrations than precipitation (Lo et al., 1997). Green-Pedersen and Pind (2000) reported that a ferrihydrite-coated montmorillonite surface possessed large specific surface area and an increased sorption capacity for Ni(II) compared to the bare surface of montmorillonite. Meng and Letterman (1996) discussed the adsorption properties of oxide mixtures and correlated the metal uptake by relative amount of metal oxide components. Meng and Letterman (1993) also reported adsorption of heavy metal ions onto the aluminum oxide-coated silica and the adsorption was modeled with uniform coverage of the oxide rather than using two distinct surfaces. Lo and Chen (1997a) determined the effect of Al oxide mineralogy, amount of oxide coating, and acid- and alkali-resistance on the removal of selenium from water. Brandao and Galembecket (1990) reported that the impregnation of cellulose acetates with manganese dioxide resulted in high removal efficiency of Cu(II), Pb(II), and Zn(II) from aqueous solutions. Al-Degs and Khraisheh (2000) had reported that diatomite and manganese oxide modified diatomite were effective adsorbents for removing Pb$^{2+}$, Cu$^{2+}$, and Cd$^{2+}$ ions. The sorption capacity of Mn-diatomite was considerably increased compared to the original material in removing the studied metals. Filtration quality of diatomite was significantly increased after modification with Mn-oxides.

Numerous researchers investigated the use of activated carbon to remove heavy metals from aqueous solutions (Alfarra et al., 2004; Kononova et al., 2005; Park and Kim, 2005; Puziy et al., 2004; Sekar et al., 2004). Granular activated carbon (GAC) used in a column process could eliminate separation problems and minimize sludge production. Activated carbon, however, showed relatively lesser adsorption capacity and affinity for
metals (Fan and Anderson, 2005). Huang et al., (1975 &1977, 1978) found that the removal of Cr(III) and Cr(VI) from aqueous solutions by different heat-treated charcoal and activated carbons depends largely on the solution pH and chromium concentrations. Oxides were widely used for the removal of heavy metal toxic ions from aqueous solutions. Relative to GAC, oxides have higher metal exchange capacities. Furthermore, oxides have the ability to remove metals even up to trace levels and the adsorbed metals can be recovered and solids can be reused. However, solid separation and sludge management after the adsorption process is seemingly difficult, because the oxides are usually in colloidal forms. One possible solution to this problem is to prepare a granular adsorbent that can be used in column process. Composite adsorbents of this type include Fe$^{2+}$ treated activated carbon (Huang and Van, 1989), Fe-coated sand (Edwards and Benjamin, 1989; Lai et al., 1994; Lo et al., 1997; Satpathy and Chaudhuri, 1995; Stahl and James, 1991a), granular iron oxides (Theis et al., 1992), Fe-coated GAC (Wang, 1995) and Mn oxide coated sand etc. (Stahl and James, 1991b).

Sand is one of the natural filter media and widely used in the waste water treatment plant for pre-filtration and it was reported that during the treatment, manganese or iron, which is present in the wastewater, is deposited on the surface of sand in the form of oxides. Recently, several researchers have developed techniques for coating metal oxides onto the surface of sand to overcome the problem of using metal oxides powders in water treatment. Many reports have shown the importance of these surface coatings in controlling metal distribution in soils and sediments (Zacharra et al., 1995; Fuller et al., 1996; Edwards and Benjamin, 1989). In recent years, coated minerals are widely studied because of their potential application as effective sorbents (Zacharra et al., 1995; Lo et al., 1997; Kuan et al., 1998).
Merkle et al., (1996 & 1997) reported that manganese dioxide coated sand was effective for removal of arsenic from ground water in column experiments. Merkle et al., (1996) developed a manganese oxide coating method on anthracite to improve the removal of Mn\(^{2+}\) from drinking water and hazardous waste effluent. They generated a filter media with an increased surface area after coating with manganese oxide and found manganese oxide coated media have the ability to adsorb and co-precipitate a variety of inorganic species. Stahl and James (1991b) found that manganese oxide coated sands generated a larger surface area and increased adsorption capability with increasing pH as compared to uncoated silica sand. The removal of As(III) and lead(II) from aqueous solutions was studied using manganese coated sand and the equilibrium study and competitive adsorption was further carried out (Han et al., 2006). The removal of copper using manganese coated sand in a liquid fluidized-bed reactor was carried out by Lee et al., (2004). Similarly, manganese coated sand was studied by Guha et al., (2001).

Iron oxide coated materials for heavy metal removal was employed successfully for the enhancement of removal capacity and efficiency comparing to uncoated filter media, such as silica sand (Sansalone et al., 1995; Sansalone et al., 1999; Khaodhia et al., 2000; Joshi et al., 1996; Benjamin et al., 1996), granular activated carbon (Reed et al., 1996) and polymeric media (Liu et al., 2001a; Edwards and Benjamin, 1989) etc. It was observed that coated media possessed with significant higher removal capacity for several heavy metals toxic ions over a wide pH range. Bailey et al., (1992) used iron oxide coated sand to remove hexavalent chromium from a synthetic waste stream. The influent contained with 20 mg/L of Cr(VI) and more than 99% of Cr(VI) was removed. It was found that iron(III) coated sand can be used for the removal of both cationic and anionic heavy metals, such as Cu(II), Pb(II),
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As(III), As(V), Sr(II) and Se(IV) (Huang and Liu, 1997; Lo and Chen, 1997a; Yang et al., 2005).

The oxidation and adsorption of Co(III)-EDTA complex subsurface materials using iron oxide coated and manganese oxide coated grains was performed by Zachara et al. (1995). Mn(II) was removed from aqueous solutions using manganese coated sand and the removal efficiency was greatly enhanced in presence of sodium hypo-chlorite (Tiwari et al., 2007b).

Iron oxides, hydroxides and oxide hydroxides consist of arrays of Fe ions and O²⁻ or OH⁻ ions. In comparison with minerals existing in soil, iron oxides have relatively high surface area and surface charge, and they often regulate free metal concentration in soil through adsorption reactions (Sewertmann and Taylor, 1989). It was affirmed that, in recent years, many researchers have applied the iron oxide to the treatment of heavy metals from metal-bearing tap or wastewater (Benjamin and Leckie, 1981b). Most of iron oxides are available only as fine powders or are being generated in aqueous suspension as hydroxide floc or gel. In such forms, they retain their desirable adsorptive properties for the trace metals but are limited to reactor configurations incorporating large sedimentation basins or a filtration unit. Under such conditions, the solid/liquid separation is fairly difficult. Besides, the iron oxide alone is not suitable as a filter medium because of its low hydraulic conductivity (Theis et al., 1992). Many researchers have studied the adsorption characteristics of anions, cations, and organics onto the iron oxide surface in recent decades. Adsorption is capable of removing metals over a wider pH range and to much lower concentrations than precipitation (Benjamin and Leckie, 1981b; Schultz et al., 1987). It was reported that iron oxide could be regenerated and reused at least 50 times without a noticeable loss in treatment efficiency (Edwards and Benjamin, 1989). Iron – coated sand was tested for removal of
cationic as well as anionic metals from synthetic and real waste waters (Theis et al., 1992; Edwards and Benjamin, 1989; Stahl and James, 1991; Bailey et al., 1992; Lai et al., 1994). The results from these studies confirm the utilization of iron-coated sand for trace removal of metal ions from water is worth to be developed for future wastewater treatment strategy. The applications of iron-coated sand are influenced by the coating techniques. Iron oxide formed from Fe(NO₃)₃ is composed of mainly amorphous iron oxides and a small amount of crystalline iron oxides (Lo et al., 1994a; Lo et al., 1994b). But the type of iron oxide coating produced depends on the physical and chemical environments at which iron oxide was prepared and coated.

1.3. ADSORPTION

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface (Glossary, 2009). This process differs from absorption, in which a fluid (the adsorbate) permeates or is dissolved by a liquid or solid i.e., the absorbent (Absorption Chemistry, 2010). The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physi-sorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction (Ferrari et al., 2010). A liquid or a solid substance which is present in the bulk of the substance is being attracted uniformly from all sides by the neighbouring molecules and hence there is no net force acting on the molecule hence there is no unbalanced force around molecule. On the other hand, if a molecule is present near the surface, such a molecule is not bonded to other molecules from all sides but has some unutilized valencies because there are no neighbouring molecules above the surface to which it can be bonded. As a result of these unbalanced forces the
molecules present at the solid or liquid surfaces tends to satisfy their residual forces by attracting and retaining on their surface, the molecules of other species when brought in contact with them. These results in increase in concentration of the substance near the surface compared with the bulk phases. A substance which has different concentration at the surface than in the bulk phases is said to adsorb and the existence of a substance at a surface in a different concentration than in the adjoining bulk phases is adsorption.

The material upon whose surface the adsorption takes place is called an adsorbent while the molecular species that get adsorbed are called adsorbate. Adsorption is not necessarily a physical phenomenon always. It maybe said a chemical process involving a chemical interaction between the adsorbent and adsorbate. When the molecules of the adsorbate are held to the surface of the adsorbent by chemical forces, the adsorption is called chemisorption.

Adsorption is different from absorption. In absorption, the molecules of a substance are uniformly distributed in the bulk of the other, whereas in adsorption molecules of one substance are present in higher concentration at the surface of the other substance. But in some cases adsorption and absorption occur together. In such cases, the substances gets uniformly distributed into the bulk of the solid but at the same time, its concentration is higher at the surface than in the bulk, such phenomenon is called “sorption”. Instead of using an adsorption, the term sorption and bio-sorption is used since the adsorption phenomenon is not clear. Bio-sorption can be defined as a non-directed physio-chemical interaction that may occur between metal species and the biological materials.
1.4. CLASSIFICATION OF ADSORPTION

Adsorption has been classified mainly on the basis of the nature of interactions between the atoms, molecules or ions of the adsorbates and the adsorbents.

1.4.1. Physisorption

Physisorption, also called physical adsorption, is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption (Oura et al., 2003; Desjonqueres et al., 1993; Hans Luth, 1993). This type of adsorption depends on the result of dispersion or Van der Waal forces of attraction between the adsorbent and the adsorbate. It is generally resulting with the binding of the adsorbate particles ion several consecutive layers which is usually favours the lowering of temperature. Physisorption is a spontaneous, rapid and reversible process, which requires small activation energy and the corresponding enthalpy change ranges up to 20 kJ/mol (Bond, 1984; Yoyutsky, 1978).

1.4.2. Chemisorption

Chemisorption is a sub-class of adsorption, driven by a chemical reaction occurring at the exposed surface. A new chemical species is generated at the adsorbent surface (e.g. corrosion, metallic oxidation). The strong interaction between the adsorbate and the substratesurface creates new types of electronic bonds - ionic or covalent, depending on the reactive chemical species involved (Oura et al., 2003). Chemisorption is based on the chemical forces which arise due to transfer or sharing of electrons between the adsorbate and the adsorbent. The energy of attachment is much greater as compared to the physisorption and may be comparable to the energies of the chemical bond formations. Chemisorption behaves to be irreversible, slow and temperature dependent which indicates the presence of
an activation energy. The enthalpy of chemisorption is usually in the range of 40 – 800 kJ/mol (Volkenshtein et al., 1949; Robers, 1935).

1.4.3. Electrostatic Adsorption

This type of adsorption is mainly due to the attractive coulombic forces between electrically charged adsorbent surface and the oppositely charged adsorbate species which is mostly observed in adsorption from aqueous solutions. It is usually the ionic exchange type; however, ion exchange need not be necessarily an electrostatic process. The ion exchange adsorption is specific, not always reversible and occurs slowly and the heat of adsorption is usually smaller than that of chemisorption (Helfferich, 1962).

In many systems, the mechanism of adsorption cannot be definitely specified and several mechanisms may be involved simultaneously (Ottewill and Shaw, 1968; Mishra et al., 1991).

The adsorption of trace elements is difficult to interpret as some of the physical methods used to distinguish among the adsorption mechanisms viz., calorimetry, infrared spectroscopy etc. fail entirely to detect micro and sub micro concentrations of the adsorbate species. However, it is well established that the mechanism of adsorption for trace elements depends upon their state in solutions. Simple ions are adsorbed by ion exchange mechanism whereby ions of the similar charge form part of the surface crystal layer of the adsorbent or the outer part of the electrical double layer which exists on the surface of most of the adsorbents (counter ions). The former mechanism is basically primary adsorption on crystalline precipitates (Wahl et al., 1951) and is mostly due to isomorphous ion replacement. The latter (secondary adsorption) can occur with the major site of the adsorbents (Grebenshesikova et al., 1972).
1.5. FACTORS INFLUENCING ADSORPTION PROCESS

Adsorption at solid – solution interface is influenced by several parameters viz., nature of adsorbent, nature of adsorbate, temperature, pH and concentration of the adsorbate and the presence of foreign species.

1.5.1. Nature of Adsorbent

The efficiency of an adsorbent depends on two factors. One is the specific surface area of the adsorbent and the other is the adsorption affinity of 1 cm$^2$ of the adsorbent. Generally, an increase in specific surface area of adsorbent enhances the adsorption due to increase in the number of sites available for adsorption (Kurbatov, 1948; Petrov, 1958). Adsorbents with higher surface charge will have a greater tendency to adsorb oppositely charged trace elements (King et al., 1974; Skulskii et al., 1971) while similar charged trace elements (adsorbate) results in lesser uptake by the adsorbent (Benes et al., 1972). The adsorption of hydrolysed or slightly dissociated species normally increases with the increase in hydrophobic character of the adsorbent (Rydberg et al., 1952).

1.5.2 Nature of Adsorbate

The adsorption process also depends on the size, shape and chemical nature of the adsorbate. The uptake of the adsorbate depends upon the polarity and the presence of active sites on the adsorbent. The presence of hydroxyl groups in a molecule is reported to enhance its adsorb ability (Stryker et al., 1968).

1.5.3. Influence of Temperature

Temperature influences the kinetics and the final values of adsorption (Benes et al., 1980). The uptake of the adsorbate normally increases with the increase in temperature which
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could be used in evaluating the activation energies (Gutsanu et al., 1990; Kikuchi et al., 1979; Kato et al., 1981; Pakholkov et al., 1983). On the other hand, the effect of temperature on trace adsorption was found to be small and is nearly constant over a wide range of temperature (Dyck, 1968; Mishra et al., 1986). It was observed that the physisorption decreased with the increase in temperature (Mishra et al., 1987a; Taylor et al., 1932). The increase in adsorption with the rise in temperature was attributed to the acceleration of some steps which are originally slow or even due to the change in the adsorption mechanism towards the chemisorption (Taylor, 1932; Mishra et al., 1992).

1.5.4. Influence of pH on Sorptive Solutions

The pH is an important parameter for adsorption of trace elements as their state in solutions is strongly depends on the pH of the solution. The pH can extensively affect the surface charge of the adsorbent which in turn direct the electrostatic adsorption of ions and colloids. Organic polymers are negatively charged in the pH range of 2–3 due to the dissociation of their surface active groups or due to adsorption of \( \text{OH}^- \) ions (Benes et al., 1971). The acidity and basicity of solution can influence the composition and properties of adsorbent surface and this in turn put forth some effect on adsorption (Rozovskaya, 1960; Suhybani, 1989; Kenta et al., 1984). The anions or cations of hydroxides used for adjustment of pH compete with trace ions in ion exchange process which is particularly observed in the adsorption of monovalent or bivalent ions (Benes and Kucerra, 1972).

Generally, the adsorption of cations takes place at higher pH values whereas the anions are adsorbed at lower pH values. Therefore, adsorption of most trace cations is observed in negligible quantity at lower pH i.e., strongly acidic solutions (Ahmad, 1969). Under certain conditions the increase in pH may even increase the uptake of anions (Burclova et al., 1973).
1.5.5. Influence of Sorptive Concentration

The adsorption at solid–solution interface obviously depends on the bulk sorptive concentrations. The concentration of trace quantity adsorption often conform either Langmuir or Freundlich adsorption isotherms. The later has been successfully utilized by several researchers for the adsorption study of cations and anions on solid surfaces (Upien, 1986; Aksoyoglu, 1989; Clark, 1970; Mishra and Tiwary, 1991). However, Freundlich isotherm fails in some cases wherein Sips formulation is obtained for a better fit to such cases (Sips, 1948).

1.6. THEORIES OF ADSORPTION

Various theories have been put forward from time to time to explain the process of adsorption which is discussed briefly below:

1.6.1. Chemical Theory

The chemisorption may involve sharing or transfer of electrons between the adsorbate and the adsorbent resulting in the formation of a chemical bond. Considering a covalent bonding model, Pauling derived an empirical formula for bonds between single atoms and extended to adsorption bonds in the case of covalent bonding (Pauling, 1939).

1.6.2. Capillary Condensation Theory

The condensation of the adsorptive species on to the pores of the adsorbent to form a thin layer of the molecules is the basis of this theory. The concept of this theory is comparable to the idea proposed by Zsingmondy (1911) and Foster (1932). The theory was extended further by Patric and Long (1925) to explain the physical adsorption. However, the elementary theory of capillary condensation does not take into account the specific action of
surfaces and it also differs from poly-molecular physical adsorption by the fact that the latter may occur on plane surface while capillary condensation cannot.

1.6.3. Residual Valence Theory

Haber (1914) proposed this theory assuming that the upper surfaces of adsorbents generally possess residual valencies, as a result of which adsorptive species are attracted towards the surface of adsorbents. This theory was further elaborated by Langmuir (Langmuir, 1918) assuming that the adsorption forces are homogeneously distributed all over the surface forming a monolayer coverage. However, the bonds are weaker than the true chemical bonds.

1.6.4. Polarization Theory

The polarization theory is based on the notations of de Boer and Zwikker (1929) and Bradly (1936) where the surface of a polar adsorbent polarizes the molecules of a non-polar adsorbate which are adsorbed in the first adsorption layer. The induced dipoles further induce secondary dipoles in the second layer and the process extends to several layers. Modern spectroscopic data point to the substantial polarization of the adsorbed molecules and atoms. This theory is successfully utilized in explaining the adsorption of organic molecules and noble gases on metals, graphite and alumina (Fridrikhsberg, 1986) which has been supported by the works of Cassel (1931) and Imre (1934).

1.6.5. Potential Theory

This theory was proposed by Polanyi (1914) and extended by several workers (Berenyi, 1920; Williams, 1918). It is based on the assumption that there is a potential field at the surface of adsorbents responsible for mono- and multi-layer adsorption. The potential
energy of interacted gas molecule with the particles of the lattice is the sum of all the individual interactions:

\[ U = \sum U(\mathbf{r}_i) \]  

Where \( U(\mathbf{r}_i) \) is the potential energy of interaction of the gas molecules with the \( i^{th} \) particle of the lattice at a distance \( \mathbf{r}_i \). \( U \) is a function of \( X, Y \) and \( Z \) coordinates of adsorbed molecule. If \( X \) and \( Y \) coordinates of the adsorbed molecule are kept constant, while \( Z \) varies, \( U(z) \) will have shape of the potential energy curve with minimum such as that given by Lennard-Jones intermolecular pair i.e.

\[ U(r) = \frac{A}{r^{12}} - \frac{C}{r^6} \]  

where \( A \) and \( C \) are the constants and \( r \) is the distance perpendicular to the surface. The value of \( U(z) \) above a particle of the solid will be different from \( U(z) \) between two particles. Specifically, \( U_m \), the potential minimum of \( U(z) \) will vary periodically in both \( X \) and \( Y \) directions. Thus, a plot of \( U_m \) against \( X \) and \( Y \) will give a curve with maxima and minima. The energy difference between the energy of minima and that of molecules in the gas phase is the energy of adsorption (\( U_0 \)) and the difference between energy of minima and maxima is the energy required for surface diffusion (\( V_0 \)). In the simple case of localized adsorption and adsorbed molecule is considered to be held at the bottom of a potential well whose depth is much greater than \( kT \). All the potential wells at the surface are assumed to be equal in depth and regularly spaced. Molecules in such positions have practically no chance of lateral movement across the surface. However, localized adsorption may be mobile or immobile depending on the nature of the surface. When the adsorptive species are free to migrate along
the surface, the adsorption is generally classified as mobile or non-localized. This theory was further modified for the adsorption from solutions of sparingly soluble solute (Polanyi, 1920).

1.6.6. BET Theory

Brunauer, Emmett and Teller (Brunauer et al., 1938) extended the Langmuir concept to the multilayer adsorptions and derived an equation which is known as BET equation. It represents the first effective attempt to explain physical adsorption from monolayer regions through the multilayer regions. The equation is:

\[
\frac{C}{(C-xC)Qc} = \frac{1}{BQ^0} + \frac{B-1}{BQ^0} \cdot \frac{C}{Qc} \tag{3}
\]

where Cs is the saturation concentration of the solute on adsorbent, C is the measured concentration in solution at equilibrium, Qc is the number of moles of solute adsorbed per unit weight of adsorbent inferring a complete monolayer on the surface, Qc is the number of moles of solute adsorbed per unit weight of adsorbent at concentration C, and B is a constant, expressive of the energy of interaction with the surface. This equation is helpful in determining the nature of adsorption isotherm, heat of adsorption and the amount of adsorbate required to form a complete monolayer. This theory has been extensively used for the determination of the surface area of solid materials.

1.6.7. Boundary – Layer Theory

This theory was reported by Aigrain and Dugas (1952) and Hauffe and Engell (1952) and Weisz (1953). The electron transfer between the adsorbing gas and adsorbent (semiconductor) is the basis of boundary layer theory of adsorption (Mott and Gurney, 1950; Garner et al., 1952) when a neutral atom ‘c’ is brought to the surface of solid (n-type semiconductor), electron near the surface is transferred from conduction band to the electron accepting level of ‘c’ giving, a negative ion ‘c’. As the process of adsorption continues, a
positive space charge is developed in the semiconductor underneath the surface and the surface accumulates the negatively charged adsorbate molecules. After the setting up of negative field, the surface layer of semiconductor starts repelling the electrons and prevents an accumulation process. In view of the fact that the electrons available from the upper conduction band or impurity levels are depleted and then adsorption remains confined to a monolayer, this type of adsorption is known as ‘depletive chemisorption’. The process of adsorption is followed by a decrease in conductivity of adsorbent. An example of such behaviour is the adsorption of oxygen on zinc oxide (Mott and Gurney, 1950). This theory predicts the direction of change of conductivity accompanying adsorption. It also explains the adsorption due to the presence of impurities in the adsorbent. The major disadvantage of this theory is that it considers only those types of adsorption processes which result from the transfer of charge.

1.6.8. Electron Theory

This theory was developed by Wolkenstein to explain chemisorptions and catalysis on semiconductors (Wolkentein and Peshev, 1965). He considered a process in which transfer of charge occurs with resulting change in conduction and also adsorption in which no transfer of charge occurs. Electron theory indicated that two or more types of adsorption may occur simultaneously. The adsorption of CO on Cu₂O and ZnO/Cr₂O₃ were explained with this theory (Green et al., 1957). Wolkenstein and Peshev, (1965) has further defined ‘weak’ and ‘strong’ chemisorption.

i) In weak chemisorption, no change occurs in the number of electrons in the conduction band or positive holes in the valence band of the material. The chemisorbed particle with its adsorption center remains electrically neutral.
ii) In strong chemisorption either donation or capture of an electron by the chemisorbed particle will occur. Thus, the number of electrons in the conduction band or positive holes in the valence band of the crystal will change. There are two types of ‘strong’ chemisorption bonds’ donor bonds when the chemisorbed particles donate electrons (capture positive holes) to the crystal and acceptor bonds, when the particles capture free electrons from the crystal. Each of these bonds may be purely ionic, purely covalent or intermediate.

1.7. ADSORPTION ISOTHERM

The adsorption of compound onto adsorbent can be described mathematically by an adsorption isotherm; adsorption isotherm simply defined as the quantity of adsorption that can be bound up on a particular of adsorbent is a function of the concentration of an adsorbate and the temperature.

Although several isotherms have been developed for use in modeling the adsorption isotherms, only two isotherms are considered the most common equation used to describe the equilibrium between an adsorbent (surface) and an adsorbate (chemical in solution). These isotherms are the Freundlich and Langmuir adsorption equations.

1.7.1. Freundlich isotherm equation

In 1906, Freundlich presented the earliest known adsorption isotherm equation. Freundlich is an empirically derived logarithmic model that attempts to factor in the effects of various adsorption energy levels. The model assumes that the number of sites associated with a particular free energy of adsorption decreases approximately as the free energy level increases, this empirical model can be applied to non–ideal sorption on heterogeneous
surfaces as well as multilayer adsorption. The model can be described by the following equation (4) (Alley, 2002; Ho et al., 2002):

\[ q_e = K_f C_e^{1/n} \] .... (4)

where:

\( q_e \) = Equilibrium loading on the adsorbent (mg/g)

\( K_f \) = Adsorption capacity at unit concentration (mg/g)

\( C_e \) = Equilibrium concentration of adsorbate (mg/L)

\( 1/n \) = Adsorption intensity

The equation fit to straight line when plotted on Log– Log basis, the above equation can be written in following form as equation (5):

\[ \log q_e = \log K_f + \left[ \frac{1}{n} \right] \log C_e \] .... (5)

1.7.2. Langmuir Isotherm Equations

In 1915 Langmuir developed equation to describe the interaction between the adsorbent and adsorbate as a linear, reversible and mono layer chemical reaction, this equation is relatively a straight forward model that assume that the adsorbent surface is completely homogeneous, that each adsorbent site can bind a maximum of one adsorbate molecule, and that their no lateral interaction take place between molecules of the adsorbate (Alley, 2000).

This model can describe theoretically by following equation (6) (Ho et al., 2005):

\[ q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \] ------ (6)

where:

\( q_e \) = Equilibrium loading on the adsorbent (mg/g)
\[ C_e = \text{Equilibrium concentration of adsorbate (mg/L)} \]

\[ q_m \text{ and } K_a = \text{characteristics Langmuir constants} \]

Constant \( q_e \) and \( K_a \) can be determined from linearized form of equation (7), represented as:

\[
\frac{C_e}{q_e} = \frac{1}{q_m + K_a} + \frac{C_e}{q_m} \quad --- \text{(7)}
\]

A plot of \( C_e/q_e \) vs \( C_e \) could indicate a straight line of slope \( 1/q_m \) and an intercept of \( 1/(K_a q_m) \). Advantage of the Langmuir equation includes simplicity and the applicability to a wide range of data. Limitations to the model include the monolayer assumption the reversibility of bonding and the constant uptake rate.

1.8. SCOPE OF THE PRESENT INVESTIGATION

Sand itself is widely used as a filter media for the treatment of wastewaters and it was found that during the treatment, manganese and iron, if present in wastewater, is to be deposited on the surface of sand in the form of their oxides. Hence, the application of iron coated sand or manganese coated sand may provide more viable, eco-friendly and cost effective treatment technology. The present research work is an alternative treatment technology for the removal of heavy metal toxic ions from the aqueous solutions by employing the artificially obtained manganese coated sand (MCS) or iron coated sand (ICS). Further, the manganese or iron coated sand is a type of silica medium coated with manganese or iron oxides, formed from the sorption of manganese or iron oxides during long-term filtration via the process of rapid sand filtration, followed by aeration on a water treatment plant. This study was conducted to build the basic data for coating hydrated manganese or
iron oxide on the sand surface to utilize the adsorbent properties of the coating and the filtration properties of the sand in the low level removal of various heavy metal ions.

The wide range of waste water treatment strategies to be adopted for the effective/efficient low level removal of several heavy metal toxic ions is a current area of research. The cost effective and more environment friendly processes are inevitable for the treatment methods. Hence keeping in view the proposed study is an attempt to exploit fully the natural sand materials in order to obtain the manganese or iron coated sand which further be used for the low level removal of several heavy metal toxic ions viz., Cr(VI), As(III), As(V), Cd(II), Cu(II) and Pb(II). The materials employed were likely to be cost effective and perhaps environmentally benign. Further, the studies were extended to understand the mechanism involved at solid/solution interface carrying the various parametric studies viz., effect of sorptive pH, concentration and ionic strength, etc.

The practical applicability of these methods could better be demonstrated under the dynamic experimentation i.e., column studies. Hence, the column experimentation were included in the present investigation. The basic data to be obtained by the column experiments could be used finally to develop the Pilot Plant or the Large Scale Treatment Plant for the treatment of waste/effluent waters contaminated of these polluting ions.