1. Introduction

1.1. Environmental issues

An environmental issue has concerned substantial attention as their harmful effects on the atmosphere and human being health. In fact, generally the urbanized countries have previously implied the fact that the particularly survival of life on earth may be endangered, if proper steps are not taken for the prevention, control and abatement of environmental issues. The impaction of man on environment and the individual activity has altered which in turn is altering the face of an earth. Growing human population and technology had been give severe pressure on earth mainly which cannot be reversed. This has created an attention among the scientists and technologists to study the environmental issue aspects, status and the removal strategies.

This is a list of environmental issues as such Climate change, Conservation Environmental degradation, Environmental health, Genetic engineering, Intensive
farming, Land degradation, Soil, Nanotechnology, Nuclear power debate, Overpopulation
Ozone depletion, Pollution.

Among them only pollution was studied in this thesis.

1.2. Pollution

Pollution is the introduction of contaminants into the natural environment that induces unfavorable change. It can take the form of chemical substances or energy, such as noise, heat or light. Pollutants, the components of pollution, can be either foreign substances/energies or naturally occurring contaminants. The major forms of pollution are listed below along with the particular contaminant relevant to each of them such as Air pollution, Water pollution, Light pollution, Noise pollution, Soil contamination, Radioactive contamination, Thermal pollution and Visual pollution.

Among them only water pollution was studied in this thesis.

1.3. Water pollution

Water pollution is one of the mainly severe threats faced at present by the mankind in our atmosphere [1]. It is defined as the taking away of waste resources into them have altered their quality and cause them to be polluted and not fitting for living beings. It has been proposed that it is the resulting universal cause of deaths and diseases, and that it reports for the deaths of more than 14,000 people daily.

Category

Surface water and groundwater have frequently been studied and handled as individual resources, even they are interrelated. Surface water oozes through the soil and
turns groundwater. Conversely, groundwater can also run surface water sources. **Origins of surface water pollution are mainly classified into two classes.**

1.3.1. **Point sources**

It concerns to contaminants that introduce a waterway from a single, specifiable source, such as a pipe. Good examples of sources in this class include discharges from a sewage treatment plant, a industry, or a urban center storm drain.

1.3.2. **Nonpoint sources**

This refers to spread contamination that does not arise from a single distinct source. NPS pollution is often the accumulative effect of small amounts of contaminants collected from a large area. A general example is the leaching out of nitrogen compounds from fertilized agricultural lands. Nutrient runoff in storm water from "sheet flow" over an agricultural field or a forest is also referred as examples of NPS pollution.

1.3.3. **Heavy metals and environmental pollution**

Water pollution due to **heavy metals** (Cu$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Ba$^{2+}$, Co$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$) has concerned significant concentration because of their detrimental effects on the environment and human health. **Any toxic metal may be called heavy metal**, regardless of their atomic mass or density. These include the transition metals, some metalloids, lanthanides, and actinides. Heavy metals are non-biodegradable and they can be conglomering in living organisms. They are universally released to the environment from various industrial activities such as leather tanning, smelting, electroplating, painting, mining, alloy and battery manufacturing, etc., creating a main threat to the environment and public health [2-4].
Heavy metals disrupt metabolic functions in two ways:

1. They accumulate and thereby disturb function in vital organs and glands such as the kidneys, bone, liver, heart, brain, etc.

2. They move the vital nutritional minerals from their place, thereby, blocking their biological function [5].

1.4. Toxicity of Heavy metals

Heavy metal is a universal common name, which related to the group of metals and metalloids with atomic density greater than 4000 kg m$^{-3}$ or 5 times more than water [6]. These are usual components of the earth’s crust. Although the minority of them (Fe$^{3+}$, Cu$^{2+}$, Zn$^{2+}$, Mn$^{2+}$) act as vital micro nutrients for living organisms and also essential to biochemical reactions, they will answer to hazardous toxic situation at superior levels [7]. The heavy metals like Cu$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Ba$^{2+}$, Co$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ and Hg$^{2+}$ etc., are tremendously detrimental to living beings even at low concentrations as a consequence of suppression of several natural protection mechanism. The perniciousness of Hg, Cu, Cr, Cd, Ni and Pd is due to their bioaccumulation trend by food chain, which induces adverse effects on human being healthiness. Generally, the heavy metals cause irritation, nerve system injuries, heart diseases, kidney malfunction, hypertension, brain damage and cancer, disturbed metabolism, renal systems cardiac strain and destruction of central nervous. Enchanting these aspects in consideration, the main aim of this study was to sequestration of Cu$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Ba$^{2+}$, Co$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$ ions from aqueous solution in batch and column process and determines the adsorption capacity
of these heavy metal ions using various ion exchangers (polymer matrix, low cost ion exchangers, zero valent nanoparticles and polymer nanocomposites).

1.4.1. Toxicity of Mercury

It is employed in float valves, mercury switches, mercury relays, thermometers, barometers, manometers, sphygmomanometers, fluorescent lamps and other strategy however worries on the element's toxicity have led to mercury thermometers and sphygmomanometers being principally phased out in clinical environments in favour of choices such as thermistor or infrared-based electronic instruments, galinstan-filled glass thermometers.

It is a neurotoxin that can reason injure to the central nervous system. High concentrations of mercury reason destruction of chest pain and dyspnoea, pulmonary and kidney function [8].

1.4.2. Toxicity of Lead

It has a shiny chrome-silver luster while it is melted into a liquid and it is used in bullets and shot, weights, as part of solders, pewter’s, lead acid –batteries, building construction, radiation shield and fusible alloys.

If consumed, it is toxic to animals as well as humans. It damages the nervous system and causes brain disorders. Too much lead also causes blood disorders in
mammals. Resembling the element mercury, one more heavy metal lead is a neurotoxin that collects both in soft tissues and the bones [9].

1.4.3. Toxicity of Copper

It is vital to the entire living organisms as a trace dietary mineral because it is a key ingredient of the respiratory enzyme complex cytochrome c oxidase. In molluscs and crustacea copper is a essential of the blood pigment hemocyanin, which is changed by the iron-complexed hemoglobin in fish and other vertebrates. The major areas where copper is found in humans are liver, muscle and bone. Copper compounds are used as fungicides, bacteriostatic substances and wood preservatives.

However the excessive ingestion of copper brings regarding serious toxicological concerns, such as convulsions, vomiting, cramps, or even death [10].

1.4.4. Toxicity of Nickel

It is one of the mainly important metals among heavy metals. Divalent nickel is discharged to environment from hydrometallurgical industry, leather tanning, electroplating, paint industry, metal finishing, mineral processing, silver refineries, zinc base casting, steam-electric power plants and storage battery industries.

Nickel and their compounds causing a variety of diseases and disorders including pulmonary fibrosis, renal edema, skin dermatitis, and gastrointestinal distress is carcinogenic, non-biodegradable, and tend to accumulate in living organism. Divalent nickel especially causes cancer of lungs, nose, and bone [11].
1.4.5. Toxicity of Cadmium

It was utilized for a long time as a pigment as well as corrosion resistant plating on steel as cadmium compounds were used to stabilize plastic. The use of cadmium is usually falling due to its toxicity and the substitution of nickel-cadmium batteries with nickel-metal hydride and lithium-ion batteries. One of its few new uses is in cadmium telluride solar panels. Even though cadmium has no known biological function in higher organisms, a cadmium-dependent carbonic anhydrase has been found in marine diatoms.

The main anthropogenic pathway of cadmium incoming environment is through wastes from industrial processes such as pigments, batteries, electroplating, alloy manufacturing, and textile operations. Cadmium entering body could reason severe damages of the kidneys, lungs, bones and hypertension [12].

1.4.6. Toxicity of Manganese

It is the next most abundant metal in an environment. Its most general mineral is pyrolusite (MnO₂). It is vital metal for the human system and enzymes activation. It has a diversity of applications in ceramics, dry battery cells and electrical coils; it is also an alloying element.

The neurological effects of breathed in manganese have been well recognized in humans constantly exposed to superior levels in the workplace. The syndrome known as “manganism” is caused by introduction to very high levels of manganese dusts or fumes and is characterized by a “Parkinson-like syndrome”, including weakness, slow speech, monotonous tone of voice, emotionless “masklike” facial expression and slows anorexia,
muscle pain, apathy, and clumsy movement of the limbs. Generally, these effects are irreversible [13].

1.4.7. Toxicity of Zinc

A lot of industrial facilities such as batteries, mining operations, metal plating, petroleum refining, tanneries, electronic and chemical plants, pigments, alloys and fertilizer release Zn (II) ions through their waste effluents.

In spite of a necessary micronutrient for life, zinc can also lead to increased thirst, neurologic symptoms, depression and lethargy ahead of the limit suitable concentration in living organism [14].

1.4.8. Toxicity of Cobalt

Cobalt and its salts are used in grinding wheels, painting on glass and porcelain, nuclear medicine, enamels and semiconductors, hygrometers and electroplating; as a foam stabilizer in beer, varnishes and paints, catalyst for organic chemical reactions, in vitamin B12 manufacture and acts as a drier for lacquers.

It has together favorable and unfavorable effects on health. The effects of sharp cobalt poisoning in humans are very severe, among them are asthma like causing heart failure, damage to the thyroid, allergy, damage to the heart and liver. It might reason mutations (genetic changes) in living cells. Exposure to ionizing radiation is related with an augmented risk of developing cancer. Several isotopes of cobalt do emit ionizing radiation [15].

1.4.9. Toxicity of Barium
Barium, since a metal or while alloyed with aluminium, is utilized to eliminate unwanted gases (gettering) from vacuum tubes, for example TV picture tubes. Barium oxide is utilized in a covering for the electrodes of fluorescent lamps, which assists the free of electrons. Barium carbonate is used in glassmaking. Being a heavy element, it enhances the refractive index and luster of the glass.

Water-soluble barium compounds are toxic. At low doses, barium ions act as a muscle stimulant, while higher doses affect the nervous system, reasoning weakness, anxiety, cardiac irregularities, tremors, paralysis, dyspnea, blindness and sensitization [16].

1.5. Heavy metal wastewater Management methods

1.5.1. Chemical precipitation

This method is effectual and considerably used this process in industry [17] since it is comparatively easy and low-cost to operate. In this processes, chemicals react with heavy metal ions to get insoluble precipitates. The forming precipitates can be divided from the water through sedimentation or filtration process. In addition to the treated water is then decanted and properly released or recycled. The common chemical precipitation processes include hydroxide precipitation and sulfide precipitation [18].

1.5.2. Chemical precipitation combined with other methods

This has been exposed to be doing well while combination with other methods [19]. Here, various reports scheduled chemical precipitation in combination with ion-exchange treatments. Ion-exchange process alone as well as followed by combining with chemical precipitation in eliminating nickel from wastewater from a rinse bath of
aluminum parts [20]. They established that the individual application of ion exchange led to the removal of nickel up to 74.8%, at the same time as using the combination of ion exchange and precipitation processes, superior removal from 94.2% to 98.3% was achieved [21].

1.5.3. Heavy metal chelating precipitation

Since be acknowledged, traditional chemical precipitation methods have numerous limitations and it is complex to meet the progressively more strict environmental regulations by application of the method to handle the heavy metal wastewaters mainly including coordinated agents. Since, various factories apply chelating precipitants to remove heavy metals from aqueous medium. Trimercaptotriazine and sodiumdimethyldithiocarbamate heavy metal precipitants are used removal of toxic metals form aqueous solution [22].

1.5.4. Membrane filtration

This methods by various kinds of membranes demonstrate enormous agree for heavy metal retention for their high effectiveness and trouble-free process. This processes used to remove heavy metals from the aqueous solution as well as wastewater are ultrafiltration [23], reverse osmosis [24], nanofiltration [25] and electrodialysis [26].

1.5.5. Coagulation and flocculation

These two methods succeeded with sedimentation and filtration is too applied to removal of heavy metals from wastewater. The destabilization of colloids through neutralizing the forces to maintain them away from each other is known coagulation. A lot of coagulants are commonly used in the wastewater treatment processes for example
ferric chloride, aluminium and ferrous sulfate ensuing in the successful exclusion of wastewater particulates and contaminants via charge neutralization of particles and in enmeshment of the contaminants lying on the formed amorphous metal hydroxide precipitates. The removals of heavy metal with coagulation of shared drain flood with two commercial coagulants, a ferric chloride solution and a polyaluminium chloride (PAC). They created tremendous heavy metal removal was attained in a fine range of coagulant about optimal coagulant concentrations [27].

Flocculation techniques are the act of polymers to form bridges between the flocs and bind the particles into huge agglomerates or clumps. When suspended particles are flocculated into bigger particles, they can frequently be eliminated or separated by filtration (or) floatation. Nowadays numerous types of flocculants, for instance polyferric sulfate (PFS), PAC, and polyacrylamide (PAM), are extensively used in the management of wastewater, though, it is virtually impractical to eliminate heavy metal wonderfully from wastewater openly through these recent flocculants. Macromolecule heavy metal flocculants is a novel kind of flocculants. A macromolecule heavy metal flocculant mercaptoacetyl chitosan by reacting chitosan with mercaptoacetic acid. They accounted that this novel flocculant could not only remove turbidity and as well remove heavy metals in wastewater [28].

1.5.6. Flotation

This process has now found wide use in wastewater treatment and applied to removal of heavy metal from aqueous medium with effervesce attachment, made in
mineral processing. Ion flotation, precipitation flotation and Dissolved air flotation (DAF) are the major flotation processes for the removal of metal ions from solution.

1.5.7. Electrochemical treatment

This method demands the plating-out of metal ions lying on a surface of a cathode as well recover metals into the elemental state. This technology involves comparatively more capital investment and the supply of expensive current, thus they haven’t been extensively used.

1.5.8. Adsorption

This technique is currently acknowledged as an efficient and profitable method for wastewater treatment. This process suggests flexibility in design and function. Besides, adsorption is reversible at times, adsorbents can be recovered with appropriate desorption method [29].

1.5.9. Ion exchange

These methods have been generally used to remove heavy metals from wastewater due to their numerous advantages, superior removal efficiency, fast kinetics and high treatment capacity [30]. Synthetic resins are universally chosen as they are effective to practically remove the heavy metals from the solution amongst the resources used in these processes [31]. Mainly used cation exchangers are strongly acidic resins by sulfonic acid groups (-SO₃H) and weakly acid resins by carboxylic acid groups (-COOH).

*Hydrogen ions in the sulfonic group or carboxylic group of the resin can act as exchangeable ions with metal cations in wastewater. Since the wastewater contains*
heavy metal surpass throughout the cations column, metal ions are exchanged for the hydrogen ions on the resin with the following ion-exchange process:

\[
nR-\text{SO}_3\text{H} + M^{n+} \rightarrow (\text{RSO}_3^{-})_n M^{n+} + n\text{H}^+ \quad (1)
\]

\[
nR-\text{COOH} + M^{n+} \rightarrow (\text{RCOO}^-)_n M^{n+} + n\text{H}^+ \quad (2)
\]

The removal of heavy metal ions with ion-exchange resins is slightly affected by definite variables like initial metal concentration, contact time, pH and temperature [32]. The power of ionic charge on the removal of Fe$^{3+}$, Ce$^{4+}$ and Pb$^{2+}$ from aqueous solution through cation-exchange resin purolite C100 was tested with [33]. In this research work, this method was followed for the removal of heavy metals from aqueous solution using the polymer matrix, low cost ion exchangers, Zero-valent nanoparticles and polymer nanocomposites.

1.6. Zero-valent nanoparticles

These have been large potential as redox active medium and catalysts because of their large high reactivity, specific surface area, shape-dependent optical, catalytic property and electronic, which have paying attention of many researchers toward design extremely efficient photo-catalytic materials for decontamination of contaminated waters and gases. The general catalytic nanoparticles comprise nanosized semiconductor materials such as ZnO [34], CdS [35], WO$_3$ [36], nano-TiO$_2$ [37], zero-valence metal such as Cu$^0$ [38], Zn$^0$ [39] and Fe$^0$ [40] and bimetallic nanoparticles such as Fe/Al [411], Zn/Pd [42] and Fe/Ni [43]. These are generally used as catalysts or redox reagents for removal of more types of environmental contaminants like azo dyes [44], organochlorine pesticides [45], PCBs (polychlorinated biphenyls) [46], halogenated
herbicides [47] and heavy metals [48]. Conversely, the employ of aqueous suspension restrictions their extensive applications due to the troubles about separation of the fine particles as well as the recycling of the catalyst. Arrest of these nanoparticles onto polymer matrix such as ion exchangers [49], polymeric membranes [50] and porous resins [51] has been existing to resolve the problems to significant extent, acting for the reduction of particle loss, hindrance of particles agglomeration and potential function of convective flow happening through self-supporting particles. Previous research work has recognized that several nanoscale metals are Fe\(^0\), Cu\(^0\) and Zn\(^0\) are very efficient in removing various organic contaminants such as chlorinated methanes, brominated methanes, other polychlorinated hydrocarbons, trihalomethanes, chlorinated ethenes, chlorinated benzenes, dyes and pesticides. The metal nanoparticles reactivity is generally very high such as nanoscale zero-valent iron (nZVI) can still self-ignite while exposed to air. Therefore, supporting the particles is essential to protect their chemical nature through bottling up oxidation until they can react with the targeted pollutants. The synthesized cation exchange resin supported nanoscale zero valent copper (nZVC) to develop the removal of carbon tetrachloride (CCl\(_4\)) from water. The employ of the cation exchange resin as a support efficiently prohibited the decrease of surface area because of the agglomeration of nZVC particles. Besides, the cation exchange resin regenerated the copper ions formed from the reaction between CCl\(_4\) and Cu\(^0\) (Zerovalent) through concurrent ion exchange. The decrease in the quantity of CCl\(_4\) in aqueous solution resulted from the shared effects of degradation by nZVC as well as adsorption with the host resin. The pseudo-first-order rate constant regularized via the surface-area as well as
the mass concentration of nZVC was about 20 times that of commercial powdered ZVC. But, these nano-adsorbents have numerous clear limitations like high energy consumption, high preparation cost and strict operational conditions. These limitations which may control function areas of nano-particles adsorbents in wastewater treatment previously turned into a severe problem cannot be unobserved. To defeat this, there is a must very hygienic, non-hazardous, bio-compatible and environment friendly materials synthesized through ‘green’ approach. The capability plants to make nanoparticles have characterized exciting loom toward the growth of natural nano-factories. This fact has brought an approaching among researchers for improvement of molecules which are specific and efficient via using well-designed and resourceful methods. Considerable efforts have been made to synthesize nanoparticles like silver, gold, platinum, palladium, etc using plants of natural origin. Previously, silver nanoparticles (AgNPs) were synthesized using various plant extracts such as Desmodium triflorum [52], Moringa oleifera [53] and so on. Until now, the AgNPs were not synthesized using Cyperus rotundus grass extract (CRGE). Hence, we report an inexpensive, versatile, and very reproducible ecofriendly method for the large-scale synthesis of AgNPs by biological reduction process using plant extract CRGE. Here, CRGE acts as a reducing and also capping agent. So far, the CRGE capped AgNPs as Ag\(^0\) (silver zero valent nanoparticles) was not utilized for heavy metals retention. \textit{Hence in the present study, we have synthesized AgNPs through green route and applied these for adsorbing heavy metals from aqueous solution.}

1.7. Polymer nanocomposites (Potential Donnan Membrane Effect)
As the particle size obtains into nanoscale, they showed to be more efficient due to the very large surface area as well as high reactivity. So far growing nanocomposite adsorbents were considered through impregnating the inorganic nanoparticles within the conventional polymers, that is, ion-exchangers [54], alginate [55], cellulose [56] and porous resins [57] to avoid problems caused through the ultra-fine particle size like transition loss and excessive pressure drops. Porous polymeric adsorbents or ion exchangers have demonstrated to be best substitutes to construct like hybrid adsorbents while considering their outstanding mechanical strength as well as adaptable surface chemistry of the polymeric supports [58]. Thus in the current study, the following macro porous cation exchangers like Resorcinol-formaldehyde resin (RFR), Para cresol-formaldehyde resin (CFR) and Phenol-formaldehyde resin (PFR) were used as polymeric host materials (supporting materials) for loading AgNPs. The immobilized charged functional groups bound to the polymeric matrix are supposed to develop penetration of inorganic pollutants of counter charges, which can be understood through Donnan membrane principle [59].

1.8. Batch studies

Batch adsorption experiments were conducted by placing a desired amount of various adsorbents in 100 ml conical flasks containing 40 ml of various concentration of metal ions solution. The flasks were agitated at 200rpm in a Remi rotator shaking machine at the constant temperature to reach equilibrium. Aliquot samples were taken from the flask at appropriate time intervals as necessary. The residual concentration of the metal ions in the aqueous phases was determined by using standard titration
techniques as per the literature [60]. The equilibrium adsorption capacity of the adsorbents was estimated with the help of following equation:

\[ q_e = (C_0 - C_e) \times \frac{V}{M} \quad (3) \]

Where, \( q_e \) is the equilibrium adsorption capacity (mg g\(^{-1}\)), \( C_e \) is the concentration of metal ion (mg L\(^{-1}\)) at equilibrium, \( V \) is the volume of solution (L) and \( M \) is the weight (g) of adsorbent. Moreover the influence of the resin dosage for ion-exchange experiments was performed in the range of 0.010 - 0.030g. The effect of grain size on adsorption capacity of RFR, LCIER and LCIER-AgNPs was also studied in the 200-300 μm range.

1.9. Adsorption Isotherms

In order to study the adsorption data, the Freundlich and Langmuir adsorption isotherms are applied.

1.9.1. Freundlich isotherm

Freundlich adsorption isotherm [61] in its linearised form is known by the equation

\[ \log q_e = \log K + \frac{1}{n} \log C_e \quad (4) \]

Where, \( q_e = (x/m) \), is the amount of metal ion adsorbed (in mg g\(^{-1}\)) per unit mass of the adsorbent at equilibrium; \( m \) is mass of the adsorbent (in g\(^{-1}\)), \( K \) and \( 1/n \) are the Freundlich constants, which are the measures of adsorption capacity (in mg g\(^{-1}\)) and intensity of adsorption, correspondingly. The value of \( 1/n \) \([0 < (1 / n) < 1]\) is a fraction, in order that, the value of \( n \) is a whole number \((n > 1)\), which is the order of adsorption. A plot of \( q_e \) versus \( C_e \) is established to be an exponential one. Though, when the values of \( \log q_e \) are plotted against \( \log C_e \) values, straight line plots are found with \( \log K \) value as the
intercept and \((1/n)\) value as the slope. Freundlich constants are determined through using linear regression analysis as well as reported.

### 1.9.2. Langmuir isotherm

Langmuir adsorption isotherm [62] is specified with the expression

\[
\frac{C_e}{q_e} = \left(\frac{1}{Q_b}\right) + \left(\frac{C_e}{Q_0}\right) \quad \text{------------ (5)}
\]

Where, \(q_e\) is the amount of metal ion adsorbed (in mg g\(^{-1}\)) at equilibrium contact time (i.e., time for maximum adsorption), \(C_e\) is the equilibrium concentration (in ppm) of metal ion and \(a\), \(b\) are the Langmuir constants correspondingly, the monolayer adsorption capacity (in mg g\(^{-1}\)) and adsorption energy (in g\(^{-1}\)). A plot of \((C_e/q_e)\) versus \(C_e\) is established to be linear with \((1/Q_0)\) as the slope and \((1/Q_0b)\) as the intercept. This plot is known as Langmuir adsorption isotherm plot. The pertinence of Langmuir isotherm demonstrates the development of unimolecular layer and then the nature of adsorption process. Then, the necessary characteristics of the Langmuir isotherm can be explained in expressions of a dimensionless constant viz., **separation factor or equilibrium parameter**, \(R_L\), which is defined with the equation [63].

\[
R_L = \frac{1}{1 + bC_i} \quad \text{------------ (6)}
\]

Where, \(b\) is the Langmuir constant (in L mg\(^{-1}\)) and \(C_i\) is the (optimum) initial concentration (in mg L\(^{-1}\)) in the adsorption studies. The value of \(R_L\) assumes the nature of adsorption isotherm as well as the feasibility of adsorption process as follows:

<table>
<thead>
<tr>
<th>(R_L) value</th>
<th>Adsorption process</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (\leq R_L &lt; 1)</td>
<td>Favorable</td>
</tr>
<tr>
<td>1 (R_L = 1)</td>
<td>Linear</td>
</tr>
<tr>
<td>(R_L &gt; 1)</td>
<td>Unfavorable</td>
</tr>
</tbody>
</table>
Numerous scientists have employed the Langmuir isotherm to investigate the formation of monolayer of adsorbate/solute and the nature and the favourability of the adsorption process by $R_L$ values.

### 1.10. Kinetics of Adsorption

Kinetic studies of adsorption are important as the data can be utilized for calculating the time required to reach equilibrium, the rate of adsorption can be applied for the following kinetic models

#### 1.10.1. Pseudo first order model

The simple kinetic model that explains the process of adsorption is the pseudo first order equation is recommended with Lagergren for the adsorption of solid/liquid systems as well as used by the author [64].

$$\frac{dq}{dt} = k_{ad}(q_e - q_t) \quad \text{(7)}$$
Where, $k_{ad}$ (min$^{-1}$) is the rate constant of the adsorption and $q_t$ and $q_e$ are the amount adsorbed at time $t$ and at equilibrium in that order. Following integration with the initial condition, $q_t = 0$ at $t = 0$, we get

$$\ln (q_e - q_t) = \ln q_e - k_{ad} t \quad \text{(8)}$$

1.10.2. Pseudo second order model

The rate limiting step for the pseudo second order reaction can be chemical sorption relating valency forces during sharing of electrons between sorbent and sorbate as covalent bonds. Primarily, it has to be assumed that the adsorption follows the Langmuir equation and this has been verified formerly [65]. The rate of pseudo second order reaction may be reliant on the amount of adsorbate on the surface of adsorbent and the amount of adsorbate adsorbed at equilibrium. The sorption equilibrium, $q_e$ is a role of temperature, initial concentration, the adsorbent dose and nature of solute-sorbent interaction. The rate expression for the adsorption is illustrated by

$$\frac{t}{q_t} = \frac{1}{k_2} \frac{q_e^2}{q_e} + \frac{t}{q_e} \quad \text{(9)}$$

Where $k_2$ is the rate constant of sorption (g mg$^{-1}$ min$^{-1}$), $q_e$ is the amount of adsorbate at equilibrium (mg g$^{-1}$), $q_t$ is the amount of adsorbate on the surface of the adsorbent at any time, $t$ (mg g$^{-1}$).

1.11. Intra-Particle Diffusion Model

The intra-particle diffusion process is constantly the rate limiting step in several adsorption processes [66]. The rate of particle transfer by this mechanism is slower than adsorption on the external surface sites of adsorbent. The linear portion of the plot for a extensive variety of contact period between adsorbent and adsorbate does not pass
throughout the origin. Such a divergence of the straight line from the origin possibly caused by the difference in the rate of mass transfer in the initial and final stages of adsorption. Intra-particle is usually described with a relationship between the solid phase concentration and the square root of time. The intra-particle diffusion model is specified by the equation:

\[ q_t = k_p t^{1/2} + c \tag{10} \]

Where, \( q_t \) is the amount of metal ions adsorbed (in mg g\(^{-1}\)) at time \( t \); and \( c \) and \( k_p \) are the intercept and intra-particle diffusion rate constant (unit: mg g\(^{-1}\) min\(^{0.5}\)), respectively. The value of intercept (\( c \)), give an idea about boundary layer thickness, i.e., greater the intercept, larger the boundary layer effect.

1.12. Column adsorption studies

Column experiment was carried out with a fixed-bed glass column with 2.0 cm internal diameter and 35cm height and packed with 2 cm (3.5g) of polymer nanocomposites. The column bed volume is 6.28 cm\(^3\). The flow circulation was enhanced with an addition of glass wool beads. Heavy metal ions solution (initial concentration= 2mg/L) and other co-ions were used as influent with high concentration than the target heavy metals and fed through the column at a constant flow rate of 5 mL/min in down-flow mode. The effluent solution was collected at different time intervals and calculated for metal ions content using EDTA titration techniques. Breakthrough curves were found by plotting volume of the influent against the proportion of metal ions concentrations in
the effluent throughout the column for the adsorption of metal ions from aqueous solution [67].

1.13. Desorption

Adsorption between heavy metal ions and adsorbent can be attained by physisorption or chemisorption or ion-exchange. If the adsorption can be built through physisorption, because the loosely bound metal ions can be effortlessly desorbed with distilled water. On the other hand, if the adsorption process is sustained by chemisorption or ion exchange or combination of both, followed by desorption to be done effectively with strong mineral acid solution. Thus, desorption study can give with a clear idea regarding the mechanism of adsorption and is useful in regeneration of the adsorbent and recovery of the metals. Here, the % of regeneration level of Ion Exchangers was studied by using the different eluting agent [68].

\[
\% \text{ of Regeneration} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100 \quad \text{(11)}
\]

1.14. Equilibrium Studies

Equilibrium studies are carried out at 30, 40, 50 and 60°C with the heavy metal ions using polymer nanocomposites. Thermodynamic parameters are calculated from the equilibrium constant \(K_{eqm}\). The values of standard free energy change \(\Delta G^\circ\), enthalpy change \(\Delta H^\circ\) and entropy change \(\Delta S^\circ\) at standard state have been calculated using the following relationships [69]:

\[
K_{eqm} = \frac{C_{aq} \text{ (solid)}}{C_e \text{ (solution)}} \quad \text{(12)}
\]
\[ \Delta G^\circ = -2.303 \, RT \, \log K_{eqm} \]  \hspace{1cm} (13)

\[ \log K_{eqm} = -[\Delta H^\circ / 2.303 \, RT] + (\Delta S^\circ / 2.303R) \]  \hspace{1cm} (14)

Where,

- \( K_{eqm} \) = equilibrium constant
- \( C_{ad} \) (solid) = Conc of metal ions adsorbed (in mg L\(^{-1}\)) in solid phase at equilibrium.
- \( C_e \) (solution) = Conc of metal ions in aqueous solution (in mg L\(^{-1}\)) at equilibrium.
- \( R \) = Universal gas constant (8.314 J mol\(^{-1}\) deg\(^{-1}\)),
- \( T \) = temperature (in K)
- \( \Delta G^\circ \) = standard free energy change (in kJ mol\(^{-1}\))
- \( \Delta H^\circ \) = standard enthalpy change (in kJ mol\(^{-1}\)) and
- \( \Delta S^\circ \) = standard entropy change (in kJ mol\(^{-1}\) deg\(^{-1}\))

The \( \log K_{eqm} \) values at 30, 40, 50 and 60\(^{0}\)C were plotted against 1/T and linear plots are attained. The \( \Delta S^\circ \) and \( \Delta H^\circ \) values were calculated from the intercept and slope of the linear correlations of \( \log K_{eqm} \) with 1/T.
1.15. **Scope of the Work**

Nowadays, most of the researchers used a polymer based hybrid nanocomposites by impregnating ecofriendly synthesized Zerovalent nanoparticles within a low cost ion exchange resin for highly efficient removal of heavy metals from aqueous solution as well as reduce the cost of the ion exchange resin and treatment process.

*The following are the aims and objectives of the present work;*

- To find out the aspects of utilizing synthetic phenolic resins, low cost plant matters and silver nanoparticles (zero valent) as a raw material for the built-up of low cost ion exchangers for removing heavy metals from aqueous solution.

- To synthesize the phenolic resins like Phenol – formaldehyde resin (PFR), Resorcinol – formaldehyde resin (RFR), P-Cresol – formaldehyde resin (PFR) by formaldehyde acts as a cross-linking agent.

- To prepare the activated carbon from Euphorbia Hirta and crateva nurvala by sulphuric acid treatment.

- To synthesize the various ion-exchangers by substituting the amount of activated carbon in the phenolic resins from 0 to 100% (w/w).
To find out the low cost ion-exchanger(best ion-exchanger) among the various ion-exchangers, the ability of the various ion-exchangers for removing heavy metal ions like (Cu$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Ba$^{2+}$, Co$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Hg$^{2+}$ and Zn$^{2+}$) from aqueous solution was explored.

To synthesize the AgNPs via green route using the plant extracts such as Cyperus rotundus grass extract (CRGE) and phyllathus emblica leaf extract (PELE) as reductant and capping agent.

To synthesize polymer nanocomposites by impregnating the synthesized AgNPs from flora extracts within the low cost ion-exchanger by poly condensation method and these was also explored for the heavy metals retention.

To characterize the AgNPs and ion-exchangers using atomic force microscope (AFM), scanning electron microscope (SEM), energy-dispersive microanalysis (EDX), X-ray diffraction spectroscopy (XRD), flourier transform infra red (FTIR), thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and UV–vis spectroscopy (UV).

To find out the optimal reaction conditions like stirring speed, resin dosage, initial concentration, grain size, contact time by efficient batch mode techniques.

To explain the adsorption mechanism. Pseudo first-order, Pseudo second-order kinetics and Webber-Morris intra particle diffusion were studied.

To match the equilibrium data obtained at different initial concentration with various isotherm models like Langmuir model and Freundlich model as well as to find out the which one of these best fits the experimental data.
To carry out the fixed-bed column adsorption studies to calculate the Breakthrough curves.

To examine the effects of Na\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\) on Hg (II) adsorption with the adsorbent along with the host cation exchanger RFR was also involved for reference to find out the % of adsorption to LCIER-AgNPs toward Hg (II) ions in the presence of competitor ions.

To calculate the thermodynamic parameters (ΔG, ΔH, and ΔS) were calculated by using Van't Hoff isotherm, Van't Hoff and Gibbs Helmholtz equation.

To study the regeneration of the ion-exchangers by using the different efficient regenerators.

1.16. References:


