2.1 LITERATURE REVIEW

In the past decades, emphasis is placed on these heavy metal ions as these are extremely toxic and present major problems when released into the environment. Heavy metals, which are toxic to environment and human health, are an important class of pollutants in water and wastewater systems. These are more than 20 heavy metals hazardous to human health are cadmium, copper, lead, chromium, mercury and nickel etc. The treatment technologies which are currently employed for the removal of these metals from aqueous solution are also critically discussed and the advantages and disadvantages of each method are highlighted. In developing countries, advanced technologies such as membrane separation, electrodialysis and filtration, etc., are normally used for the removal of heavy metal ions from industrial wastewater. However, these treatments cannot be applied on a large scale because of high technical levels and insufficient funds. Adsorption is one of the most effective and simplest approaches in removing toxic heavy metal ions from aqueous systems. Extensive research has been focused in introducing new adsorptive materials which improve these metals from wastewater effluents before their discharge into water bodies system. Since, polyaniline and its copolymer have effective binding nature by forming selective bond with certain types of metal cations. Polyaniline based on conducting polymeric adsorbents have been emerging as potential to
alternative to other adsorbents. Removal of metal ions by adsorption process using polyaniline and its copolymer has several advantages over the conventional adsorbents; the synthesis of conducting copolymers containing hetero atoms such as imine, amide, sulfur and oxygen groups in the polymer backbone has gained industrial importance. Adsorption using conducting copolymer and its composites is an economical method, since conducting copolymer has high adsorption capacity and to get easily re-generable. A detailed survey of literature involving important amine functionalized polymers and its copolymer composites and the metal ions separated are given below.

Farrell et al (2004) Polyaniline film was prepared and used as adsorbent for the removal of Cr(VI) from aqueous solution and they are suggested that the mechanism of adsorbent.

Pourshaban et al (2013) investigated the adsorption studies that have been carried out to determine the effect of contact time, adsorbent dose, and pH on the removal of Co(II) by using polypyrrole as an adsorbent.

Guo et al (2011) focused on synthesized bulk-quantity of one-dimensional polyaniline (1D PANI) nanowire/tubes with rough surface were prepared by a simple chemical oxidation method and Cr(VI) removal rapidly and effectively in one step from aqueous solution.

Bhaumik et al (2012) studied successful synthesis of the polypyrrole-polyaniline nanofibers for the first time by simultaneous in situ chemical polymerization technique and applied as a promising adsorbent for the removal of Cr(VI) from aqueous solution.
Manju et al (2002) investigated an adsorbent for heavy metals by introducing carboxylate functional group into polyacrylamide-grafted hydrous iron(III) oxide. The product exhibits a very high adsorption potential for Pb(II), Hg(II) and Cd(II).

Ansari (2006) Suaw dust/polyaniline adsorbent is simple to prepared and it can be used successfully for the removal of Cr(VI) ion from aqueous solutions. They suggested that the sorption capacity of polyaniline toward Cr(VI) is greatly affected by pH of treated solution.

Yang et al (2007) studied the modification of activated carbon by polyaniline for enhanced adsorption of As(V) and it has been an effective adsorbent for the removal of arsenate ions from aqueous solutions.

Han et al (2012) investigated the polyaniline (PANI) hollow nanospheres with controllable in continuous nano cavities ranging in size from 10 to 50 nm as a novel hollow nanostructure that have been successfully fabricated by chemical polymerization of aniline with chloroaurate acid as the oxidant and citric acid as the doping acid. From the results, they conclude the adsorbents have very good potential of higher levels of adsorption and desorption of Pb ions when modified materials are used as adsorbents.

Jiang et al (2012) examined the preparation of novel polyaniline/calcium alginate sorbent with milli/nano hierarchical structure, which realizes the homogeneous distribution of PANI nanofibers on a large scale, shows high Cu(II) and Pb(II) removal percentage in a relatively wide pH range (3-7).

Kolaei et al (2012) studied the polyaniline/polystyrene (PAn/PS) nanocomposite was prepared in aqueous solution by the polymerization of
styrene and aniline using potassium iodate and ammonium peroxydisulfate as oxidants in the presence of surfactive dopant sodium dodecylbenzenesulfonate and poly(vinylpyrrolidone) as surfactant. The capability of separating Cd(II) ions was studied and the results were compared with those obtained with other adsorbents.

Sufia Hena (2010) examined an adsorption capacity of Cr(VI) onto chitosan coated with poly 3-methyl thiophene synthesized chemically in a batch system by considering the effects of various parameters like contact time, initial concentration, pH and temperature.

Zhang et al (2007), Multi-amine functionalized mesoporous silicas have been prepared by a post-grafting process using silane coupling agents. This method has been attributed to highly order hexagonal pore structure, which has been retained after the grafting. From the conclusion point, multi-amine grafted composites show almost equal affinity to Hg(II), Pb(II), Zn(II), Cu(II) and Cd(II) in wastewater samples and can effectively remove them rather completely.

Zhang et al (2012) successfully prepared the Fe$_3$O$_4$–SiO$_2$-poly(1,2-diaminobenzene) sub-micron particles with a core–shell structure with high saturated magnetization and used for the removal of As(III), Cu(II) and Cr(III) ions from aqueous solutions.

Shin & Jang (2007) studied the fabrication of Fe$_3$O$_4$–PEDOT nanoparticles using an acid-mediated seeded polymerization. Fe$_3$O$_4$ nanoparticles encapsulated with PEDOT were used as an efficiently separable and reusable adsorbent of heavy metal ions under an external magnetic field and had high uptake capacities for different heavy metal ions (Ag(II), Pb(II) and Hg(II)).
Bhaumik et al (2011) synthesized and examined the PPy/Fe$_3$O$_4$ nanocomposite and used as an effective sorbent for the removal of Cr(VI) form aqueous solution.

Murugesan et al (2011) studied the removal of Pb(II), Cu(II) and Cd(II) ions onto polyazomethineamides (PAMA) has been investigated using batch adsorption techniques. The extent of adsorption was investigated as a function of pH, adsorbent dose, contact time and initial metal ion concentration.

Navarro et al (2001), Influence of anions on the equilibrium and kinetic uptake of heavy metals such as Cu(II) and Co(II) from an aqueous solution by a novel nitrogen-type chelating adsorbent was evaluated. Equilibrium experiments revealed that stoichiometric amounts of metals and anions are adsorbed by the resin.

Ansari et al (2008), Sorption or silver ion uptake by the adsorbents (Polypyrrole/Sawdust and Polyaniline/Sawdust) employed in this investigation seems to be occurred via complex chemical reactions such as reduction-oxidation, complex formation and chelating.

Omraei et al (2011) studied that the polypyrrole/sawdust showed considerable potential for the removal Zn(II) from aqueous solutions. Desorption of Zn(II) polypyrrole/sawdust has been studied using various solvents (alkaline, bases and water). Maximum desorption efficiency was 75% by using NaOH. Also polypyrrole/sawdust has been applied for the removal of Cr(VI), Zn(II), Ni(II) and Cd(II) from plating wastewater that its ability was considerable.
Chandra et al (2011) examined the pyrrole polymerized along graphene sheets shows an increased surface area and the composite shows highly selective adsorption capacity for Hg(II).

Rutkowsk et al (2008), Microparticles of poly(1,8-diaminonaphthalene) (PDAN) were prepared by chemically oxidative polymerization by (NH$_4$)$_2$S$_2$O$_8$. The effect of pH on the sorption of Cd(II), Cu(II), Ni(II), Mn(II), Zn(II) and Pb(II) on poly(1,8-diaminonaphthalene) was examined by the batch procedure.

Li et al (2004), Poly(1,8-diaminonaphthalene) fine particles have been synthesized successfully by a facile chemical oxidation polymerization of DAN with (NH$_4$)$_2$S$_2$O$_8$ or FeCl$_3$ as oxidant with a high yield and productivity. They evaluated that silver-ion adsorbability of the particles can be further maximized by carefully controlling the adsorption time, the dose, size of the particles, the temperature and pH of Ag(I) solution.

Li et al (2013) studied the composite of polyaniline and reduced graphene oxide (PANI/RGO) was prepared through polymerization of aniline in the presence of graphene oxide, and further reduction by hydrate hydrazine. It was utilized as the effective adsorbent towards the adsorption of Hg(II) in aqueous solutions.

Pourhashemi et al (2012), Preparation of polypyrrole/poly (vinyl alcohol) nanocomposite as adsorbents were discussed and the capability of separating nickel from aqueous solution was studied. Batch sorption studies have been carried out to determine the effect of agitation time, adsorbent dose and pH on the removal of nickel by polypyrrole.
Katal et al (2011) studied the polypyrrole from a molecular properties perspective and its effects on the removal efficiency also have to be considered for precise practical applications.

Shao et al (2012) studied the PANI/MWCNT magnetic composites were synthesized by using plasma induced polymerization technique. From the results of UV–vis spectra, XPS, TGA and FE-SEM characterizations they found that PANI has been modified onto MWCNTs. PANI/MWCNTs magnetic composites have very high adsorption capacities in the removal of Pb(II) ions from large volumes of aqueous solutions and PANI/MWCNTs magnetic composites can be separated and recovered from solution by simple magnetic separation.

Ghorbani et al (2011) prepared polyaniline (PANI) and its nanocomposite containing rice husk ash (RHA) and their capability for the removal of Hg(II) from aqueous solution was studied.

Li et al (2011) investigated the composite PANI/HA was prepared by adding humic acid (HA) into the chemical polymerization process of aniline monomers. Hg(II) ions and Cr(VI) anions were selected to evaluate the adsorption properties of PANI/HA and the adsorption data were analyzed.

Huang et al (2007) focused on nitric acid, hydrochloric acid and EDTA chosen as desorbent to systematically evaluate the adsorption/desorption performance of the Pb(II), adsorbing fine microparticles of poly(m-phenylenediamine).

He et al (2012) examined the hierarchical structural of polyaniline-lignine composite that has been successfully prepared using aqueous
ammonia solution as polymerization medium. From the conclusion the composite exhibited a strongly reactive sorption characteristic for silver ions.

Li et al (2005) studied the series of high-performance copolymer microparticles from SDP and DAN monomers. They have been synthesized successfully by a facile chemical oxidation precipitation polymerization with \((\text{NH}_4)_2\text{S}_2\text{O}_8\) as an oxidant. The Ag(I) reactive adsorbability of the microparticles was optimized by carefully regulating the SDP/DAN ratio, particle size and Ag(I) solution pH. This clearly shows, the introduction of SDP units into DAN polymer chains and the diminution of the particle size can effectively increase the capacity and rate of Ag(I) adsorption.

Ballav et al (2012) evaluated the glycine doped polypyrrole as a promising adsorbent for Cr(VI) removal and was synthesized by in situ polymerization. They provided the mechanism of Cr(VI) adsorption that was governed by ionic interaction as well as reduction of Cr(VI) to Cr(III).

Han et al (2011) examine two kinds of different-shaped poly(o-phenylenediamine) (PoPD) polymers: solid and hollow sub-microspheres with both size of about 700 nm synthesized by a solution route without any additional directing agents. There are employed as efficient adsorbents for removal of Pb(II) ions from water.

Zhang et al (2011) studied the method of pH manipulation which has been used to improve chemically oxidative polymerization of m-phenylenediamine (mPD) through concurrent addition of NaOH when adding oxidant \((\text{NH}_4)_2\text{S}_2\text{O}_8\). From the results synthesized PmPD possesses better Ag(I) adsorption performance when lowering its oxidation state and the adsorption process includes redox reaction, chelation and physical adsorption.
Li et al (2009), synthesized poly(o-phenylenediamine) microparticles through a chemically oxidative polymerization of poly(o-phenylenediamine) and the strong adsorbability of Ag(I) ions on to them was systematically examined. PoPD/Ag nanocomposites were facilely prepared through the reactive sorption method.

Li et al (2011) studied the preparation of poly(aniline-1, 8-diaminonaphthalene) and its application as adsorbent for selective removal of Cr(VI) ions. The adsorption behavior of Cr(VI) onto PAN/DAN was then examined using batch and fixed-bed column sorption techniques.

The fine PpPD and PmPD microparticles have been successfully synthesized by a facile oxidative precipitation polymerization procedure by Huang et al (2006). The adsorption of Pb(II) ions onto the microparticles has been optimized by regulating the pH and concentration of the Pb(II) solution, as well as the adsorption time and microparticle dosage.

Li et al (2010) evaluated the Poly[aniline(AN)-co-5-sulfo-2-anisidine(SA)] nano grains with rough and porous structure, demonstrating ultra-strong adsorption and highly efficient recovery of silver ions.

Vukovic et al (2010) studied the adsorption properties of raw-MWCNT were greatly improved by oxidation, as well as by amino-functionalization. It was found that the adsorption capacities change with increasing temperature, whereby the amino-functionalized MWCNT had the best adsorption capacity for Cd(II).

Gu et al (2013) examined the synergistic interactions between as-received multi-walled carbon nanotubes (MWNTs) and toxic hexavalent chromium (Cr(VI)) in solutions of different pH were investigated that aimed
to functionalize the nanotubes and remove the toxic Cr(VI) by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), Raman spectroscopy and transmission electron microscopy (TEM).

Lu et al (2007) evaluated the novel copolymer nanoparticles with intrinsically high stability and also good long-term stability/redispersibility in pure water or other media have been successfully synthesized by using chemical oxidative precipitation polymerization from aniline and sulfophenylene diamine monomers in aqueous HCl in the absence of any external emulsifier or stabilizer. The sorption mechanism of lead and mercury ions on the particles is proposed.

Huang et al (2012) proposed the novel copolymer microparticles having both strong adsorbability and rapid adsorption rate towards Pb(II), Hg(II) and also Cr(VI) have been productively synthesized by chemical oxidative polymerization of m-phenylenediamine (mPD) and p-sulfonic-m-phenylenediamine (SPD) in pure water.

Min et al (2011), novel method for the shape-controlled synthesis of poly(phenylenediamine) (PpPD) polymer microstructures using a UV lamp as the oxidation energy source and poly(N-vinylpyrrolidone) (PVP) as the surfactant. The as-obtained PpPD polymer microstructures show excellent adsorption ability in the removal of lead ions, which might be very useful in many practical applications, including water purification and waste treatment.

Yao et al (2011) studied the hierarchical porous polypyrrole (PPy) nanoclusters composed of small PPy nanospheres were successfully prepared in one-step by a reactive-template method without any surfactants. To test the feasibility of using the PPy nanoclusters in real applications, the capacity of
nanoclusters as a heavy metal ion remover was explored. The resulting PPy nanoclusters showed an excellent ability to remove Cr(VI) ions in aqueous solution.

Nabid et al (2011) evaluated that the sorbents made from modified multi-walled carbon nanotubes and conducting polymers (PANI and PEDOT) were used for solid-phase extraction. The Au(III) ions are adsorbed as a result of the interaction with the electron pairs of =N- and -S- groups.

Wu (2007) evaluates the Cu(II) adsorption efficiency of as-produced carbon nanotubes (CNTs) and those modified by HNO$_3$ and NaOCl. They are concluded that the adsorption capacity of Cu(II) ion as-produced and modified CNTs increased with the pH and temperature. However, the effects of the ionic strength on the adsorption of Cu(II) on as-produced and modified CNTs were negligible.

Velickovic et al (2012) expressed the iron(III) oxide coated e-MWCNTs show good adsorption affinity for arsenic(V) and lower affinity for As(III) in a wide range of initial pH values.

Rao et al (2007) studied the technical feasibility of various kinds of raw and surface oxidized carbon nanotubes (CNTs) for sorption of divalent metal ions (Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II)) from aqueous solution is reviewed.

Kosa et al (2012), Multi-walled carbon nanotubes (MWCNTs) were modified with 8-hydroxyquinoline and used for the removal of Cu(II), Pb(II), Cd(II) and Zn(II) from aqueous solutions.
Salam et al (2011) examined the nanocomposite made of multi-walled carbon nanotubes and chitosan (25:75 wt%) was prepared. The MWCNTs/chitosan nanocomposite was used for the removal of copper, zinc, cadmium and nickel ions from aqueous solution.

Kumar et al (2013) proposed on dodecyl benzene sulfonic acid (DBSA) doped polyaniline/multi-walled carbon nanotubes (DP/MWCNTs) nanocomposite was prepared by in-situ oxidative polymerization. DP/MWCNTs was found to be ideal adsorbent for the removal of Cr(VI) as compared to pristine and oxidized MWCNTs.

Li et al (2003) studied the individual and competitive adsorption capacities of Pb, Cu and Cd by nitric acid treated multi-walled carbon nanotubes (CNT).

Tofighy et al (2011) examined the removal of some divalent heavy metal ions (Cu(II), Zn(II), Pb(II), Cd(II) and Co(II)) from aqueous solutions using carbon nanotube (CNT) sheets. Preference of adsorption onto the oxidized CNT sheets can be ordered as Pb(II)>Cd(II)>Co(II)>Zn(II)>Cu(II) respectively.

Stafiej et al (2007) studied that, carbon nanotubes (CNTs) were employed as adsorbent to study the adsorption characteristics of some divalent metal ions (Cu, Co, Cd, Zn, Mn and Pb). The effect of solution conditions such as pH and metal ions concentration was investigated. At pH 9 the affinity order of the metal ions towards CNTs is Cu(II) > Pb(II) > Co(II) > Zn(II) > Mn(II).
2.2 SCOPE OF THE PRESENT STUDY

The main objective of the present work is to synthesize o-MWCNT doped copolymer nanocomposites containing hetero atoms that can act as ligands and to polymerize them using \textit{in-situ} chemical oxidative polymerization technique. These o-MWCNT functionalized copolymer nanocomposites are used for the removal of divalent metal ions from aqueous media. These co-polymeric nanocomposite adsorbents, possessing sulfur, oxygen and nitrogen functionalized chelating groups can act as metal-complexing ligands. Hence, this work is focused on the development of chelating polymeric nanocomposites with oxidized MWCNT which can be used as adsorbents for the effective removal of metal ions from aqueous media. The metal ions that have been chosen for the present investigation are Pb(II), Ni(II) and Cd(II).

The scope of the present investigation is as follows:

- To prepare oxidized multi-walled carbon nanotubes using strong oxidized agent H$_2$SO$_4$ and HNO$_3$ in the ratio of 3:1.
- To synthesize polyaniline/o-MWCNT and polypyrrole/o-MWCNT polymer nanocomposites using simple \textit{insitu} chemical oxidative polymerization techniques.
- To prepare oxidized MWCNT doped co-polymeric nanocomposites such as poly(aniline-co-diamino diphenyl sulfone)/o-MWCNT, poly(aniline-co-diamino diphenyl ether)/o-MWCNT, poly(pyrrole-co-diamino diphenyl sulfone)/o-MWCNT and poly(pyrrole-co-diamino diphenyl ether)/o-MWCNT using \textit{insitu} chemical oxidative polymerization techniques.
To elucidate the structure of the copolymers and its nanocomposites synthesized using infrared spectroscopy in Attenuated Total Reflectance mode (ATR), Diffuse Reflective Spectra of Ultra Violet-visible spectroscopy (DRS UV-vis) and Raman spectroscopy.

To confirm the structural modification of the copolymer nanocomposites such as polyaniline/o-MWCNT, polypyrrole/o-MWCNT, poly(aniline-co-diamino diphenyl sulfone)/o-MWCNT, poly(aniline-co-diamino diphenyl ether)/o-MWCNT, poly(pyrrole-co-diamino diphenyl sulfone)/o-MWCNT and poly(pyrrole-co-diamino diphenyl ether)/o-MWCNT using X-Ray Diffraction analysis (XRD).

To determine the thermal stability of copolymer nanocomposites such as polyaniline/o-MWCNT, polypyrrole/o-MWCNT, poly(aniline-co-diamino diphenyl sulfone)/o-MWCNT, poly(aniline-co-diamino diphenyl ether)/o-MWCNT, poly(pyrrole-co-diamino diphenyl sulfone)/o-MWCNT and poly(pyrrole-co-diamino diphenyl ether)/o-MWCNT using Thermogravimetric analysis (TGA).

To investigat the surface morphology of copolymer nanocomposites and metal adsorbed copolymer nanocomposites using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM). After that adsorption polymeric nanocomposites towards their removal of heavy metals were confirmed by the Energy Dispersive X-ray analysis (EDX) and also re-evaluated from the results of Selected Area Electron Diffraction (SAED) pattern.

To determine the adsorption capacity of copolymer nanocomposites for heavy metal (Pb(II), Ni(II) and Cd(II))
ions removal from aqueous solution and to study the effect of various adsorption parameters on the adsorption process such as:

- Solution pH
- Initial metal ion concentration
- Adsorbent dosage
- Contact time
- Temperature

- **Adsorption kinetic models** – to study the adsorption mechanism of selected adsorbents with divalent metal ions, using the pseudo-first order, pseudo-second order and Elovich models.

- **Adsorption isotherm models** – to evaluate the adsorption behaviour of the selected adsorbents, with the Langmuir, Freundlich, and Redlich-Peterson, adsorption isotherm models, using MATLAB R2009a.

- **Thermodynamic studies** – to study the thermodynamic nature of the adsorption (exothermic or endothermic) of selected adsorbents.

- **Recyclability** - to elucidate the adsorption-desorption capacity of the adsorbents to be reused for further adsorption process.

In the present study, polyaniline/o-MWCNT, polypyrrole/o-MWCNT, poly(aniline-co-diamino diphenyl sulfone)/o-MWCNT, poly(aniline-co-diamino diphenyl ether)/o-MWCNT, poly(pyrrrole-co-diamino diphenyl sulfone)/o-MWCNT and poly(pyrrrole-co-diamino diphenyl ether)/o-MWCNT are used as adsorbents for the removal of metal ions such as Pb(II), Ni(II) and Cd(II) from aqueous media.