CHAPTER 2

2.1 Introduction

Extensive industrial applications of heavy metals and their indiscriminate indecent disposal into water followed by ensuing its accumulation into water resources leads to continuous deterioration of water quality as well as pose serious health hazards to humans and animals [Gómez et al. 2014]. These metallic species exert detrimental effects due to their persistent nature as well as their build-up in food chain [Maksin et al. 2012]. Exposure to such metals even at trace level is a risk for living beings.

2.2 Conventional adsorbents for removal of heavy metals from aqueous solutions

Therefore, numerous techniques have been used for efficient removal of heavy metals among which adsorption is considered to be the most effective technique which is non-destructive in nature, involves low initial cost, simplicity of design, ease of operation, large scale applicability, insensitivity to toxic substances, no harmful by products formation and almost complete removal of pollutants even at trace level from dilute solutions [Mahmoodi et al., 2010; Al-Othman et al., 2012; Albadarin et al., 2012; Li et al., 2013; Gupta et al., 2013; Gusain et al., 2014]. Significant work has been carried on the abatement of different contaminants from water by utilizing adsorption method. Initially, activated carbon [Aggarwal et al., 1997; Rao et al., 2006; Kadirvelu et al., 2001; Mohan et al., 2001], was utilized for the removal of contaminants from water, which has

been supplanted by some low cost adsorbing materials. A number of other adsorbents, e.g. fly ash [Rao et al., 2002; Diamantopoulos et al., 1993; Kapoor et al., 1996], chitosan [Covas et al., 1992; Rorrer et al., 1993], kaolinite [Yavuz et al., 2003], zeolite [Ayuso et al., 2003; Sheta et al., 2003], montmorillonite [Bhattacharya et al., 2007], sphagnum moss peat [Sharma et al., 1993] wollastonite [Sharma et al., 1990], bentonite [Viraraghvan et al., 1994], sawdust [Memon et al., 2007], sea weeds [Vijayaraghavan et al., 2005], soya cake [Daneshwar et al., 2002], red mud [Pradhan et al., 1999] and alumina [Sing et al., 2004; Sanchez et al., 2007; Wu et al., 2000] have been incorporated by various workers and reported for the removal of metallic pollutants from aqueous solutions and wastewaters.

2.3 Literature review: A brief overview of metal oxide nanoparticles utilized as adsorbents for removal of metallic species from aqueous solutions

For removal of heavy metals from aqueous solutions by adsorption, the most frequently used nano-adsorbents include iron oxides (FeO), silica (SiO_2), manganese oxides (MnO_2), aluminium oxides (Al_2O_3), and titanium oxides (TiO_2). Iron is known to be one of the most ubiquitous elements on the earth. The widespread availability of resources as well as ease in synthesis, render nano-sized ferric oxides (FeOs) to be one of the low-cost adsorbents for toxic metal abatement. Since elemental iron is eco-friendly, nano iron-oxides can be directly employed at contaminated sites with negligible risks of secondary contamination [Deliyanni et al., 2004]. The extensively studied nano iron-oxides for heavy metals removal from water/wastewater include goethite (α-FeOOH)

[Jiang et al., 2013], hematite (α-Fe_2O_3) [Chen et al., 2010], amorphous hydrous Fe oxides [Fan et al., 2005], maghemite(γ-Fe_2O_3) [Hu et al., 2005; Hu et al., 2006], magnetite(Fe_3O_4) [Mandavian et al., 2010; Wang et al., 2010; Badruddoza et al., 2011; Liu et al., 2008; Huang et al., 2009; Guan et al., 2007]. The removal of various metallic pollutants onto numerous nano-adsorbents through the process of adsorption has been tabulated in Table 2.1.

Arsenic (V) removal on 16 nano-particles of metal oxides was reported by Hristovski et al., (2007), out of which TiO_2, Fe_2O_3, ZrO_2, and NiO, were the most important one. All nano particles were found to be highly efficient with removal capacities of 98% except for ZrO_2. The adsorption data followed the Freundlich model for all the nano-particles.

Mostafa et al., (2010) described adsorption strategy of As (V) onto nano-sized iron oxide coated quartz (IOCQ) and reported 100% arsenic (1000 µg/L) removal within 5.0 min. The adsorption data followed Langmuir isotherm model and according to the authors, the reported method was quite suitable and the adsorbent is effective for the removal of arsenate from drinking water. Tu et al., (2013) described the adsorption of Arsenate on Fe_3O_4 nano-particles at 27°C and at pH 3.0, 7.0 and 11.0 with adsorption capacities of 14.35, 10.12 and 4.88 mg/g respectively.

Investigation on the abatement of Cd^{2+} ions from mixed maghemite-magnetite of average surface area 49.5 m^2/g and particle size of 20-80 nm as an adsorbent was carried out by Chowdhury et al., (2013). The results showed that 0.8 g/L of maghemite-magnetite particles removed up to 1.5 mg/L of Cd^{2+} ions from the aqueous solution. The

adsorption rate of Cd(II) ions was fast initially, and about 40% of total Cd(II) ions were removed within 5 min. Thereafter, the adsorption capacity increased slowly with contact time before reaching a plateau after 2 h, and then remained constant. Generally, the removal of Cd(II) ions by mixed maghemite-magnetite increased with an increase in the pH of the adsorbate solution and adsorbent dosage whereas decreased with an increase in initial concentration of Cd ions. Adsorption of Cd(II) ions by mixed maghemite-magnetite was found to follow the pseudo-second-order kinetics model with correlation coefficient value (R^2) being above 0.99. The adsorption equilibrium data were fitted well by Langmuir isotherm model with regression coefficient (R^2) value of 0.9931 indicating a monolayer adsorption on a uniform surface with a finite number of adsorption sites. Intra-particle diffusion studies suggested that adsorption of cadmium is partly diffusion controlled and partly due to an electrostatic effect along with specific adsorption involving the adsorption of Cd^{2+} and $CdOH^+$ on mixed maghemite- magnetite nanoparticles in the alkaline pH range. Nano zinc oxide (n-ZnO) particles via sol-gel method were synthesized by Srivastava et al., (2013) and investigated its applicability in cadmium removal from aqueous solutions. The prepared nanoparticles were of 17-50 nm in size. A high removal of Cd (II) ions i.e., 92% from its aqueous solutions with initial metal concentration of 200mg/L by n-ZnO particles was achieved within 1 hr of contact time that supported its requisition in treatment of effluents containing Cd (II) ions.

Fe$_3$O$_4$ and MnFe$_2$O$_4$ nano-particles were investigated for the removal of Cr (III) or Cr (VI) ions under light and dark conditions by Luther et al., (2013). These particles were synthesized via precipitation method and their corresponding size was found to be

22.4±0.9 nm (Fe_3O_4) and 15.5±0.5 nm ($MnFe_2O_4$). The pH of the solution played a significant role in the binding of chromium (III) and chromium (VI) ions where optimum binding of Cr (III) and Cr (VI) was observed at pH 6 and pH 3.0 respectively. Adsorption isotherm studies were performed under light and dark conditions at 23ºC in order to determine the removal capacity of the synthesized nano-particles and the results of the experiment had been tabulated in Table 1.7.

An insight into the binding capacity of these nano-particles showed that the binding of chromium (III) and chromium (VI) to the Fe_3O_4 and $MnFe_2O_4$ nano-materials have opposite behaviour with greater binding to Fe_3O_4 in comparison to $MnFe_2O_4$ nano-particles, under both the conditions. The reason behind this difference in the binding capacity under light and dark conditions may be explained by the surface chemistry and the interaction of light with the surface of the material and the chromium ions. The binding of metal ions to nano-materials is affected by the surface charge of the nano-material which could be affected by the presence or absence of light. The increase in capacity noticed under the dark reaction condition may be a synergistic effect of surface charges and the absence of light during the experimentation. The influence of pH on the binding capacity also showed the opposite behaviour as it was noticed that Cr (VI) displayed greater binding to both nano-materials at low pH and decreased to zero binding above pH 6.0, whereas, Cr(III) was bound to a very low extent at pH 2.0 and increased to a maximum around pH 6.0. The isotherm studies depicted that the binding of both these ions followed the Langmuir isotherm model. In order to understand the mechanism of binding, the data obtained through the thermodynamic studies has been taken into account

that suggested that probably, the reaction has two different mechanisms for the binding of chromium (VI), possibly through physical adsorption and through some type of exchange mechanism. However, chromium (III) binds to the nano-materials through an exchange mechanism as the entropy of reaction was found to increase under all reaction conditions.

A 100% removal of Cr (VI) ions from aqueous solution onto iron nano-particles of 15 nm prepared via a simple sol-gel method was reported by Sharma et al., (2009). Various experimental parameters such as initial metal ion concentration, contact time, adsorbent dosage, pH and temperature on the removal of chromium were evaluated and authors found that the removal of chromium increased from 88.5% to 99.05% when its initial concentration was decreased from 15 to 5mg L^{-1} at optimum conditions. The adsorption was found to be highly pH dependent and the maximum removal was obtained at pH 2.0. The removal process was found to the kinetics of both, pseudo-first-order and pseudo-second-order models with the values of R^2 being 0.997 and 1.0 respectively. Intra-particle diffusion studies reflected its influence on the removal process. The thermodynamic results obtained through experimentation supported the fact of increased adsorption on increasing temperature and revealed that removal process was feasible, spontaneous and endothermic in nature.

Sorption of Pb(II) ions on nano-sized ZnO nanoparticles prepared via gel combustion method has been explored by Venkatesham et al., (2013). The average particle size and BET specific surface area of the synthesized zinc oxide was estimated as 40 nm and 80.425 m^2 g^{-1} respectively. The influence of pH, metal ion concentration and adsorbent

dose on the adsorption process was examined and it was found that adsorption of Pb was maximum for the lower concentration of Pb solution, acidic solution (pH 4.0) and becomes constant in basic solution and also adsorption shows an increment with increase in the adsorbent dosage i.e maximum at 1.0 g. The correlation coefficient (R^2) values obtained from Langmuir and Freundlich adsorption isotherm viz., 0.9987 and 0.9999 respectively, were almost the same. Therefore, both the adsorption isotherms perfectly fitted to Pb (II) adsorption on nano-ZnO particles.

TiO$_2$ nano-crystals have been employed as an adsorbent by Ghasemi et al., (2012) for abatement of Hg (II) ions from aqueous solutions. The synthesis involves the hydrolysis of TiCl$_4$ at room temperature and results showed that the 13.2% of particles consisted of anatase and 86.8% rutile phase with average grain size of 8.8 nm and 10.2 nm respectively. These nano-crystals having specific surface area of $98.743 m^2/g$ showed more than 96% percentage removal of Hg (II) ions. The influence of various parameters viz., initial metal concentration, pH, temperature and contact time of adsorption process were investigated and results of experiment revealed that adsorption process attained equilibrium at 420 min with optimum adsorption at pH 8.0. It was explored by the authors that the solution pH strongly affected the removal process. Freundlich isotherm with correlation coefficient value being R^2 0.995, was found to be best fitted to the experimental data, which fits well to multilayer adsorptions on heterogeneous surfaces. The kinetics studies of adsorption showed the involvement of pseudo-second-order with value of k$_2$ 2.8126 $\times 10^{-3}$ g mg^{-1} min^{-1}, at 303 K.

Srivastava et al., (2011) synthesized nano-Alumina via sol-gel method and investigated its applicability in mitigation of Ni (II) ions from aqueous solutions. It was found through experimentation that sorption of Ni (II) ions is dependent upon initial Ni (II) solution and increased from (96.60 to 99.0) % by decrease in concentration from (75 to 25) mg^3 L $^{-1}$ at 25 °C at an equilibrium time of 120 min. The agitation speed was found to have sound effect on the removal of Ni (II) ions and optimum removal was achieved at 100 rpm. The kinetic data of the adsorption experiment well supported the pseudo-second order with high correlation coefficient value (R^2) of 0.999. In examining adsorption isotherm, various isotherm models viz., Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin were considered and interestingly it was found that the equilibrium data fitted well to all the isotherm models considered during experimentation with one particular model suitable at some temperature while other model at some other temperature. The activation energy of the sorption process was calculated and was found to be 8.96 kJ mol^{-1} indicating the physi-sorption nature of adsorption. The values of the coefficient of mass transfer for the systems were evaluated and found significant that indicates the feasibility of a sufficiently rapid transfer of adsorbate species from the bulk to the surface and/or solid/liquid interface. The authors claimed that the nano-alumina is quite efficient candidate for removal of Ni (II) ions from aqueous solution and it can be used for designing treatment plants for the removal of Ni(II) from water and wastewater.