Chapter 2

LITERATURE REVIEW

2. LITERATURE REVIEW

Precipitation (Esalah *et al.* 2000;Mirbagheri and Hosseini 2005), reverse osmosis (Al-Rashdi *et al.* 2011;Hintermeyer *et al.* 2008), coagulation-flocculation (Fu and Wang 2011;Truitt and Weber 1979), ion exchange (Gode and Pehlivan 2003;Wong *et al.* 2014), nanofiltration (Ballet *et al.* 2004;Muthukrishnan and Guha 2008), adsorption (Gupta *et al.* 2012;Gupta and Nayak 2012), electrocoagulation (Bazrafshan *et al.* 2008;Vasudevan *et al.* 2011a) and electrodialysis (Lambert *et al.* 2006;Marder *et al.* 2003;Rodrigues *et al.* 2001) is in use for abatement of chromium and cadmium. Each technology has its own merit and demerit.

2.1. Precipitation

Precipitation is effective tool to remove chromium from aqueous solutions (Fu and Wang 2011). Chemicals used in precipitation react with heavy metal ions to form insoluble precipitate. Hydroxide precipitation or sulphide precipitation is commonly in use (Fu and Wang 2011). It is popular due to ease of operation and low cost. The solubility of most species gets reduced and forming precipitate in the pH range of 8 to 11 (Fu and Wang 2011). Chromium is precipitated with the help of lime by Mirbagheri and Hosseini (2005). Chromium precipitation by lime was preceded with its reduction to chromium (III) state with ferrous sulphate. The reduction was most successful in the pH range of 2 to 2.3. Afterwards, it gets precipitated with lime and caustic soda. Precipitation was faster for chromium with lime than soda process (Mirbagheri and Hosseini 2005).The optimum pH for chromium removal was found to be 8.7. Cadmium was removed with sodium di-(n-octyl) phosphinate as precipitating agent (Esalah *et al.* 2000). The removal of cadmium increased with rise of amount of precipitating agent up to the molar ratio of 2. The highest removal (%) with sodium di-(n-octyl) phosphinate is achieved at molar ratio of 2. The concentration of cadmium decreased from 660 mg L^{-1} to 0.24 mg L^{-1}. Sodium di-(n-octyl) phosphinate increased the pH of the solution. This is due to the dissociation of hydroxo-complexes produced in the precipitation. The removal of cadmium decreased with decrease in pH of the solution. This happened due to precipitation of ligand at lower pH (Esalah *et al.* 2000).

2.2. Ion exchange

Ion exchange involves the use of resin having capability to exchange with metallic ions in the contaminated water. The advantage of ion exchange resin is that it has high removal efficiency with fast kinetics. Resins with sulphonic acid groups and carboxylic acid groups were used as cation exchangers (Fu and Wang 2011). The hydrogen ions of carboxylic or sulphonic groups act as the exchangeable ions with metal cation. Factors like pH, initial concentration, contact time and temperature serve as the variables affecting the removal of metals from contaminated water. Gode and pehlivan (2003) reported 85 to 90% removal of chromium from aqueous solution in pH range of 3-6. The removal of chromium was completed in 80-120 minutes. The chelating ion exchangers form heterocyclic chelates with chromium. The removal of chromium decreases at high pH values. At low pH, hydrogen ions effectively compete with chromium for binding sites, resulting in low removal. So, chromium shows maximum affinity in narrow pH range and a maximum removal at pH 4.5. The effect of temperature on removal of chromium is quite small as compared to other factors (Gode and Pehlivan 2003). Equilibrium for cadmium removal by iminodiacetate resin was achieved in 24 h (Wong *et al.* 2014). A maximum adsorption capacity was achieved at pH 5. Maximum adsorption capacity of 2.18 mmol/g was achieved at this pH and it declines on either side of pH 5 (Wong *et al.* 2014). Dowex 50W synthetic resin (Gode and Pehlivan 2003) displayed equilibrium time of 60 min. The removal of cadmium was achieved at pH 8-9 and reaction is favoured at higher temperatures.

2.3. Reverse osmosis

Reverse osmosis process uses a semi permeable membrane. The contaminant is allowed to pass through the membrane. The contaminant is not able to pass through the membrane, but the water is able to pass through. The limitation of reverse osmosis lies in the fact that it requires high power for pumping pressures and restoration of membranes (Fu and Wang 2011). Chromium removal by reverse osmosis was achieved with the help of polyacrylamide membrane. The efficiency of removal was high ca. 100% (Hintermeyer *et al.* 2008). The time required to reach the steady state declines with increase of cross flow velocity and pressure applied in the system (Das *et al.* 2006).Promoters decline the flux density and time required to reach the steady state (Das *et al.* 2006). The permeate flux increases about 64% on increasing cross flow velocity from 7 to 9 L/min. The permeate quality improved marginally with cross flow velocity and pressure. A 94 % to 100% removal of cadmium was achieved with the help of reverse osmosis (Al-Rashdi *et al.* 2011). Cadmium concentration was reduced from 165 to 0.003 mg L^{-1} (Slater *et al.* 1987). Rejection rate in case of cadmium slightly increased on raising pH from 2.5 to 7.2 using FILMTEC FT-30 membrane. Increase of operating pressure from 200 to 900 psi and feed concentration of 163 mg L^{-1} reduced the permeate cadmium concentration from 0.164 mg L^{-1} to 0.003 mg L^{-1}. The system is also utilized at pilot scale. At 600 psi and pH of 3 and feed concentration of 900 mg L^{-1}, the permeate concentration was 0.153 mg L^{-1}. It shows usability of membrane at wide range of concentration (Slater *et al.* 1987).

2.4. Nanofiltration

Nanofiltration uses steric and electric effect to remove the pollutants from water (Kurniawan *et al.* 2006). A Donnan potential is generated between the charged anions in the nano filtration membrane and the co-ions in the contaminated water. The small pore and surface charge on the membrane reject the charged solutes which are smaller than the membrane pores. Along with the bigger neutral solute, salts are also rejected (Kurniawan *et al.* 2006). Nanofiltration requires lower pressure than reverse osmosis making it more preferable due to lower cost. Nanofiltration can treat up to a metal concentration of 2000 mg L^{-1}. Nanofiltration also works at wider range of pH. Cadmium is removed at acidic pH (Ballet *et al.* 2004), whereas, chromium is removed at basic pH more efficiently (Muthukrishnan and Guha 2008). However, chromium and cadmium in aforementioned studies are also satisfactorily removed at both acidic and basic pH Ballet *et al.* (2004) and Muthukrishnan and Guha (2008). The rejection rate depends on the species of contaminants to be removed. The rejection rate for cadmium is as follows $CdSO_4$ > $CdCl_2$ > $Cd(NO_3)_2$. Sulphate anion is excluded more than the monovalent anion due to bivalent charge on sulphate anion. The nitrate ion is less hydrated than chloride which led to less rejection of cadmium ion associated with nitrate. The ionic strength also affects the rejection of contaminant. The charge on the surface of membrane hindered the electrostatic effects of the membrane. Increased sodium ion concentration neutralized the negative charge on membrane and reduced the rejection of cadmium associated with different anions (Ballet *et al.* 2004).

2.5. Coagulation - Flocculation

Coagulation-Flocculation is a two step process. In first step i.e. coagulation the charge on particles is neutralized. After neutralization of charge, particle are able to stick together (Wang *et al.* 2007). A rapid mixing is followed to disperse the coagulant and promotes particle collisions. This is followed by flocculation; where a gentle mixing is done. It leads to the formation of flocs and afterwards, the flocs get settle down. A removal of 91 % of chromium was achieved with the help of ferric chloride as coagulant (Amuda *et al.* 2006). Removal was mostly achieved in the pH range of 10-11. The dose of coagulant affects the removal process; coagulant of 500 mg L^{-1} concentration is required to remove 91% chromium (initial concentration 0.66 mg L^{-1}) as compared to ca. 30 % removal at 100 mg L^{-1} coagulant dose. Addition of polymer with coagulant increased the removal efficiency. On addition of polymer (ferric chloride dose as coagulant 200 mg L^{-1}, polymer dose 5 mg L^{-1}) the removal was increased from ca. 50 to 84%. On further increasing polymer dose to 10 mg L^{-1}, removal further increased to 93%. Sludge generation decreased with addition of polymer with coagulant (Amuda *et al.* 2006). A high removal of 90- 95% for chromium was achieved at pH 10 (Fu and Wang 2011). Fulvic acid was found to help in the removal of cadmium by coagulation process (Truitt and Weber 1979).

2.6. Electrocoagulation

Coagulants are generated in situ in electrocoagulation. The generation is done electrically from aluminium or iron electrodes (Bazrafshan *et al.* 2008;Fu and Wang 2011). The accumulation of metal takes place at anode. Chromium is removed by electrocoagulation with the help of iron and aluminium as sacrificial electrodes. Apart from pure metals, alloys are also used as anode. Alloy of Al-Zn-In is also used as anode material (Vasudevan *et al.* 2011b).The pH influences the electrocoagulation process. At an initial pH < 7, generation of hydrogen increased at cathode. However, in alkaline media i.e. pH >8 the final pH did not vary much and influenced the electrocoagulation process (Bazrafshan *et al.* 2008). The rise in concentration increased the removal time or electrical potential applied (Bazrafshan *et al.* 2008).Current density or electrical potential applied increases the removal efficiency. At higher electrical potential, oxidation of metal at anode increases, which results in greater amount of precipitate. Hence, the removal (%) is raised. The material used for electrocoagulation as anode affects the removal process significantly. The removal of chromium with iron as anode was better than aluminium (Bazrafshan *et al.* 2008). Cadmium removal by electrocoagulation is also achieved with alternating current. The direct current is also used, besides the alternating current for electrocoagulation. The direct current reduces the efficiency of removal process of cadmium removal. Bicarbonate, phosphate and arsenate reduce the efficiency of removal in electrocoagulation process (Vasudevan *et al.* 2011a).

2.7. Electrodialysis

Electrodialysis is another membrane technology. The process uses charged membranes and separation of ions occurs with electricity as the driving force from one solution to another (Fu and Wang 2011).This process used both anion and cation exchange membranes. Chromium and cadmium were removed successfully with nafion exchange membrane (Lambert *et al.* 2006;Marder *et al.* 2003;Rodrigues *et al.* 2001). The removal (%) increased with higher current densities applied in electrocoagulation process, even when current efficiency is lower (Marder *et al.* 2003). The larger ion is difficult to move through the membrane (Marder *et al.* 2003).

2.8. Limitations of removal technologies of chromium and cadmium

The aforementioned technologies for removal of chromium and cadmium from aqueous effluents are blemished with limitations. In precipitation technology there is generation of low density sludge, which can lead to disposal problems. Presence of complexing agents in water inhibits metal hydroxide precipitation (Fu and Wang 2011). Ion exchange method cannot handle concentrated metal solutions and is non selective with high sensitivity to pH (Barakat 2011). Regeneration of ion exchange leads to release of harmful chemicals into environment. Reverse osmosis is expensive due to high energy requirement (Li *et al.* 2014). The process requires regular maintenance and expensive membranes. Reverse osmosis and nanofiltration are also marred with membrane fouling (Greenlee *et al.* 2009;Kurniawan *et al.* 2006). Coagulation is less preferred due to generation of sludge (Verma *et al.* 2012). Electrochemical method like electrodialysis and electrocoagulation incur high initial capital cost, high maintenance and operation costs (Fu and Wang 2011). Precipitate formation in ion exchange membrane in electrodialysis reduce the membrane area for effective removal (Marder *et al.* 2003) and also leads to reducing its life cycle and increase of operational costs.

2.9. Adsorption

Adsorption refers to the pile up of substance on to liquid solid interface or gas solid interface. The material which gets piled up at the interface is known as adsorbate and the surface on to which it's is piled up is called adsorbent (Yagub *et al.* 2014). Adsorption is classified into chemical and physical adsorption. The physical adsorption involves physical forces between adsorbate and adsorbent i.e. weak van der Waals' force between adsorbate and adsorbent. Chemical adsorption involves formation of strong chemical bonds between adsorbate and adsorbent. Adsorption process is cost effective, least energy sensitive and removes even low concentration of contaminants. Low cost dolomite (Albadarin *et al.* 2012), modified corn stalk (Chen *et al.* 2012), activated carbon (Al-Othman *et al.* 2012), chitosan (Vieira *et al.* 2011), nano zerovalent iron (Boparai *et al.* 2011), nano alumina (Sharma *et al.* 2010) and nano hydroxyapatite (Asgari *et al.* 2012) , functional mesoporous silica, activated carbon (Machida *et al.* 2012), cerium oxide and titanium oxide (Contreras *et al.* 2012) have been used as adsorbents for removal of chromium and cadmium from aqueous solutions and water/wastewaters. In the current study nano crystalline zirconia and iron oxide/hydroxide are used for the removal of chromium and cadmium from aqueous solutions. Iron based materials are easy to recover after adsorption due to magnetic property. Zirconia is biocompatible, chemically inert and has high thermal stability (Aboushelib *et al.* 2008;Deshmane and Adewuyi 2012;Hisbergues *et al.* 2009).

2.10. Occurrence of iron and zirconia

India has 3400 thousand metric tons of zirconium reserves and annually produces 40 thousand metric tons (USGS 2016). The world reserves of zirconia account for 78,000 thousand metric tons. The annual production of zirconium is 1410 thousand metric tons.

India has 28.52 billion tonnes of iron resource and produced 150 million tonnes in 2013. The world annual production stands for 2950 million tonnes in 2013 (Rao and Sharma 2016). The world total resource of iron accounts for more than 230 billion tones (USGS 2016).

2.11. Adsorption experiments

Classically, experimentation is conducted to optimize the response by variation of one parameter at a time, while keeping all other parameters constant. Chromium and cadmium are removed by classical method using various adsorbents (Al-Saadi *et al.* 2013;Di Natale *et al.* 2015;Ihsanullah *et al.* 2015;Zhang *et al.* 2013). Classical method is time intensive study and does not present the proper depiction of quantitative interactions among various parameters (Garg *et al.* 2008). In addition to this, comparison of data is difficult, in addition there are concerns relating to sensitivity of particular variable, effect of process variable on quality characteristics of response (Nwabueze 2010). A large number of combinations of process variables are required to examine relationship between them (Nwabueze 2010). To overcome these drawbacks, experimental response is optimized by varying variables collectively. One of the statistical method of experimentation to optimize response by collective variation of input variables is response surface methodology (RSM) (Hameed *et al.* 2009). RSM is a compilation of statistical and mathematical tools employed to optimize the response administered by numerous independent variables. It has been helpful for modeling and analysis of problems in which a response of interest is controlled by several variables and its aim is to optimize the response (Montgomery 2012). The intention to use the RSM is to provide a suitable path with highest probability of attaining the yield. The system optimized by RSM is formulated as mathematical model (Nwabueze 2010). The easy availability of computers with required computing strength, large and complex system can be modelled and optimized (Nwabueze 2010).

RSM includes two designs: Box–Behnken design (BBD) and Central composite design (CCD) (Raja *et al.* 2011). In BBD, cubic points (+1 or -1) are used, whereas in CCD, axial points (α) are used in addition to cubic points. So, BBD has 3 degrees of freedom (-1, 0, +1) and CCD has five degrees of freedom (-α, -1, 0, +1, +α).

The value of α is calculated is as follows:

llows:

$$\alpha = (2)^{\text{number of variables}/4} \tag{2.1}$$

There are number of studies for adsorption of chromium via response surface methodology (Anupam *et al.* 2011). Response surface methodology is used for removal of chromium by various adsorbents like powdered activated carbon (Anupam *et al.* 2011), immobilized cyanobacterium (Kiran *et al.* 2007), chitosan (Aydın and Aksoy 2009) and maghemite nanoparticles (Ahmadi *et al.* 2014). Cadmium removal is also optimized with the help of response surface methodology. The adsorbents used for cadmium removal using response surface methodology are carbon aerogel (Goel *et al.* 2006) , straw carbon (Kannan *et al.* 2004), activated carbon (Alslaibi *et al.* 2014) and polymers (Alizadeh 2011). In the present study also, optimization for removal (%) with nano crystalline iron oxide/hydroxide and zirconia was done by response surface methodology.

2.12. Kinetics and isotherm of adsorption experiments

Mechanism of adsorption, surface property, capacity of adsorption and rate of adsorption is easily determined by isotherm and kinetic parameters (Gimbert *et al.* 2008). Isotherm and kinetic parameters for adsorption are frequently determined by linear fitting of the data (Dehghani *et al.* 2016;Khan *et al.* 2015). However, the linear regression is marred by change of error structure, violation of error variance (Foo and Hameed 2010) due to transformation of native equation into linear equation (Foo and Hameed 2010). This led to the utilization of non-linear models. Non- linear models had an advantage that error distribution does not change as in the linear model (Dubey *et al.* 2016). Nonlinear curve fitting for isotherm and kinetic modeling is used by different methods and software like error function using Solver add-in of Microsoft Excel and Curve fitting of Microcal origin software (Ho *et al.* 2002;Hossain *et al.* 2013;Shin *et al.* 2011).Recently rigorous error functions like sum of the square of the errors (ERRSQ), Marquardt's percent standard deviation (MPSD),average relative error(ARE), hybrid fractional error function(HYBRID), sum of the absolute errors (EABS) have greatly addressed the error biases by minimizing the error distribution between experimental and predicted isotherm data (Foo and Hameed 2010). These nonlinear analysis methods led to the different estimation of parameters. So, a comparative study is conducted via different methods to reach the optimum isotherm and kinetic parameter determination.

2.13. Thermodynamics

Thermodynamic parameters like change in free energy, enthalpy and entropy give essential requisite for the design and management of adsorption based treatment plants (Salvestrini *et al.* 2014). Several techniques were employed to estimate the thermodynamic parameters. Among them Langmuir constant method and partition methods were used apart from others (Salvestrini *et al.* 2014). Langmuir constant method involves the use of Langmuir constant b (L/mg) to calculate K_L (thermodynamic equilibrium constant), whereas, the partition method uses the ratio of adsorbed amount of adsorbate to non-adsorbed mass of adsorbate as K_L.

The Langmuir constant was suggested to be numerically equal to neutral and dilute solutions and for charged solutions there is inclusion of activity coefficient in calculation of change in free energy (Liu 2009).However, the partition method does not include any variation in dilute, neutral or charged species of adsorbate (Salvestrini *et al.* 2014).Here, the difference in thermodynamic parameters obtained by aforementioned methods were studied.

2.14. Summary

Precipitation, reverse osmosis, coagulation-flocculation, ion exchange, nanofiltration, adsorption, electro coagulation, electrodialysis and adsorption are common methodologies used for removal of chromium and cadmium from water wastewater. However, adsorption process is cost effective, least energy sensitive and removes even low concentration of contaminants. In the present study, nano crystalline zirconia and iron oxide/hydroxide are used as adsorbents for the removal of chromium and cadmium from aqueous solutions. Adsorption experiments were performed using response surface methodology (RSM). Mechanism of adsorption, surface property, capacity of adsorption and rate of adsorption is determined by isotherm and kinetic parameters. Isotherm and kinetic parameters for adsorption were determined by linear and non linear curve fitting of data. In addition to this comparison of linear and non linear curve fitting methods were studied. Thermodynamic parameters were determined by langmuir constant and partition methods. Here, the differences in thermodynamic parameters obtained by aforementioned methods were studied.