CHAPTER 2

Review of Literature

2.1 General Description of Mercury and Nickel

2.1.1 Discovery and Naming
Mercury was known to the Romans, Chinese, Hindus, Egyptians, and Greeks before 2000 BC and stored in small glass tubes in an Egyptian tomb from 1500 BC. A Greek philosopher Theophrastus (327-287 BC) penned that cinnabar was found mainly in the silver mines. Thirty thousand years ago, cinnabar (HgS) was used by the Palaeolithic painters as a red pigment to decorate the caves in France and Spain. These cinnabar produces mercury after heating in a crucible. The chemical symbol for mercury (Hg) comes from “hydrargyrum” the Latin word, which means liquid silver.

Nickel was discovered in a mineral (niccolite) by Swedish mineralogist and chemist Axel Fredrik Cronstedt in 1751. The element was named after the German word “kupfernickel” which means devil’s copper or old Nick’s (St Nicholas’s) copper.

2.1.2 Occurrence
Mercury is known to be present rarely to about 0.5 ppm in the earth’s crust (Pacyna et al., 2006). It is rarely found as a natural metal, usually found as a compound in livingstonite, cinnabar, corderoite and other minerals among which cinnabar (HgS) is known to be the common ore (Rytuba, 2003). Ores of mercury are generally found in orogenic belts where the rocks of high density are enforced to Earth’s crust frequently in volcanic regions or hot springs. In Spain and Peru, mercury was widely used for extracting silver from the mines. It was reported that from Peru, 100,000 tons or more mercury were mined (Kim et al., 2000). China was known to be the topmost producer of mercury in 2005 thereby contributing almost 2/3rd of the global share. Other countries are also believed to produce mercury from copper electroextraction process and recovery from industrial effluents.

Nickel is present in the inner and outer cores of the Earth and is commonly found in combination with iron and sulfur, sulfur alone, arsenic and sulfur, arsenic alone in the
form minerals such as pentlandite, millerite, galena and nickeline respectively (Brillo and Egry, 2003). It is found as alloys such as taenite and kamacite in iron meteorites. The majority of nickel is extracted from two kinds of ores; magmatic sulfide deposits in which pentlandite is the principal ore and the second one is laterite where limonite and garnierite are the principal ores (Rasmussen et al., 1988).

2.1.3 Chemistry

Mercury occurs in two states of oxidation viz., I and II where mercury(II) is the most common and mainly found in nature as well. Higher oxidation states such as mercury(IV) fluoride are rare but have been detected under odd conditions (Wang et al., 2007). Mercury when exposed to air at raised temperature for longer duration, the main oxide form of mercury, mercury(II) oxide is formed which returns to the elements when heated upto 400°C. Mercury being a soft metal, reacts with heavier chalcogens to form stable derivatives. Mercury(II) salts reacts with ammonia to form different complex derivatives including fusible white precipitate ([(Hg(NH₃)₂]Cl₂) and Millon’s base (Hg₂N⁺). Potassium tetra-iodomercurate(II) (HgI₄²⁻) also called as Nessler’s reagent is rarely used to test ammonia as it has a tendency to form intensely colored Millon’s base. Mercury derivative namely mercury fulminate is known to be used in explosives. Salts of mercury(II) can directly react with the aromatic rings (McAuliffe, 2016). Organomercury compounds do not react with water. Organomercury is generally represented by the formula HgRX or HgR₂ known to be solid in nature where X represents acetone or halide and R represents an alkyl or aryl group. Compounds possessing the formula CH₃HgX have a generic term called methylmercury, considered as a bio-accumulative toxic substance frequently encountered in contaminated water and are produced by process called biomethylation.

Nickel primarily occurs as divalent compounds as +2 is the most common oxidation state of the element. Certain compounds of nickel exist with oxidation state of -1 to +4. The characteristic colors of nickel compounds are green and blue and are mostly found in hydrated form. Nickel hydroxide occurs as green crystals and is precipitated when mixed with alkali solution. It readily dissolves in ammonium hydroxide and acids but not soluble in water. Nickel oxide occurs as green powder which turns yellow upon heating. This compound is obtained by heating nickel nitrate, hydroxide or carbonate. Nickel oxide is soluble in acids but insoluble in water (Jolly, 2012). Nickel reacts with fluorine gas (F₂)
which makes nickel as the main metal involved in making fluorine containers. The dibromide (NiBr$_2$), di-iodide (NiI$_2$) and dichloride (NiCl$_2$) compounds are formed when nickel reacts with bromine (Br$_2$), iodine (I$_2$) and chlorine (Cl$_2$) respectively. Nickel slowly dissolves in dilute sulfuric acid to form solutions comprising aqueous Ni(II) ion along with hydrogen gas (H$_2$). Nickel(II) reacts with anions including carbonate, hydroxide, sulfate, halides and carboxylates to form various compounds. Nickel reacts with halides to form compounds among which nickel(II) chloride is the most common.

2.1.4 Industrial Uses

The main uses of mercury are in manufacturing of electronic and electrical components, fluorescent lamps in gaseous form, instruments and related products. It is used in thermometers. Mercury is widely known as a constituent in dental amalgams. An organic mercury compound called thiomersal is used as preservative in all vaccines. Thiomersal in vaccines for children of six years have been used in trace amount but could result in autism, though no supporting record of such incident was reported (Parker et al., 2004). Thiomersal is used widely in mascara production. The addition of mercury in skin care products or cosmetics was banned first in Minnesota in 2008. Merbromim an organomercuric disodium salt is usually marketed as Merbromine, Supercrome, Cinafacromin, Mercurochrome, Sodium mercurescein, Asceptichrome and Brocaset as a topical antiseptic to treat minor burns, wounds and scratches. It is also useful in treating infections of finger and toe nails as it is considered to be lethal to bacteria. Merbromim is known to be available in most of the countries. Cinnabar, the common ore of mercury is widely used in traditional medicines but it has been reviewed that cinnabar when used in higher dose or taken for longer duration, can lead to mercury poisoning (Liu et al., 2008). Mercury in gaseous form is used in electron tubes including mercury arc rectifiers, thyratrons and ignitrons. The addition of gaseous form of mercury to the cathode region of argon-filled lamps increases electrical conductivity and ionization. Mercury(II) fulminate, a mercury compound is an explosive, mainly used in firearms as a primer of cartridge. Mercury battery known as a non-rechargeable electrochemical battery is widely used in variety of applications. Its long shelf life and constant output of voltage added to its usage in camera lights and in hearing aids. But the use of mercury cell was banned due to the rising problem of mercury contaminated
landfills. The largest industrial use of mercury is involved in the electrolysis process for separation of sodium and chlorine from brine (chloralkali process).

Nickel containing products play a significant role in our day-to-day lives. Compared to other materials, nickel bearing products have more strength at low and high temperatures, toughness, improved corrosion resistance and electronic and magnetic properties. It is mostly used for coatings, alloying elements and making batteries. Other uses include medical equipment, transport, kitchen wares, jewellery, power generation, mobile phones and buildings. The use of nickel is conquered by the production of ferronickel for stainless steel, alloy steels, non-ferrous alloys, plating, batteries and foundry. Many industrial products such as alnico magnets, rechargeable batteries, coinage, stainless steel, microphone capsules, plumbing fixtures are being produced from nickel. Nickel cast irons and nickel steels are the chief uses of nickel. It possesses toughness, tensile strength, elastic limit and used for plating. Nickel is used as a substitute for making silver item because of its resistance to corrosion. Nickel and its alloys mainly Raney nickel, a nickel-aluminium alloy are used as catalysts for hydrogenation. Nickel mesh or nickel foam is widely used for fuel cells in the gas diffusion electrodes (Reck et al., 2008). Nickel is used in several rechargeable batteries which are used in power tools, emergency power supply, transport and in electronics. Nickel powder is used for powder metallurgy alloys.

2.2 Health Issues

2.2.1 Toxic Effects of Mercury

Mercury is known to persist in the environment causing long term pollution problems. The compounds of elemental mercury have no recognized metabolism and can be transformed into very high toxic forms by biological and other methods. Methylmercury can be biomagnified via food chains thereby returning mercury to human being. Mercury is known to be a carcinogen, teratogen and causes cytochemical, histopathological and embryocidal effects (Miretzky and Cirelli, 2009). Any form of mercury is considered to be poisonous mostly distressing the neurologic systems, gastrointestinal (GI) and renal organ. Mercury poisoning causes a disease called hydrargyrias carrying kidney, brain and lungs. Mercury inhalation can cause harmful effects on lungs, kidneys, nervous, immune, digestive systems and can also be fatal. In humans, the initial symptoms include numbness of the limbs and lips. Permanent damage occurs to the central nervous system, as the sickness progresses.
The victim experiences loss of motor coordination, visual constrictions and in the final stages loss of taste, hearing, and memory occurs prior to death (Sari and Tuzen, 2009; Arias et al., 2017). There is report that methyl and elemental mercury have higher tendency for binding proteins affecting the renal, peripheral and central nervous systems (Shokrollahi et al., 2009). Mercury salts are corrosive to the gastrointestinal tract, eyes and skin. It can also cause kidney toxicity if consumed. Dermal exposure, ingestion or inhalation of various mercury compounds may cause behavioral or neurological disorders. The symptoms include chest pain, insomnia, tremors, memory loss, headaches, dyspnea, cell damage, neuromuscular effects and cognitive dysfunction (Jeong et al., 2007).

2.2.2 Toxic Effects of Nickel

Nickel is naturally available in both water and food but the level is increased to a large extent by pollution caused by human. The atmosphere becomes nickel contaminated mainly by fossil fuel combustion and metal refining. Humans can absorb nickel via skin contact with jewelry, detergents, coins and shampoos. The harmful health effects such as cancer of nasal sinus and lung, reduced lung function and chronic bronchitis have been reported in human who have inhaled dust containing nickel compounds such as nickel subsulfide and nickel refinery dust (Malkoc, 2006). Department of Health and Human Services (DHHS) of the U.S. has reported nickel metal and nickel compounds as a potent carcinogen leading to cancer in lungs, stomach, larynx, prostate, bone and nose (Kwak et al., 2011). Damage to nasal cavity and lung inflammation occurs at high concentration of nickel compounds. Damage to liver, stomach, kidneys, immune system and reproduction has been reported in rats and dogs after ingestion of nickel at a level greater than the permissible limit.

The most frequent effect of nickel exposure in human is nickel itch, an allergy caused when in contact with jewelries and nickel coins (Ijagbemi et al., 2010). An uptake of excessive amount of nickel can cause cancer, heart disorders, lung embolism, respiratory failure, chronic bronchitis, asthma, skin rashes, headache, nausea, vomiting, cyanosis, sickness, dizziness and extreme weakness (Fouladgar et al., 2015; Shivhare and Sharma, 2012).
2.3 Conventional Methods for Removal of Mercury and Nickel from Aqueous Medium

2.3.1 Removal of Mercury

Huge amounts of mercury are known to be released into aquatic systems from erosion, chloralkali plants, atmospheric deposition, cement manufacture, metal smelters, urban discharges, mining, combustion of fossil fuels, metal refining, wood pulping and electrical instruments (Martínez-Juárez et al., 2012; Boening, 2000). Numerous technologies have developed to eradicate mercury ions from aqueous medium. Conventional methods that are used for removal of mercury from the metal contaminated waters include coagulation, ion exchange, flocculation, complexation, sequestration, reverse osmosis, evaporation, adsorption and chemical precipitation (Tuzen et al., 2009; Khoramzadeh et al., 2013).

Adsorption of mercury from aqueous medium onto dead protonated Ulva lactuca biomass was reported (Zeroual et al., 2003). At pH 3.5, 5.5 and 7 the maximum mercury uptake values were 27.24, 84.74 and 149.25 mg/g respectively.

Al Rmalli et al. (2008) reported the biosorption of mercury onto a biosorbent obtained from leaves of castor tree (Ricinus communis L.) from aqueous environment. The biosorption process was studied at various pH (2 to 8) and maximum mercury uptake capacity was noted as 37.2 mg/g at pH 5.5. Sorption equilibrium was attained in one hour and the data were fitted to equilibrium models viz., Freundlich and Langmuir models.

The adsorption behaviour of modified chitosan resin for Hg(II) in aqueous medium was investigated by batch method (Donia et al., 2008). The maximum uptake value (2.8 mmol/g) was noted and thermodynamic and kinetic studies showed that the process of adsorption was exothermic and well followed pseudo-second order model.

Tuzen et al. (2009) reported the application of the lichen biomass (Xanthoparmelia conspersa) for mercury removal from aqueous medium. The equilibrium data well fitted Langmuir model when compared to Freundlich model and maximum mercury uptake was noted to be 82.8 mg/g. Also, the experimental data fitted pseudo-second order kinetic model and the thermodynamic studies suggested the sorption of Hg(II) ions as spontaneous and exothermic.

Anagnostopoulos et al. (2012) reported the adsorption behaviour of mercury onto malt spent rootlets (MSR), a known brewery by-product. The effects of contact time,
solution pH, and initial metal concentration were studied. Kinetic studies exhibited that adsorption of mercury was a rapid process and controlled by both intra-particle and film diffusion and the equilibrium data fitted to the Langmuir model thereby defining a monolayer adsorption mode.

The biosorption of mercury(II) onto 14 different fungal biomasses was reported (Martínez-Juárez et al., 2012). The remaining concentration of mercury ions in the solution was determined spectrophotometrically at wavelength of 492nm using dithizone as the complexing agent which is indicated by the formation of orange colour in the solution. *M. rouxii* IM-80 showed the maximum removal of mercury (95.3%). The highest adsorption was noted at pH 5.5, at 30°C after 24 hours.

Dried *Vibrio parahaemolyticus* PG02 was used to remove mercury from synthetic effluent (Jafari and Cheraghi, 2014). Kinetic data revealed that biosorption of Hg(II) was well described by pseudo second order model. The equilibrium data well fitted Langmuir model and maximum uptake was reported to be $9.63 \times 10^{-4}$ mg/g at 35°C and pH 6.0.

Liu et al. (2017) reported synthesis and application of DNA functionalized graphene nanoparticles, a novel bio based nanomaterial for detection and removal of mercury(II). The graphene oxide was reduced when combined with Fe$_3$O$_4$, which was further functionalized with Hg$^{2+}$-specific thymine oligonucleotide (T-DNA). T-DNA is known to interact with Hg$^{2+}$ and change the structure from random coil to hairpin resulting in the increase of SYBR Green I fluorescence. This aided in determination of mercury(II). The removal of mercury(II) was attained due to the large surface area offered by the graphene oxide nanoparticles. The results suggested that these nanomaterials could exhibit a removal efficiency above 80% and quick separation from the solution.

### 2.3.2 Removal of Nickel

Removal of nickel has been a principal concern in treating wastewater because of its widespread applications in industries (Kwak et al., 2011). Nickel is present in wastewaters released from industries such as mining, electroplating, metal finishing, smelting, galvanization, plastic manufacturing, nickel-cadmium batteries manufacturing and porcelain enameling (He et al., 2014). A wide range of techniques viz. coagulation, ion exchange, evaporation, precipitation, ultrafiltration, electrodialysis, reverse-osmosis and
Adsorption have been used for Ni(II) removal from industrial wastewater in order to decrease their impact on the environment (Can et al., 2006).

Adsorption of nickel(II) on natural and acid treated forms of brown algae (Sargassum sp.) was investigated (Kalyani et al., 2004). Equilibrium data were evaluated using isotherm models (Langmuir and Freundlich). It was observed that both the models represented data satisfactorily. The nickel uptake capacities of 181.2 and 250.0 mg/g was noted in case of native and acid modified form of algae respectively.

Nickel removal from electroplating wastewater was examined in a column packed with acid washed crab shells (Vijayaraghavan et al., 2005). Effluent collected from two sources were used to analyze the removal capacity of crab shells and it was noted that the crab shells exhibited the uptake values of 15.08 and 20.04 mg/g for source 1 and 2 respectively.

Ipek (2005) investigated Ni(II) removal from aqueous medium by reverse-osmosis (RO) which was performed at various conductivity, pH, metal and EDTA concentrations. Removal efficiency in the pretreatment units (PU) with granular activated carbon (GAC) and filtration (F) was also studied. Ni(II) was removed (23-25%) using PU and the rejection of Ni(II) was found to be more than 99.2% by PU+RO based on the experiments related to the effect of initial metal concentration on rejection. It was further noticed that the rejection of Ni(II) increased from 99.2% to 99.7% when 240 ppm of EDTA was added into the aqueous solution.

The removal of nickel from aqueous medium using maple sawdust was reported (Shukla et al., 2005). The effects of solution pH, adsorbent dosage and initial sorbate concentration were investigated in batch mode. Maximum removal of nickel(II) was noted at pH 9.0.

The adsorption behaviour of pomegranate (Punica granatum) peel waste for Ni(II) from aqueous solution was evaluated (Bhatnagar and Minocha, 2010). Batch experiments were conducted. The process of adsorption was described by the pseudo-second-order kinetic model. The data conformed Langmuir isotherm model with maximum uptake of 52.0 mg/g. Study of thermodynamics revealed that the adsorption process was spontaneous and endothermic in nature.
The removal and recovery of nickel(II) from electroplating wastewater was studied using biomass of *E. coli* and compared with Amberlite resin (Kwak et al., 2011). On the basis of Langmuir isotherm model, better performance with an uptake of 30.48 mg/g was exhibited by Amberlite resin compared to the biomass which showed an uptake of 26.45 mg/g. The fast achievement of equilibrium by both the sorbents confirmed their feasibility in industrial application. In regeneration studies, a better nickel recovery efficiency was found by the waste biomass than the commercial resin (only 50%) which demonstrated its environmental friendliness and economy.

Shih et al. (2013) investigated the remediation of nickel from plating wastewater via Fered-Fenton method and chemical precipitation. This method was adopted to remediate the nickel citrate and alkaline precipitation was used to eliminate the nickel ions that were released. Nickel citrate, the target pollutant was oxidized using electrochemical reactor, mounted with two cathodic net and four anodic rods. Nickel was released (99.9%) from the chelated form and was recovered by deposition at cathodic region followed by alkaline precipitation.

Poly(ethyleneimine)-functionalized silica hybrid was successfully synthesized by surface grafting method for Ni(II) removal from aqueous environment (He et al., 2014). Among the isotherm models, Langmuir model was noted to be more favorable and in case of kinetic models, the data followed pseudo-second-order. Study of thermodynamics proposed that Ni(II) adsorption on PEI-functionalized hybrid silica was endothermic and spontaneous.

Liu et al. (2017) reported Ni(II) removal from municipal sludge using an electrokinetic process. Optimum parameters for the experimental setup was found to be 0.200 mol/L HNO₃ electrolyte concentration in the anode chamber; 0.800 mol/L NaNO₃ electrolyte concentration in the cathode chamber and 2.0 mA/cm² of current density. Under optimized conditions, the efficiency for nickel removal was noted to be in the range of 46.6-75.1%. When three sludge chambers were equipped in the electrokinetic system and the pH of the sludge was adjusted to 3.8, the current efficiency was found to increase and the specific energy consumption was decreased.
Table 2.1 Summary of adsorption capacity/removal efficiency obtained for the adsorbents reported in the previous studies

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>Uptake (mg/g)</th>
<th>Removal (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(II)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Conventional method</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ulva lactuca biomass</td>
<td>149.25 mg/g</td>
<td>-</td>
<td>Zeroual et al. (2003)</td>
</tr>
<tr>
<td>Leaves of castor tree (Ricinus communis L.)</td>
<td>37.2 mg/g</td>
<td>-</td>
<td>Al Rmalli et al. (2008)</td>
</tr>
<tr>
<td>Lichen biomass (Xanthoparmelia conspersa)</td>
<td>82.8 mg/g</td>
<td>-</td>
<td>Tuzen et al. (2009)</td>
</tr>
<tr>
<td>Fungal biomass M. rouxii IM-80</td>
<td>-</td>
<td>95.3%</td>
<td>Martínez-Juárez et al. (2012)</td>
</tr>
<tr>
<td>DNA functionalized graphene nanoparticles</td>
<td>-</td>
<td>80%</td>
<td>Liu et al. (2017)</td>
</tr>
<tr>
<td>Ni(II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural brown algae (Sargassum sp.)</td>
<td>181.2 mg/g</td>
<td>-</td>
<td>Kalyani et al. (2004)</td>
</tr>
<tr>
<td>Acid treated brown algae (Sargassum sp.)</td>
<td>250.0 mg/g</td>
<td>-</td>
<td>Kalyani et al. (2004)</td>
</tr>
<tr>
<td>Acid washed crab shells</td>
<td>20.04 mg/g</td>
<td>-</td>
<td>Vijayaraghavan et al. (2005)</td>
</tr>
<tr>
<td>Pomegranate (Punica granatum) peel waste</td>
<td>52.0 mg/g</td>
<td>-</td>
<td>Bhatnagar and Minocha (2010)</td>
</tr>
<tr>
<td>Biomass of E. coli</td>
<td>26.45 mg/g</td>
<td>-</td>
<td>Kwak et al. (2011)</td>
</tr>
<tr>
<td>Amberlit resin</td>
<td>30.48 mg/g</td>
<td>-</td>
<td>Kwak et al. (2011)</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>-</td>
<td>25%</td>
<td>Ipek (2005)</td>
</tr>
<tr>
<td>Chemical precipitation</td>
<td>-</td>
<td>99.9%</td>
<td>Shih et al. (2013)</td>
</tr>
<tr>
<td>Electrokinetic process</td>
<td>-</td>
<td>75.1%</td>
<td>Liu et al. (2017)</td>
</tr>
</tbody>
</table>

2.4 Nanobiocomposites-A Novel Approach for Removal of Heavy Metals

2.4.1 General Description of Nanobiocomposites

Nanotechnology mainly refers to manipulation of matter at the molecular or atomic scale and usage of structures and materials having dimension in the range of 1 to 100 nm. Nanoparticles due to their nanosized dimension, offers unique physico-chemical properties viz. high reactivity and surface area to volume ratio. Nanoparticles are reported to display unique interactions with various pollutants present in waters, soils and gases (Mascianguoli and Zhang, 2003; Klefenz, 2004; Zhang and Fang, 2010). Small size of the particles brings several issues such as mass transport and extreme pressure drops while used in the flow through system. Nanoparticles may cause harmful effects to ecosystems and human health when released to environment. Therefore, an effective method to overcome these issues is to produce a hybrid composite either by coating or impregnating nanoparticles onto larger
sized solid particles. Use of polymeric hosts may be an option for long term use because of their controllable pore size, surface chemistry and mechanical strength.

Nanobiocomposites are prepared by addition of nanoparticles or nanofillers to biopolymer matrices thereby offering a very promising material. They are stable, ecofriendly in nature and show more biodegradability. The hybrid composite maintains the intrinsic properties of nanoparticles. The polymeric matrices provide higher processability, stability and other improvements triggered by the interaction between nanoparticle and matrix. Nanoparticles that are generally used include zero-valent metals (Xu et al., 2010; Xiong et al., 2007; Liu et al., 2010; Lin et al., 2005), single-enzyme nanoparticles (SENs) (Kim and Grate, 2003) and metal oxides (Cumbal and Sengupta, 2005; Katsoyiannis and Zouboulis, 2002; Sylvester et al., 2007). The mentioned nanoparticles could be loaded onto cellulose or carboxymethyl cellulose (CMC) (Guo and Chen, 2005; Dong et al., 2011), porous resin (Blaney et al., 2007; Shu et al., 2010), alginate (Zouboulis and Katsoyiannis, 2002; Chico et al., 2009; Ngomsik et al., 2009), chitosan (Wu et al., 2009; Yang et al., 2009; Zhu et al., 2009). Properties viz. chemical stability, wettability, templating effect, hydrophilic/hydrophobic balance, bio-compatibility, mechanical, thermal, electronic and optical properties should be considered while selecting the polymeric hosts.

2.4.2 Biopolymers

Biopolymers are well-defined as natural polymers which are formed during the growth cycles of organisms under natural conditions. They are formed by metabolic processes that occurs within the cells. Recently, biopolymers have gained more importance due to increasing environmental concern. They have been widely used for heavy metal removal and also other pollutants from aqueous environment. Biopolymers are having important properties such as hydrophilicity, biodegradability. The presence of various functional groups make them advantageous for applications (Zhou et al., 2016).

2.4.2.1 Starch

Starch is a renewable biopolymer which is cost effective, abundant and biocompatible. It is composed of both linear and branched chain of polysaccharides such as amylose and amylopectin. The characteristics of native starch can be changed significantly by chemical modification to provide new and improved properties. Starch can be modified via carboxymethylation which is an etherification process where the hydroxyl groups of starch
are replaced by an anionic carboxymethyl groups. Reports are available for the application of starch and the modified products of starch in the field of heavy metal removal (Igura and Okazaki, 2012; Sancey et al., 2011). An important class of starch derivatives are represented by cross linked starch adsorbents which are formed by crosslinking the polymer covalently with the help of some crosslinking agents. They produce a 3-D network structure and swell in the aqueous medium without being dissolved (Cirni, 2005). Li et al. (2008) reported that Co(II), Cu(II) and Ni(II) can be adsorbed to crosslinked starch microspheres efficiently over a varied range of temperatures within few minutes.

2.4.2.2 Cellulose

Cellulose is the most abundant, cost effective and renewable biopolymer available for synthesis of various functional polymers. It is the main structural constituent of plant cells and broadly used in various industrial applications. Cellulose is obtained mostly from cotton and wood whereas cellulose pulp is produced from agricultural products viz. crop straws, stalks and bagasse. They can also be produced from non-plant resources especially tunicates and bacteria. The cellulose obtained from bacteria is termed as bacterial cellulose. Cellulose has a molecular structure comprised of β-D-glucopyranose units linked covalently via acetal functional groups present between C1 and C4 carbon atoms (Malmström and Carlmark, 2012). A strong interaction occurs between the neighbouring cellulose molecules via intermolecular hydrogen bonding due to the presence of hydroxyl groups. This molecular structure provides cellulose its distinctive properties such as degradability, chirality and hydrophilicity. Cellulose is ribbon shaped which allows the twisting and bending of molecule. Attempts have been made to convert cellulose into compounds which are able to adsorb metal ions from aqueous medium (Donia et al., 2012). One method involves modification of cellulose by introducing metal binding or chelating functionalities. Chemical properties of cellulose viz. elasticity, hydrophilic or hydrophobic character, ion exchange capability, adsorptive ability, thermal resistance and resistance to microbial attack can be modified. The other method is focused on the grafting of monomers to cellulose either by functionalization of grafted monomers with chelating agents or directly introducing metal binding ability (O’Connell et al., 2008). Reports are available where modified cellulose are used for removal of different contaminants from water (Hubbe et al., 2011).
2.4.2.3 Chitin and Chitosan

Chitosan is a copolymer obtained as N-deactivated chitin derivative which is found in insects, mollusks and crustacean (Wu et al., 2017; Khairkar and Raut, 2014). Chitin is composed of linear chain of acetylglucosamine groups and obtained from the shells of shrimps or crab by extracting the proteins followed by its treatment using calcium carbonate. The resultant chitin is then deacetylated with 40% NaOH at 120°C for 1-3 hours which yields 70% deacetylated chitosan (Kumar, 2000). In recent years, chitin has gained importance due to their unique properties viz. biodegradable, biocompatible, high mechanical strength and non-toxic nature with brilliant adsorption properties. All these characteristics make it appropriate as adsorbent for various applications viz. packaging, biosensors and in wastewater treatment as an adsorbent (Khairkar and Raut, 2014). Chitosan is reported as potential adsorbent for heavy metal removal from wastewater.

2.4.2.4 Alginate

Alginate is a biopolymer extracted from brown algae and is largely composed of α-L-guluronate and (1-4)-linked β-D-mannuronate units (Yang et al., 2012). Alginate is reported to have characteristics like non-toxic, efficient, high molecular weight and cost effective. Jung et al. (2015) investigated the application of alginate beads for divalent heavy metal adsorption. The presence of functional groups (hydroxyl and carboxyl) on the surface of alginate beads are capable of removing metal ions by ion exchange process. Alginate has been used as an immobilizing agent, and plays an important role on adsorption of metal ions. There are reports signifying the removal efficiency of alginate for various heavy metals by linking it with activated carbon (Hassan et al., 2014) and carbon nanotubes (Li et al., 2010). Since sodium alginate is less stable and water soluble, it cannot be used directly for adsorption of various pollutants from aqueous medium (Gopalakannan and Viswanathan, 2015). Number of attempts have been made to increase the stability and adsorption capacity by producing polymeric complexes (Jiang et al., 2012) and cross linking with metal ions of higher valence (Singh et al., 2014).

2.4.3 Nanofillers

Nanofillers are known to enhance the mechanical, optical, thermal and electrical properties of biomaterials into which they are fused. They are classified into three categories namely i) one dimensional nanofillers (plates, shells and laminas); ii) two dimensional nanofillers
(nanofibers and nanotubes having diameter less than 0.1 μm) and iii) three dimensional nanofillers (isodimensional nanoparticles). Here diverse nanofillers have been presented which are used for the production of nanobiocomposites.

2.4.3.1 Cellulose Based Nanofillers

The nanofibers produced from cellulose are considered to be attractive for its use for reinforcements during the preparation of nanobiocomposites. The two different types of nano-reinforcements that are obtained from cellulose are cellulose microfibrils and cellulose nanowhiskers (Azizi Samir et al., 2005). Cellulose microfibrils comprises bundles of elongated molecules that are stabilized via hydrogen bonding. These fibrils have a dimension of length in micrometer range and diameter in the range of 2-20 nm consisting of both crystalline and amorphous regions. Isolation of crystalline regions is possible by different methods and the resulting material is known as cellulose nanowhiskers. The most widely used technique for extracting these nanowhiskers is acid hydrolysis in which the amorphous regions are removed and the crystalline region remain unaltered. The diameter of nanowhiskers range from 8-20 nm and length from 500 nm to 1-21 m (de Souza Lima and Borsali, 2004).

2.4.3.2 Carbon Nanotubes

There are three kinds of carbon nanotubes viz., single wall carbon nanotubes (having diameter between 1 and 2 nm), double wall carbon nanotubes (diameter between 2 and 4 nm) and multi-wall carbon nanotubes (diameter between 4 and 150 nm). CNTs are formed by an electric discharge process at high temperature of 3000 to 4000°C under helium and by a catalytic vapor decomposition process at temperature ranging from 600-1000°C. They have been employed as functional fillers in polymer nanocomposites which not only enhanced mechanical/thermal properties but also resulted in additional properties such as moisture resistance, fire retardant, barrier performances and electromagnetic shielding (Baur and Silverman, 2007). The limitation during the production of CNT/polymer nanocomposites is their dispersion within the matrix as the carbon nanotubes tends to remain in bundles due to their strong van der Waals interactions and high aspect ratio. Number of treatments have been employed to improve their solubility: (i) physical treatments (plasma modification and sonochemical oxidation), (ii) formation of long alkyl/polymer chains onto CNTs and (iii) surface oxidation by acid treatment.
2.4.3.3 Nanoclays
In the silicate layers of nanoclays, the crystal arrangement is made up of two atoms coordinated tetrahedrally which is incorporated to the edge shared octahedral sheets. These sheets are composed of either aluminum or magnesium hydroxide. The tangential dimensions of these layer range from three hundred angstroms to few microns and have a thickness of one nanometer. Depending on the source of clay and preparation technique, a variation in the layer dimensions may occur. These silicate layers exhibit higher aspect ratio and surface area (Alexandre and Dubois, 2000).

2.4.3.4 Functional Nanofillers

Hydroxyapatite is a known biocompatible and bioactive ceramic found in teeth and bones which shows advantages of nontoxic behavior and osteoconductivity (Jevtic et al., 2008). The chemical representation of HAp with hexagonal crystalline structure is \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \). Various properties such as thermal stability, solubility, morphology and crystal structure (crystallinity, size, shape) determines the functionality of hydroxyapatite.

Layered double hydroxide (LDH) is usually stated as a mineral which occurs naturally (Reddy et al., 2013). LDH displays positively charged host lattices and this exclusive feature permits an interesting chemistry between layers and interlayers which can be used in various applications.

2.4.3.5 Nano-Oxides

Nanoalumina are used as fillers having size ranging from 20 nm to micrometers and are composed of crystalline spherical particles of \( \text{Al}_2\text{O}_3 \). In order to enhance catalytic properties in some circumstances, alumina nanoparticles are used as inert fillers. Nano-antimony-tin oxide is a tetragonal crystalline particle with a diameter of 15 nm, generally used as a flame retardant (Poizot et al., 2000).

2.4.3.6 Other Nanofillers

Metallic nanoparticles such as nanozinc, nanogold and nanosilver are used as nanofillers. These nanoparticles exhibit catalytic behaviour which tend to enhance the antibacterial properties at the surface. They are mostly employed in the synthesis of nanocomposites due to their magnetic and electrical properties. Silsesquioxanes are macromolecules which are used as nanofillers in the polymer matrix. They are chemically represented as \( \text{R-SiO}_{3/2} \) where \( \text{R} \) represents an organo- or alkyl functional groups. Their size in the range of
nanometer and high 3D symmetry makes them the building blocks for the synthesis of nanocomposites. The most commonly found silsesquioxanes are octasilsesquioxanes of \([\text{ROSiO}_{1.5}]_8\) and \([\text{R-phenylSiO}_{1.5}]_8\) type and polyhedral oligosilsesquioxanes (POSS) (Phillips et al., 2004). They are mainly used for the synthesis of 3-D structured monoliths, fibre reinforced and thin film nanocomposites. Boehmite, an aluminium hydroxide mineral which can be obtained either naturally or via chemical synthesis from saturated solutions is used as a nanofiller in nanocomposites. It is chemically represented as \(\gamma\text{-AlO(OH)}\).

2.4.4 Preparation Techniques of Nanobiocomposites

Nanobiocomposites are prepared following different techniques such as direct-compounding and in-situ synthesis.

2.4.4.1 Direct Compounding

This method is widely used for the synthesis nanobiocomposites due to its ease in process, suitable for massive production and comparatively cost effective. At first the nanofillers/nanoparticles and biopolymer solutions are separately prepared and are mixed by fusion, mechanical forces or emulsion (Daming et al., 2003). However, this method gained limited success because of some limitations. To overcome the limitation, several surface modifications can be done during synthesis of nanoparticles and also alterations in temperature, time and shear force were done in order to attain fine diffusion of nanoparticles in biopolymer matrices (Zha et al., 2010). Addition of appropriate compatibilizers or dispersants were done to enhance the dispersal of particle and the adhesion between biopolymer matrix and nanoparticles (Yu et al., 2008). Salam et al. (2011) reported the synthesis of multi-walled carbon nanotubes/chitosan nanobiocomposite following direct compounding technique. Two suspensions were made separately and then mixed mechanically. The resulting nanobiocomposite exhibited a great efficiency for the removal of nickel, zinc, copper and cadmium from the aqueous environment. An approach for the synthesis of a nanobiocomposite consisting of cellulose as biopolymer matrix and TiO\(_2\) nanoparticles using supercritical CO\(_2\) was described (Yu et al., 2008). It was observed that supercritical CO\(_2\) affected the interactions between TiO\(_2\) particles and the molecular chains of cellulose. Mallakpour and Madani (2016) reported the synthesis of functionalized MnO\(_2\) nanorod/chitosan hybrid composite for Pb(II) removal. Here, the composite was prepared with an approach of direct compounding where
functionalized alpha manganese dioxide nanorod was prepared separately and was added to the chitosan solution followed by crosslinking reaction using glutaradehyde (GA). Functionalization of $\alpha$-MnO$_2$ using $\gamma$-aminopropyl-triethoxysilane (APTS) was carried out in order to ensure the uniformity in its dispersion within the chitosan matrix. TGA analysis suggested that 20 wt% of APTS was attached on the surface of $\alpha$-MnO$_2$ nanorods. It was noted that crosslinking with GA reduced crystallinity of chitosan and increasing the content of GA improved the stability of the hybrid composite.

2.4.4.2 In-situ Synthesis

Under in situ synthesis, metal ions serve as nanoparticle precursors, are preloaded within biopolymer matrix and uniformly distributed. Then, precursors were subjected to the corresponding gas or liquid containing OH$^-$, S$_2^-$ etc. to synthesize the nanoparticles. Wu et al. (2009) reported in situ synthesis of chitosan nanobiocomposite incorporated with copper nanoparticles using Cu(SO$_4$)$_2.5$H$_2$O as a precursor which was applied for Cr(VI) removal. In-situ synthesis of chitosan zinc-oxide nanoparticles composite for the removal of permethrin pesticide has been reported (Dehaghi et al., 2014). In this study, ZnO nanoparticles were synthesized by treating ZnO powder with 65% nitric acid in the chitosan solution followed by addition of NaOH solution. Results suggested that the 0.5g of hybrid composite was able to remove 99% of the pesticide at room temperature and pH 7.0. Removal of lead(II) ions was done using novel triethylene-tetramine grafted magnetic chitosan composite which was synthesized via in situ synthesis. Magnetic nanoparticles were prepared in the chitosan mixture and was used for Pb(II) removal (Kuang et al., 2013). An uptake of 370.63 mg/g of Pb(II) was noted under optimized conditions ($t=1.5$h, $T=298K$, $C_0=200$ mg/L, pH=6 and adsorbent dosage= 500 mg/L). An adsorbent, iron oxy-hydroxide loaded cellulose beads was synthesized via in-situ method where FeCl$_3.6$H$_2$O served as a precursor for both arsenate and arsenite removal (Guo and Chen, 2005). The uptake capacity for arsenate and arsenite at pH 7.0 was noted as 33.2mg/g and 99.6 mg/g respectively. The data was well explained by pseudo-second-order kinetic model suggesting chemisorption as underlying phenomenon. This study also indicated that arsenite adsorption by the adsorbent was favoured in wide range of pH (5-11) whereas removal of arsenate was found to be effective at acidic pH. Both batch and column mode trials suggested that arsenite was removed more efficiently than arsenate by the adsorbent.
2.4.5 Environmental Applications of Nanobiocomposites

Nanobiocomposites have been applied towards reduction of pollutants from environmental sources such as industrial effluents or groundwater, soils and gases. The mechanisms involved in this application are adsorption and catalytic/redox degradation. Some polymer nanobiocomposites are widely applied for detection and subsequent removal of contaminants at trace levels and also in green chemistry in order to lessen the release of contaminants into environment.

2.4.5.1 As Catalyst

Nanoparticles (NPs) incorporated in nanobiocomposite can serve as redox active media and catalysts because of their high reactivity, surface area, catalytic and electronic property. These properties have gained importance in designing highly efficient catalytic materials for purification of polluted water. The common catalytic nanoparticles used include zero valence metal such as Fe$^0$, Zn$^0$, Cu$^0$ (Liu and Zhang, 2010; Lin et al., 2005), bimetallic nanoparticles such as Zn/Pd (Rivero Huguet and Marshall, 2009), Fe/Pd (Dong et al., 2011), Fe/Al (Chen et al., 2008), Fe/Ni (Barnes et al., 2010) and nano semiconductor materials such as nano-CdS (Zhu et al., 2009), ZnO (Daneshvar et al., 2004) and TiO$_2$ (Konstantinou and Albanis, 2004). Immobilization of nanoparticles onto biopolymer matrix have been reported to resolve the environmental issues to large level owing to their ability in reducing particle loss and inhibition of agglomeration of particles (Mittal and Mishra, 2014). It has been reported that nanoparticles (zero valence metal and bimetallic) viz. Zn$^0$, Cu$^0$, Fe$^0$, Pd/Zn and Fe/Pd are efficient in removing various pollutants including heavy metals (Wu et al., 2009). The reactivity of some nanoparticles is considerably very high. Nanoscale zero valent iron (nZVI) has the ability to ignite on its own when in contact with air. Therefore, the nanoparticles are required to be supported to matrix to conserve the chemical property until they come in contact with the contaminants being targeted. Dong et al. (2011) reported the Fe/Pd nanoparticle stabilization using carboxymethyl cellulose (CMC) for para-nitrochlorobenzene reduction via catalysis. Dechlorination in batch experiments suggested that trichloroethene (TCE) was degraded by CMC-stabilized nanoparticles 17 times faster when compared to unstabilized Fe/Pd bimetallic nanoparticles. Moreover, the CMC-stabilized nanoparticles exhibited an improved chemical reactivity, soil transport and stability.
2.4.5.2 As Adsorbent

Adsorption is considered as one of the simplest and effective method used in gas and water purification for the removal of recalcitrant and toxic pollutants. Metal oxides such as Mn(IV) (Trivedi et al., 2001), Fe(III) (Jang and Dempsey, 2008) and M(HPO$_4$)$_2$ where M= Ti, Zr, Sn (Jia et al., 2008) are environmentally non-toxic inorganic particles and widely used for the higher removal of targeted pollutants as effective adsorbents. Moreover, when these particles are used in nanoform they become more efficient due to their high reactivity and surface area. In order to avoid negative impacts resulted due to the extreme particle size viz. pressure drops and transition loss, nanobiocomposites were prepared by infusing nanoparticles onto biopolymers such as alginate (Zouboulis and Katsoyiannis, 2002), chitosan (Liu et al., 2015), cellulose (Guo and Chen, 2005) etc. The functional groups that are charged and bounded to biopolymer matrix are alleged to boost diffusion of pollutants having counter charges (Cumbal and Sengupta, 2005).

Chitosan is widely used adsorbent for metal cation removal because of the existence of amino (-NH$_2$) and hydroxyl (-OH) groups in huge numbers which serve as reaction and coordination sites (Liu et al., 2015). The adsorption characteristics of chitosan towards heavy metals includes (a) flexibility in the structure of chitosan chain (b) presence of functional groups such as primary hydroxyl, amino and acetamido groups (c) its high reactivity (d) hydrophilicity due to the presence of hydroxyl groups (Miretzky and Cirelli, 2009).

Alginate offers the ability to bind metal ions onto their surface thereby leading to the removal of metal ions from aqueous environment due to the presence of carboxylate groups in the polymer structure (Ngomsika et al., 2006). Toress et al. (2005) reported the adsorption of silver and gold ions from aqueous media using Ca-alginate beads. It was noted that the metal uptake capacity of alginate beads was significantly affected by solution pH. The involvement of both hydroxylic and carboxylic functional groups present in alginate beads in the adsorption process was confirmed from the FTIR spectra. Verma et al. (2017) reported the application of functionalized Fe$_3$O$_4$ nanoparticles/Ca alginate beads towards removal of Pb(II) ions. The data well fitted to pseudo second order kinetic model and after 100 min, equilibrium was attained. The adsorption data was defined by Langmuir isotherm model exhibiting maximum uptake of 555.5 mg/g.
Cellulose is the most widely available and promising low cost raw material for the synthesis of various functional polymers. Since virgin cellulose cannot be applied in adsorbing or chelating metal ions, attempts have been to modify cellulose physically or chemically and utilize the same for the adsorption of heavy metal (Donia et al., 2012). Modified forms of cellulose have been widely used for various pollutant removal from aqueous medium (Anirudhan et al., 2009).

2.4.5.3 As Sensor
Sensors which are capable of detecting contaminants at trace levels can protect the environment. Availability of a sensitive and inexpensive methods for pollutant detection would lead to significant improvement in control of process, manufacturing, monitoring of ecosystem and in making environmental decision. Nanoparticles are widely used for detecting pollutants because of their high specific area and biocompatibility. Since large segment of the atoms are present on the surface of the nano materials, the properties such as inward distance of surface charge layer becomes crucial (Tseng and Ellenbogen, 2001). However, nanoparticles also have some disadvantages such as aggregation and slow diffusion. The most efficient method to overcome such drawbacks is to immobilize nanoparticles onto the biopolymer matrix. Since the physico-chemical properties of biopolymer can be modified, they can be used for the construction of sensors (Adhikari and Majumdar, 2004). A novel strategy for sensing heavy metal ions using gold nanoparticles that were capped with chitosan was reported (Sugunan et al., 2005). In this case, glutamate ions were utilized to cap the surfaces of nanoparticle. The cationic nature of chitosan permitted the attachment of the biopolymer towards the negatively charged gold nanoparticles via electrostatic interactions. The use of chitosan serves two purposes, (a) to provide enough steric hindrance thereby ensuring colloid stability (b) functionalization of the nanoparticles to serve as sensors. The sensitivity of gold nanoparticles towards agglomeration and the well-known chelating properties of chitosan have been utilized to detect trace levels of metal ions (Zn$^{2+}$ and Cu$^{2+}$) in aqueous solution. A hybrid composite composed of chitosan, glucose oxidase and gold nanoparticles was reported as biosensor for quantitative measurement of glucose (Luo et al., 2004).
2.5 Adsorption Equilibrium Models and Kinetic Models

Adsorption equilibrium modeling is needed for experimental data analyses and to understand the process mechanisms, optimizing processes and predict answers to operational changes (Limousin et al., 2007). Various isotherm models viz. Dubinin–Radushkevich (D–R) (Dubinin, 1960), Langmuir model (Langmuir, 1918), Freundlich model (Freundlich, 1906), Sips model (Sips, 1948) and Toth model (Toth, 1971) are used to find out the adsorbent potential during adsorption. Freundlich and Langmuir isotherm models are commonly used equilibrium models for heavy metal adsorption. Langmuir isotherm model suggests for homogeneous adsorption mode whereas the Freundlich isotherm model assumes heterogeneous mode of adsorption.

Reports are available on the application of isotherm models on Hg(II) adsorption (Zeroual et al., 2003; Al Rmalli et al., 2008; Tuzen et al, 2009; Anagnostopoulos et al., 2012; Jafari and Cheraghi, 2014; Bao et al., 2017) and Ni(II) adsorption (Kalyani et al., 2004; Bhatnagar and Minocha, 2010; Kwak et al., 2011; He et al., 2014; Mangaleshwaran et al., 2015; Lakhdhar et al., 2016).

Various kinetic models viz. zero order (Covelo et al., 2004), pseudo first order (Ho, 2004), first order (Gupta et al., 2001), second-order (Cheung et al., 2001), Fractional power (Aharoni et al., 1991), pseudo-second-order (Ho and Mckay, 1999), Elovich (Low, 1960) have been used to determine rate and mechanism of the adsorption process (Das et al., 2010; Wang et al., 2011; Das et al., 2012). There are various reports on the application of kinetic models on Hg(II) adsorption (Donia et al., 2008; Anagnostopoulos et al., 2012; Jafari and Cheraghi, 2014; Kyzas et al., 2014) and Ni(II) adsorption (He et al., 2014; Salihi et al., 2016).

2.6 Modification of Nanobiocomposites

Metal affinity of the adsorbents can be manipulated by various modification techniques viz. treating with alkali, acid, detergent etc. which may improve the metal removal efficiency of adsorbents (Aqeel Ashraf et al., 2012). Waste textile cellulose fibers were converted into a high performance heavy metal adsorbent fibers (Bediako et al., 2016). The surface of Lyocell materials was modified by introducing carboxyl sites for binding heavy metals via carboxymethylation. This reaction had been largely useful as a chemical method to produce carboxymethyl cellulose (CMC) for its application toward heavy metal removal
and also in food and pharmaceutical industries (Hebeish et al., 2013). β-cyclodextrin is a cyclic oligosaccharide having a polar cavity along with number of hydroxyl functional groups outside and inside the cavity. It has been reported that both organic and inorganic pollutants can form complex with -OH groups present on the surface of β-CD (Malefetse et al., 2009). Recently, immobilization or grafting of β-CD with various supporting materials and functional groups has been applied for the improvement of uptake capacity for heavy metal. Sikder et al. (2014) coupled CM β-CD with functionalized chitosan followed by entrapment of Fe⁰ nanoparticles within the complex and employed this composite for copper(II) and chromium(IV) removal from real wastewater. A complete disappearance of Cu(II) and Cr(VI) was noted due to both adsorption and reduction of metal ions with the oxidation of iron. In order to improve the adsorption capacity and selectivity of magnetic chitosan for the heavy metal removal, modification of surface with new functional groups such as isatin (Monier et al., 2010), xanthate (Zhu et al., 2012), ethylenediamine (Hu et al., 2011), α-ketoglutaric acid (Zhou et al., 2009) and thiourea (Fan et al., 2011) has been reported. Triethylenetetramine is reported to be composed of both primary and secondary amine groups which are known to remove heavy metals through surface complexation (Chen et al., 2015). The synthesis of a chitosan derivate grafted with triethylenetetramine using epichlorohydrin as a cross linking agent to compare its adsorption efficiency and performance with raw chitosan towards the removal of cobalt(II) was reported (Liao et al., 2016). The adsorption capacity was noted to increase in case of crosslinked chitosan derivative (59.51 mg/g) when compared to raw chitosan (30.45 mg/g). Sulfonation has been reported recently as an effective chemical treatment for the better metal ion removal. Sulfonation imparts negatively charged -SO³⁻ groups on the surface of the adsorbent which allows to bind positively charged metal ions via electrostatic interaction (Suopajärvi et al., 2015, Dong et al., 2016).

2.7. Mechanism of Adsorption
The adsorption mechanisms are mostly based on the chemical and physical interactions that occur between heavy metal ions and functional groups on the adsorbent surface such as ion exchange, electrostatic interactions, metal reduction, complexation and chelation of metal ion (Ozer et al., 2005). Various factors viz. metal solution chemistry, type of the biomaterials, environmental conditions etc. influence the adsorption mechanism (Das et
Biomaterials have shown the ability to adsorb heavy metal ions from aqueous medium because of the presence of hydroxyl, amino, carboxyl and phosphate groups to which metal ions could bind (Anagnostopoulos et al., 2012). There are three steps involved in sorption of pollutant onto the adsorbent; the passage of the pollutant from aqueous phase to the adsorbent surface, adsorption onto the surface and pollutant transport within the adsorbent (Barakat, 2011). Adsorption mechanism can be classified into physical adsorption and chemical adsorption depending on the nature of forces that exist between adsorbent and adsorbate. Chemical adsorption mechanisms include chelation, complexation and micro-precipitation, while physical adsorption mechanisms generally involve electrostatic forces and ion exchange. Numerous low-cost adsorbents that are derived from natural material, agricultural waste or modified biopolymers are utilized for heavy metal remediation from metal-polluted wastewater.

2.7.1 Mechanism of Mercury(II) Adsorption

Vieira et al. (2011) investigated the mechanism of mercury(II) adsorption on pristine chitosan film and glutaraldehyde and epichlorohydrin crosslinked chitosan films using XPS analysis. Glutaraldehyde crosslinked chitosan film exhibited the good capacity to adsorb mercury(II) ions when compared to all the three adsorbents even though a reduction in the concentration of C atom was noticed in all the cases. A decrease in the intensity of C atom to 286.3 eV was noted in glutaraldehyde-crosslinked chitosan which suggested that adsorption of mercury occurred on the structure from primary aldehyde and amino terminal. In case of epichlorohydrin crosslinked and natural chitosan films, a possible interaction could also be suggested between mercury(II) ions and unreacted hydroxyl and amino groups.

The mechanism of mercury(II) adsorption by malt spent rootlets (MSR) was investigated using FTIR analysis (Anagnostopoulous et al., 2012). The spectra of mercury bound MSR revealed that the functional groups viz. carboxylic acids, amines and phosphonates are involved in the adsorption process as the intensities of various bands were found to be lower than those of MSR before mercury adsorption.

Kyzas et al. (2014) reported the use of chitosan as a filler of graphite oxide (GO) to prepare graphite oxide/chitosan composites to improve mercury(II) adsorption properties. Hydroxyl, carboxyl and epoxy functional groups of graphite oxide interacted with amino
(-NH\textsubscript{2}) groups of chitosan thereby creating new active sites for adsorption of mercury(II). The possible interactions between the composites and mercury(II) were elucidated via various characterization techniques (FTIR, XRD, SEM/EDAX, DTG).

Multiwalled carbon nanotubes were employed for mercury(II) removal (Alijani et al., 2015). Mechanism of mercury adsorption was found to be complex as both the chemical and physical mode of adsorption were involved at the same time.

Bao et al. (2016) studied the mechanism of Hg(II) adsorption on mercapto amine-functionalised silica-coated magnetic nano-adsorbents (MAF-SCMNP) using FTIR and XPS analysis. The FTIR spectra of Hg(II) loaded MAF-SCMNP showed new peak at 1637 cm\textsuperscript{-1} which can be accredited to nitrogen atoms on the adsorbent surface known to form coordination bonds with metal ions. This could be possibly due to the adsorption of mercury ions onto imine groups present on MAF-SCMNP. Moreover, the disappearance of the peak at 2538 cm\textsuperscript{-1} occurred mainly due to ion exchanges between the thiol functional groups and Hg(II) ions. XPS spectra of MAF-SCMNPs-Hg revealed the presence of Hg peak (101.8 eV) in addition to the peaks of N (399 eV), C (285 eV), O (531 eV) and S (163 eV) for MAF-SCMNPs. These results confirmed that Hg\textsuperscript{2+} ions might be loaded onto the surface of MAF-SCMNP via the formation of coordination bonds between Hg(II) ions and nitrogen and sulphur atoms present on the surface.

### 2.7.2 Mechanism of Nickel(II) Adsorption

Kwon and Jeon (2013) reported the application of sericite for nickel(II) removal from actual wastewater. Results suggested that functional groups such as aluminols and silanols enhanced nickel adsorption via covalent bonding. It was also suggested that when sericite comes in contact with nickel(II) ions, the alkali earth ions (Mg(II) and Ca(II)) found in sericite could be replaced by Ni(II) via ion exchange mechanism.

Adsorption of nickel onto silica hybrid adsorbents was investigated by Xu et al. (2016). The adsorbents were prepared via sol gel process by the reaction of N-[3-(trimethoxysilyl)propyl] ethylene diamine with crosslinking agent (epichlorohydrin). The nickel(II) adsorption was well defined by pseudo-second-order kinetic model which indicated adsorption mechanism as diffusion-chemisorption.

Ndayambaje et al. (2016) reported the adsorption of nickel(II) using polyacrylonitrile (PAN) nanofibers which was chemically modified with the chelating
ligand 2-(2'-pyridyl)imidazole (pim). The ligand was attached to the PAN nanofibers via nucleophilic addition of pim to the nitrile groups present on PAN and the conversion of nitrile groups was gravimetrically measured using FT-IR and acid adsorption measurement. The adsorption of nickel was suggested to take place by forming a complex with the chelating ligand attached on the PAN nanofibers.

Yang et al. (2016) reported nickel(II) adsorption onto Ca(OH)$_2$ modified green tea waste. In the pH range (2-8), Ni(II) adsorption onto the adsorbent was solely governed by van der Waals force as repulsion occurred between positively charged adsorbent and Ni$^{2+}$ ions. Nickel(II) adsorption onto modified green tea waste was well described by Freundlich model and kinetic data by pseudo-second-order model.

2.8. Metal Removal in Column Mode

Metal removal using adsorbents is based on batch studies which offer essential information regarding the efficiency of sorbate-sorbent system. This data could not be appropriate in case of continuous system (Oguz, 2014). Continuous flow processes are the most appropriate systems for the heavy metal removal as they can achieve high yield, simple to function and can be scaled up easily at industrial-scale (Dhoble et al., 2017). Packed bed columns are most useful in treatment of wastewater at large-scale. They have diverse advantages over the treatment carried out in batch mode. In packed bed column, the protocol of separation stages can be mechanized and higher grades of purification could be attained in single step process. It is also known to be effective for cyclic sorption and desorption studies, as it best uses the concentration difference which is known as the driving force for metal adsorption. It also permits effective use of adsorbent capacity and provides effluent of improved quality. A large capacity of wastewater can be treated continuously using a definite quantity of adsorbent in the column and also reuse of the adsorbent is possible (Lee et al., 2017).

The adsorbent efficiency could be estimated from breakthrough curve of concentration of effluent where an S-shaped curve is spotted. Various models viz. Yoon-Nelson, Bohart-Adams, Yan, Thomas, Clark and Wolborska have been used for the prediction of breakthrough curve obtained during adsorption in a packed bed column (Borna et al., 2016). Among these, the Thomas and Bohart-Adams models have been
commonly used for the determination of distinctive parameters during the process of targeted contaminant adsorption (Vijayaraghavan and Yun, 2008).

Kazemi et al. (2016) studied the removal of mercury in column mode using functionalized activated carbon (AC) derived from sawdust. The effects of flow rate, Hg(II) concentration and column bed height on the breakthrough curve were studied in a packed-bed column adsorption. It was observed that the uptake capacity estimated by both Thomas and Yan models was found to be satisfactory.

Duan et al. (2016) attempted to remove mercury in column mode using sand coated with pyrite particles. The column kinetics for mercury removal were studied by Thomas and Yan model where the Yan model predicted a better data than the Thomas model. The effect of pH was noted to largely affect the efficiency of mercury removal. With a decrease in pH, the breakthrough curves were observed to shift to the left indicating that the capacity of mercury removal decreased. Moreover, an increase in the steepness of the breakthrough curves was observed at low pH indicating a faster kinetics.

Functionalized multi-walled carbon nanotubes (MWCNTs) were reported to remove mercury from synthetic wastewater in column mode (Hadavifar et al., 2016). Column studies were conducted using thiolated multi-walled carbon nanotubes (MWCNTs-SH) using a bed height: 14 mm, flow rate: 1 ml/min and influent concentration: 20 mg/L. The obtained breakthrough curves were analyzed and data well fitted for both Thomas and Yan model with R² value ranging from 0.98 to 0.99 which signified that in a fixed bed column both models were appropriate to define Hg(II) adsorption onto MWCNTs-SH.

The adsorption potential of polyurethane foam cube for nickel removal was investigated in a packed bed column (Mangaleshwaran et al., 2015). The removal efficiency was noted to increase with lower flow rate: 2 ml/min and higher bed height: 10 cm. It was concluded that adsorption method is a suitable alternative method to remove metal ions from industrial effluents in large scale.

Mishra et al. (2016) reported nickel(II) removal from wastewater by modified biomass of *Hydrilla verticillate*. Effect of column parameters viz. particle size, bed height, flow rate and influent concentration were studied and was found to be favorable at smallest particle size (0.25-0.50 mm), maximum bed height (25 cm), lowest metal concentration (5
mg/L) and minimum flow rate (10 ml/min). Thomas and Bed Depth Service Time (BDST) models were used for the analysis of the breakthrough curves and the data well fitted to both the models.

2.9. Desorption and Regeneration

Desorption is an important step involved in the process of adsorption which permits adsorbent reuse and recovery of the sorbates (Lee et al., 2017). Regeneration experiments are generally carried out using mild bases and acids. It is necessary that desorbing agent used should not hinder the adsorbent and in some cases, it was noted that the desorbing agent may hamper the efficiency of the adsorbent.

Donia et al. (2008) reported the elution of adsorbed mercury from Schiff base modified magnetic chitosan resin. Sorption/desorption of Hg(II) loaded resin was carried out for three cycles using potassium iodide (0.1 M) at a flow rate of 1 ml/min. It was observed that the breakthrough curves for Hg(II) recovery exhibited no significant changes after successive cycles indicating that the resin had better efficiency and durability for repeated use.

Arencibia et al. (2010) reported the desorption of mercury(II) bounded to functionalized silica using 1M solution of different desorbing agents such as potassium thiocyanate, potassium bromide, hydrobromic acid and thiourea. A significant amount of mercury was removed by all the chemical agents, HBr being the best showing the regeneration percentage up to 65%. Complex formation between bromide and mercury such as HgBr$_2^-$ and HgBr$_3^-$ favored the removal of mercury.

Desorption of mercury from malt spent rootlets using 0.1 M solution of EDTA, NaCl, HNO$_3$ and HCl was investigated (Anagnostopoulos et al., 2012). Out of four eluting solutions, highest removal (54%) of the adsorbed Hg(II) was observed in case of HCl.

Kazemi et al. (2016) reported the desorption of mercury from functionalized activated carbon using several bases (NaCO$_3$, NaOH and KOH) and acids (H$_2$SO$_4$, HNO$_3$, H$_3$PO$_4$ and HCl). It was observed that desorption of mercury treated by base eluents was relatively low (approximately 15% in case of all) when compared to acid eluents (21, 27, 35 and 46% for H$_3$PO$_4$, HNO$_3$, H$_2$SO$_4$ and HCl respectively).

Mangaleshwaran et al. (2015) reported the regeneration of polyurethane foam cube by eluting the bound nickel ions with HCl (1M) and it was noted that until fifth cycle, the
uptake capacity remained same. However, a decrease in Ni(II) removal was noticed in further cycles.

Desorption of adsorbed nickel(II) ions from modified biomass of *Hydrilla verticillata* was carried out using 0.1M HNO$_3$ (Mishra et al., 2016). The biomass can be reused upto 10 cycles in continuous process of adsorption/desorption as suggested from the results.