SYNTHESIS AND CHARACTERIZATION OF ZINC OXIDE NANOPARTICLES AND ITS APPLICATION IN WATER PURIFICTION

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ABSTRACT

The synthesis of Zinc Oxide (ZnO) nanoparticles is designed by sol-gel method in the thesis. The reaction temperature is maintained at room temperature and the reaction time is constant for the preparation of ZnO nanoparticles. The precursor salt concentration is also kept fixed for the synthesis procedure. The calcination temperature is maintained at 450°C. The different types of characterization techniques such as XRD, FTIR, FESEM and EDX for ZnO nanoparticles have been completed.

Water pollution is one of the global issues and there is increase in heavy metals, bacteria and other contaminants in water bodies with time. Cadmium is one of the heavy metals which lead to toxic effects in humans even present in small concentration. In the thesis work, removal of cadmium ions, Cd (II) is done with the help of synthesised ZnO nanoparticles by adsorption process. The antibacterial property of ZnO nanoparticles is also evaluated by varying three different concentrations of ZnO nanoparticles. The efficiency of ZnO nanoparticles as an adsorbent is investigated for removal of Cd (II) ions from synthetic water. Batch mode experiment is performed to evaluate the effect of various parameters of the adsorption process.

The parameters such as pH of the solution and amount of adsorbent dose are studied and removal efficiency of Cd (II) ions and adsorption capacity of Cd (II) ions by ZnO nanoparticle is calculated from the measurement data. The isotherm, kinetics and thermodynamics parameters of adsorption process for Cd (II) ions are also determined in the study. The adsorption isotherm data is found to be agreed with Langmuir isotherm model. Pseudo second order model is best described the adsorption kinetics value with high regression coefficients. Thermodynamic study results reveal that the adsorption process is endothermic and spontaneous. This suggests the positive outcome for the removal of cadmium ions from aqueous solution by zinc oxide nanoparticles.

The efficiency of ZnO nanoparticles is also tested for removal of Cd (II) ions in real water sample analysis such as tap water and pond water collected for the adsorption experiment. The nanoparticle is found to be effective in removing Cd (II) ions from the two samples. It is found from the analysis that the prepared ZnO nanoparticles can be utilized for the removal of heavy metal ions such as Cd (II) ions from aqueous solution and collected any type of real water. Therefore, it can replace the conventional adsorbent for the removal of heavy metal ions.

CHAPTER 1:

Introduction

1. INTRODUCTION

This chapter describes about the nanotechnology, different types of nanomaterials and its advantages in today's world. There are various types of nanoparticles and one of the most significant nanoparticles is Zinc Oxide nanoparticles and its applications, advantages. The different methods which can be used to synthesize and characterize Zinc Oxide nanoparticles is also described. The ways in which water gets polluted and its harmful effects are also explained here. Heavy metals are one of the pollutants among them; cadmium is really toxic and harmful. This chapter also includes nanotechnology approach to water purification and various ways to remove cadmium from water. The most common way to remove cadmium is adsorption and nanomaterials can be used as an adsorbent for cadmium removal.

1.1. NANOTECHNOLOGY

Nanotechnology is termed as the manipulation and implementation of matter at the nanoscale. It is also defined as the understanding, control and restructuring of matter in the size range of 1-100 nm. Nanotechnology refers to the unique phenomenon of technology that enables novel applications in real world. Nanoscience is the science behind it. Richard Zsigmondy proposed first the concept of "nanometer" for describing the size of particle. Richard Feynman presented a lecture titled "There's Plenty of Room at the Bottom", during the 1959 American Physical Society meeting at Caltech, in which he presented the idea of manipulating at the atomic or molecular level. So he is considered as the father of modern nanotechnology. The general physical, chemical, electrical, biological and optical properties of matter at the nanoscale are unique and different from those at larger scale. These properties can be utilised for commercial application and betterment of the society [1, 2]. Nanotechnology has provided solution to various environmental, medical and industrial problems through integration into larger system which includes electronics, drug delivery, energy, water, biotechnology, national security and information technology [1].

Nanotechnology provides huge scope of applications in the field of agriculture. There are various challenges in agricultural field such as deficiency of nutrient, low efficiency, shortage of water, and decline in crop yield which can be met with the help of nanotechnology [3]. Due to diverse field of applications in nanotechnology, it can be useful in textile industry. The products of nanotechnology such as nanocomposite, nanofiber and nanoparticle can be easily functionalized and incorporated with textiles to enhance the performance [4]. Nanotechnology provides new opportunity in pharmaceutical specialised area for drug delivery, steam cell therapy, disease treatment, and molecular diagnostics and in gene therapy. The different types of pharmaceutical nano-systems are liposome and dendrimers [5]. Nanotechnology is also used for the renewable energy sources such as solar energy, wind energy turbines, ocean energy and related technologies such as production of hydrogen, solar

cell and fuel cell. It has the ability to increase efficiency, energy efficiency and conservation [6].

Demand of water is rising due to growth of population, climate change and decreasing quality of water. It is of utmost importance to meet the need of clean and affordable water. There is a necessity of treating water especially in affected areas where lack of treatment facilities exists. Nanotechnology can be appeared as a significant technology in water treatment for the removal of heavy metal from water because of high treatment efficiency and cost effective. The limitations of conventional methods of water treatment can overcome with the help of nanotechnology [7].

1.2. NANOMATERIALS

Nanomaterials are defined as materials which have the size, in the range of 1-100nm, atleast in one or more dimension. Different properties of nanomaterials are dependent on the size and shape of the nanomaterial. The unique properties of nanomaterials have made these materials gain significant interest [8]. Nanomaterials are classified on the basis of dimension and material type.

Based on the dimension of nanomaterials, nanomaterials are divided into four dimensions: zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanomaterials. **Zero-dimensional (0D) nanomaterials** are type of nanomaterials which have dimensions in nanoscale and point like structure. Examples of nanomaterials are hollow spheres, quantum dots, etc. **One dimensional (1D) nanomaterial** is nanoparticles which have dimensions in nano range with one dimension in other scales. Examples of one-dimensional nanomaterials are nanotubes, nanorods, nanofiber and nanowire. **Two-dimensional (2D) nanomaterials** are type of nanomaterials which contain one dimension in nanoscale (1-100nm) and other two dimensions are larger than nanoscale. Examples of two-dimensional nanomaterials are nanofilms, nanolayer, nanocoatings and nanoplate. **Three-dimensional (3D) nanomaterials** are nanomaterials with all three dimensions larger than nanoscale but contain various constituents in nanoscale. Examples of three-dimensional nanomaterials are nanocomposite, nanotubes, fullerene, honeycombs, etc. [9]

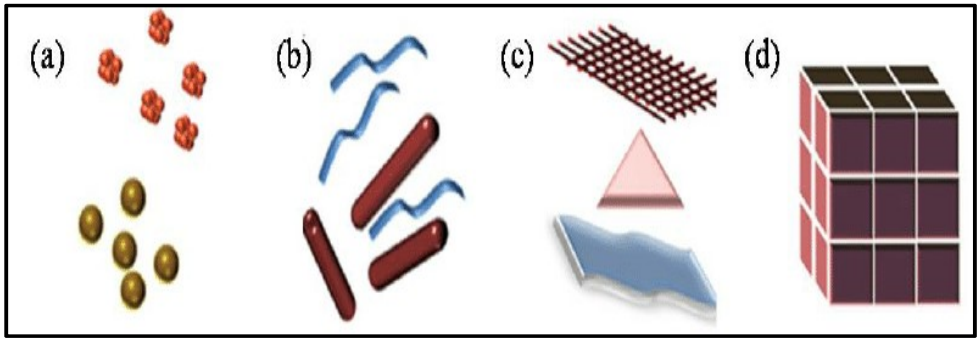

Figure 1.1. Nanomaterials are classified as (a) OD nanomaterials (b) 1D nanomaterials (c) 2D nanomaterials and (d) 3D nanomaterials [55].

Based on the different types of nanomaterials, nanomaterials are divided into various materials: **Carbon based nanomaterials** are nanomaterials which have different form of carbon and have different morphological character. Carbon-based nanomaterials can be classified as fullerene, carbon nanotubes (CNT), graphene sheets, graphite and nanodiamond. The different properties of carbon nanotube can be obtained by physical and chemical modification of CNT. Graphene sheets have unique properties such as high chemical reactivity, large surface area and good stability. Fullerene and its derivatives can neutralize nitrogen and oxygen. **Inorganic-based nanomaterials** are metal nanoparticle such as gold, silver, iron and other metals and metal-oxide nanoparticle such as TiO_2, ZnO, MnO_2 and other metal oxide. The optical, chemical and electrical properties of metal nanoparticle can be varied by varying the size of these nanoparticles. Metal nanomaterials show catalytic activity and absorb light by inter-band transition and intra-band transition. The band gap energy of metal oxide nanomaterials are influenced by the surface change properties. **Composite nanomaterials** are nanomaterials which consist of various phases, with one of the phase are in nanoscale. Chitosan-tripolyphosphate/ TiO_2 nanocomposite is a nanocomposite. Nanocomposite materials have different properties such as optical property, flexural strength, and water adsorption and wear properties because of the combination of various materials. **Ceramic nanomaterials** are material which is composed of ceramics, having dimensions smaller than 100nm. It is also classified as heat-resistant, inorganic and non-metallic solids. Nanoceramic materials have increased electrical, optical, structural, ferromagnetic, ferroelectric and structural properties. **Semiconductor nanomaterials** are materials with band gap energy of less than 4eV. Silicon, germanium, gallium and arsenide are semiconductors. The physical and chemical properties of the semiconductor nanomaterials are altered because of the quantum size effect [8].

1.3. SYNTHESIS METHODS OF NANOMATERIALS

Nanomaterials can be synthesised in the two methods which are bottom-up and top-down methods.

Bottom-up methods refers to the aggregation of small particles like atom, molecules and forming nanoscale range crystals. The different types of process that are involved in bottom-up approaches are:

- **Chemical vapor deposition (CVD):**

Chemical vapor deposition plays significant role in the synthesis of carbon-based nanomaterials. A sample material is deposited as a thin film on the substrate surface in a vapor medium via the chemical reaction in this method. CVD has an advantage of producing thin film with uniform thickness [10].

- **Hydrothermal and solvothermal methods:**

The heterogeneous reactions occur in a sealed vessel in solvent medium at high pressure and temperature to their critical point is called hydrothermal process. The only difference between solvothermal and hydrothermal method is that solvothermal process is carried out in non-aqueous medium. These methods are really useful in producing various morphologies of nanomaterial such as nanorods, nanowire, nanosheets, etc [11].

- **Sol-gel Method:**

This method is used for the synthesis of oxides, composites, and organic and inorganic nanomaterials. At first, hydrolysis process occurs in which metal alkoxide react with water or alcohol in presence of acid or base and then polycondensation occurs. The liquid phase of the solution changes into the gel due to polycondensation that is by the removal of water molecules in the solution. The gel phase converted into powder phase after the condensation of all water molecules. Heat treatment is required to get the fine crystalline powder. [12]

Top down approach of nanomaterial synthesis refers to the division of bulk materials into nanoscale materials. This method is also known as the destructive method of nanomaterial synthesis. The different processes involved in top down method of synthesis are:

❖ **Mechanical milling:**

This method is suitable for large scale production. Mechanical milling is the process in which bulk material can be reduced to form nanoscale materials and hence used to blend two different phases. It is also utilized for the production of nanocomposites. The principle of this process is kinetic energy transfer from the ball to the sample during the rotation of the milling bowl. These balls are made up of steel and tungsten. [10]

❖ **Laser Ablation:**

In this process, when powerful laser beam strikes the target material, there is a generation of nanoparticles. Electrons remove from the precursor due to the penetration of laser light results a high electric field. Energy transfer occurs as the generated free electron collides with atom of the sample. This result in the vaporization of the precursor [10].This method can be utilized in producing wide variety of nanomaterials such as metal nanoparticles, nanocomposites, and carbon nanomaterial. The properties of nanoparticles are affected by the wavelength and refractive index of the laser. [11]

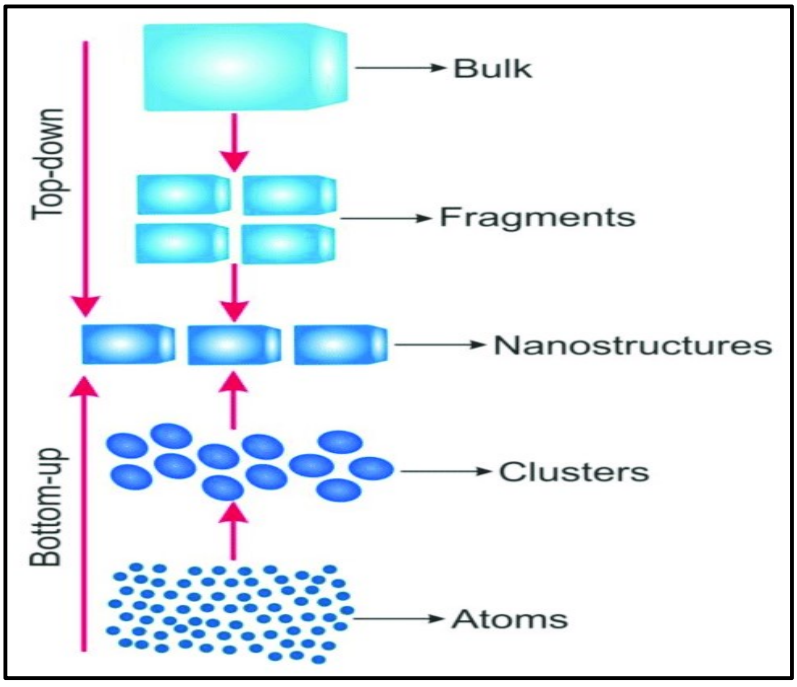

Figure 1.2. Schematic representations of synthesis methods of nanostructures [56].

❖ **Lithography:**

Lithography is used to fabricate integrated circuits for decades. This is used for creating pattern of nanometer size using a focused light beam or electrons. Lithography is divided into two types- masked lithography and maskless lithography. Photolithography, soft lithography and nanoimprint lithography are different types of masked lithography. Masked lithography utilizes masks or mold for fabrication of pattern. In maskless lithography, pattern is carried out without the involvement of mask and these include electron beam lithography, focused ion beam lithography. [10]

❖ **Sputtering:**

Sputtering is a process in which solid surface is bombarded with high energy particles such as plasma or gas in order to produce nanomaterials. [11]

❖ **Electrospinning:**

Electrospinning is one of the simple top down method and can be used to produce nanofiber from polymers [11].

The application of nanomaterials is very wide and can be used from medical field to modern industry. Nanomaterials such as magnetic ferrites can be used in electronic devices such as sensor, biosensors, units of computer, in recording media, and high density storage. Nanomaterials can also be utilized for the preparation of batteries and supercapacitors in the form of electrode. Nanomaterials such as gold, silver nanoparticle, quantum dots and metal oxide nanoparticle can also be applied for diagnosis and drug delivery action. Nanomaterials such as metal nanoparticle, carbon based nanomaterial can also act as catalyst. Nanomaterials such as metal oxide nanoparticle, nanocomposites are also useful in the treatment of wastewater [12].

1.4. NANOPARTICLES

Nanoparticles are defined as solid particle or dispersed particulate with a size in the range of 1-100 nanometer (nm). Some of the nanoparticles are:

Aluminium oxide nanoparticles (Al_2O_3) are significant nanoparticles as a catalyst component, ceramic material in industries and adsorbent. Alumina nanoparticles are coated with other materials as a support in the field of catalysis to produce another material with strong mechanical properties. Zirconium dioxide nanoparticles or Zirconia (ZrO_2) can be used as an

electrolyte, ceramic structure, a catalyst and as a sensor. Zirconia nanoparticle has enhanced sintering behaviour so it can be used in oxygen permeation membrane. Zirconia has improved optical properties and wide band gap because of the decrease in size as a nanoparticle. Cerium oxide nanoparticles or ceria have higher electrical conductivity than bulk materials. Ceria nanoparticles have the property to absorb and store hydrogen. Ceria is applied in fuel cell and automotive catalyst by doping it with a second metal and thermal stability is achieved. Titanium oxide is used as a catalyst in various industries, in electronic devices, as a cosmetics, sensor, food additive, in painting, in medicine and treatment of diseases [13]. Silver (Ag) nanoparticles can be used as antimicrobial agent in many applications such as biomedical, textiles and coatings. Ag nanoparticles can be used in pharmaceutical and biomedical industries because of the antibacterial properties. Gold (Au) nanoparticles have properties of nontoxicity, photothermal, detection ease, high functionalization ability which can easily help in developing antibacterial agents and antifungal activities [14]. Magnetic iron oxide nanoparticles can be utilized in various applications related to catalyst, recording media, in magnetic resonance imaging, ferrofluids, as therapeutic agents for treatment of cancer, magnetic seals and inks. Magnetic nanoparticles coated with polymers have enhanced chemical stability and can be exploited in wastewater treatment of industries [15]. Silicon nanoparticle shows amazing electronic and optical properties for photovoltaic application. Silicon nanoparticle, nanowire and nanotubes are widely used for lithium-ion battery applications. Silicon based tandem cells can be used for solar cell battery application [16]. Zinc sulphide nanoparticles are great carriers of photoluminescence because of the high surface to volume ratio and show large band gap. Zinc sulphide nanoparticles possess exceptional physical and chemical properties including increased quantum size effect, low melting point, high catalytic activity, various surface and volume effect, high chemical activity, and increased thermal resistance. Zinc sulphide nanoparticles can be utilized in various applications such as biosensor, field emitter, catalyst and semiconductor. [17]

1.5. ZINC OXIDE NANOPARTICLES

Zinc oxide nanoparticles are defined as multifunctional, promising inorganic nanomaterials with wide variety of application in diverse fields. Zinc oxide nanoparticles are characterized by wide band gap and high binding energy which has significant effects on the electric conductivity and optical absorption properties. Zinc oxide nanoparticles are doped with other metal helped in increasing conductivity. There is a strong ionic bonding between zinc and oxygen of Zinc oxide nanoparticles but it shows light covalent character. Zinc oxide nanoparticles have gained more attention among various nanoparticles [18]. Zinc oxide nanoparticles can appear one dimensional, two dimensional and three dimensional structures. Zinc oxide nanomaterials arise in one dimensional structure as needles, nanorods, tube, wire, belts etc. In two dimensional, Zinc oxide nanomaterials have the shape of nanosheets and nanoplate. Zinc oxide in three dimension structures appears as the shape of flower, snowflakes, coniferous, etc. Crystal of zinc oxide exists in two main forms as hexagonal wurtzite and cubic zinc blende [19]. Zinc oxide nanoparticles act as suitable additive for

textiles because of its safety and compatibility with human skin. Zinc oxide nanoparticles have improved antibacterial activity compared to its microparticles because of the increase surface area of nanoparticles [14]. Zinc oxide nanoparticles have revised electrical properties which makes it applicable in electronics. There are numerous techniques to configure Zinc Oxide nanowire as Field Effect Transistor. The synthesis routes, size, shape and surface defects decide the photoluminescence emission of zinc oxide nanoparticle shows in the UV and visible region. Zinc oxide nanoparticles can be applied in energy harvesting, photodetectors, biosensors and thermal imaging [19]. Zinc oxide nanoparticles have electrostatic properties which make it useful for biomedical application. The catalytic, electrical, electronic and photochemical properties of zinc oxide nanoparticles make it considerably useful. The large surface area and high catalytic activities of zinc oxide nanoparticles add an advantage for its application in catalytic reaction. Size of Zinc Oxide Nanoparticles is directly related to its cytotoxic properties against cancerous cell. Zinc oxide nanoparticles show photocatalytic activity which can be used for purification of water. Zinc oxide nanoparticle is used as fertilizer in agriculture for yielding the growth of food crops. Zinc oxide nanoparticles can be applied in preservation of food because of its antibacterial properties. Zinc oxide nanoparticles are used in cosmetic industry as sunscreen and facial cream because of its ability to absorb UV irradiation and optical properties. Zinc oxide nanoparticles exhibit antibacterial, antimicrobial, antifungal and antitumor properties. Zinc oxide nanoparticles have semiconductor properties which gives it ability to generate reactive oxygen species (ROS). [20]

1.6. SYNTHESIS METHODS FOR ZINC OXIDE NANOPARTICLE

The methods for synthesising zinc oxide nanoparticles can be divided into solid phase, liquid phase and vapor phase. The physical methods for synthesising zinc oxide nanoparticle are physical vapor deposition, arc plasma method, thermal evaporation and ultrasonic irradiation. The chemical methods for synthesising zinc oxide nanoparticles are microemulsion, sol-gel, precipitation, chemical reduction, hydrothermal method, solvothermal method and chemical vapor deposition. The biological methods for synthesising zinc oxide nanoparticles are plant extracts, microorganisms, and biotechnology and biochemistry methods [21]. The simpler and effective techniques to synthesise zinc oxide nanoparticles are:

- **Sol-gel method:**

The advantages of preparing zinc oxide nanoparticle from sol-gel method are simple methods, low cost, authenticity, and relatively mild synthesis conditions which enable the zinc oxide surface modification with specific selected compounds. Ristić et al. obtained zinc oxide nanocrystalline by sol-gel method. Zinc 2-ethylhexanoate (ZEH) in propan-2-ol solution added to tetramethylammonium hydroxide solution. The suspension was left for 30 minutes and then washed the solution with methanol and water. Zinc 2-ethylhexanoate

quantity does not affect the particle size of zinc oxide nanoparticles. The high pH of tetramethylammonium hydroxide may affect the ohmic conductance of nanoparticle [22]. The sol-gel process includes the formation of colloidal solution (sol) which converts into gel and then solid form. The process involves hydrolysis, condensation and polymerization. The precursors in this method used are metal alkoxide or equivalent chlorides in an aqueous medium or alcohol. The factors which affect the growth of zinc oxide nanoparticles are nature of the solvent, nature of the alkyl group, temperature, molar ratio of water to alkoxide and alkyl group nature. [21]

- **Mechanochemical process:**

The synthesis of zinc oxide nanoparticles by mechanochemical process is different from ball milling process. Ball milling process includes the reduction of powder particle below inert temperature which ultimately leads to the formation of nanosized particle within microsized particles [19]. Mechanochemical process involves high energy and low temperature for a reaction to initiate through ball powder collision in a ball mill. It is very simple cheap techniques for producing zinc oxide nanoparticles on a large scale. Solid such as NaCl acts as a reaction media and separates the formed nanoparticle which is added to the system. The main difficulty of this method is the uniform crushing of the powder. The quantity of impurities increases by increasing milling time. There is a minimum tendency for the agglomeration of particles. The uniformity of the crystalline structure and morphology obtained by this method is high [22]. Ao et al. proposed the mechanochemical method and synthesised an average size 21nm of Zinc Oxide crystal. The precursor used was zinc carbonate and carried out the milling process for 6 hour. The calcination temperature is 600°C which yielded hexagonal structure of zinc oxide. The size of ZnO depends on the calcination temperature and milling time revealed by the test. There is a reduction of crystallite size with increase in milling time while crystallite size increases with increase in calcination temperature. [22]

- **Controlled Precipitation:**

Controlled precipitation is one of the techniques for synthesising zinc oxide nanoparticles with desirable properties. This method involves synthesis of zinc oxide nanoparticles in which zinc salts precursor such as zinc acetate dihydrate, zinc nitrate, zinc sulphate react with alkali reducing agents. Precipitate is then formed which is further washed with water or alcohol in order to remove impurities. The precipitate was dried to get solid powder. Metal oxide nanoparticles. Zinc oxide nanoparticles are formed by further calcination. The obtained zinc oxide nanoparticle with different morphologies depends upon different parameters such as pH, concentration of the solution, calcination temperature and washing medium [21]. Kumar et al. formulated zinc oxide nanoparticles by using zinc sulphate heptahydrate and

sodium hydroxide as precursor. Characterization results indicated that the morphology of synthesised nanoparticles depend upon the temperature of calcination. The morphologies of samples were nanoflakes at 300°C and 500°C while it changed into spherical nanoparticle by increasing the temperature to 700°C [21]. Wang et al. carried out controlled precipitation of zinc oxide by using zinc sulphate heptahydrate and sodium bicarbonate. Membrane reactor was used, consisting of two plates of polytetrafluoroethane with stainless steel as a dispersion media. The size of zinc oxide nanoparticles obtained was from 9 to 20nm. Temperature, calcination time and concentration of the solution affected the size of the particle [22].

❖ Hydrothermal method:

The hydrothermal is simple and environmentally friendly technique which does not require organic solvents use or further processes such as calcination and grinding. The substrate mixture is heated to a temperature of 100-300°C in an autoclave and then, left for several days. Crystal nuclei are formed as a result of heating followed by cooling which then grow. The advantages of this process are high crystallinity degree of the product and high metal purity. Chen et al. have proposed synthesis of zinc oxide nanoparticles by hydrothermal reaction using zinc chloride and sodium hydroxide in a ratio of 1:2. Filtered and washed the zinc hydroxide precipitates. Hydrothermal heating takes place in an autoclave for a set time at a particular temperature and then cooling. Zinc oxide is the final product of the process. The efficiency of the process is reduced by increasing the pH of the solution which increases the crystallinity and size of the particles. [22]

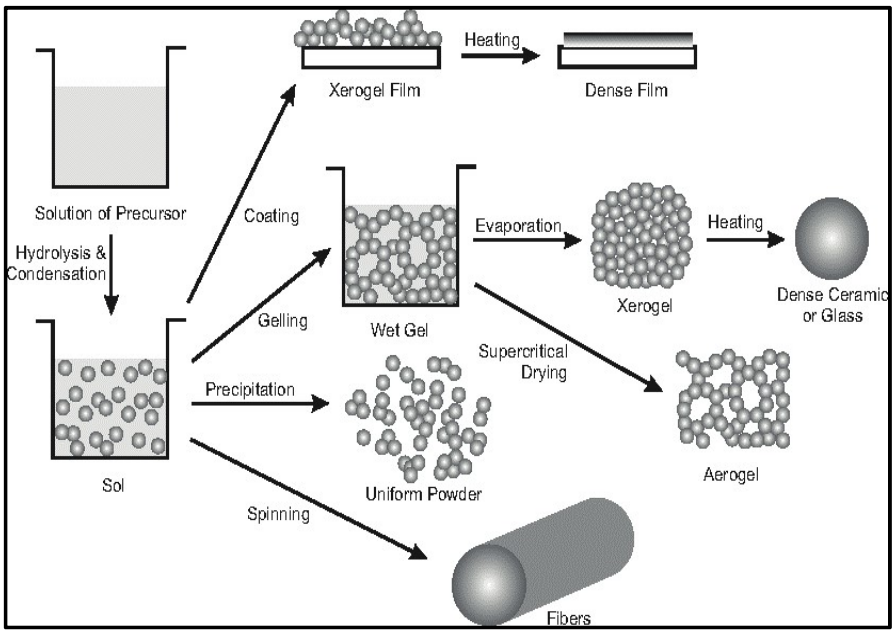

Figure 1.3. Steps of different Sol-Gel process [57].

❖ **Microemulsion:**

Emulsion is basically defined as a continuous liquid phase dispersed in second discontinuous liquid phase. This technique can be divided into two groups based on the external phase which are oil-in-water and water-in-oil emulsion. Water is hydrophilic, high polar liquid and oil is hydrophobic, non polar liquid. Emulsion systems were used by Vorobyovo et al. in their work. An interphase reaction takes place between zinc oleate dissolved in decane with sodium hydroxide dissolved in water and zinc oxide precipitate is formed. The obtained zinc oxide powder was analysed by SEM and XRD which was followed by removal of solvent by drying at room temperature. The reaction took place in both water and organic phases. The size of the particles and location of their phases are affected by various conditions of the process such as temperature, ratio of two phases. Different particle shape of zinc oxide can be obtained with diameter depending upon the condition of the process [22].

❖ **Thermal decomposition:**

This process does not require any expensive raw materials or complex instruments for the large scale production of zinc oxide nanoparticles so it is low cost and easy handling process. Solution and solid phase thermal decomposition process can be used for the synthesis of zinc oxide nanoparticles. This method does not require any catalysts, surfactants or organic solvents for the synthesis of zinc oxide nanoparticles. Zinc oxide nanoparticles with 27-35nm crystal size by thermal decomposition were prepared by Little et al. The aqueous solution of zinc oxalate was used in three steps. At first, het the solution at 100°C for removing water and for complete dehydration, it was heated at 200°C. Finally heat the powder at 450°C. [23]

1.7. CHARACTERIZATION METHODS OF ZINC OXIDE NANOPARTICES

The characterizations of nanoparticles are done on the basis of size, shape, surface charge, porosity and average diameter. The advanced techniques that are used for characterization of nanoparticles are scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), dynamic light scattering (DLS), and X-Ray diffraction (XRD). After synthesis of nanoparticle, their crystal structure and chemical composition are thoroughly studied.

❖ **X-Ray Diffraction (XRD):**

X-Ray Diffraction (XRD) is mostly used techniques for the characterization of nanoparticles and used to study the various range of structural information in crystalline sample. The information that XRD provides are arrangement of the crystal structure, lattice parameters of crystalline sample, mean shape and size of nanoparticles, nature of the phase and size of crystalline grains. The particles composition can be found by comparing the position and intensity of peaks with the reference data available from Joint Committee on Powder Diffractions Standards (JCPDS) database [24]. The Scherer equation is used to find this parameter by using the widening of the most intense peak of XRD measurement of a sample. The full width at half maximum is determined by the size of the crystal planes that gives rise to specific reflections because every peak is related to specific crystals direction. XRD pattern gives different sizes for different crystallographic directions which are related to unique shape of the crystal. The Scherer equation is defined as the following expression (Eq. 1.1) [25]:

$$D_{hkl} = \frac{(k\lambda)}{(\beta_{hkl}\cos\theta)} \quad \text{..... (1.1)}$$

where, D_{hkl} is the size of crystal in the perpendicular direction to the lattice planes, hkl are miler indices of the planes belong to the analysing peak, k is a numerical constant known as the crystallite shape factor, λ is the wavelength of incident X-rays, θ is the Bragg angle and β_{hkl} is the Full Width Half Maxima of the diffraction peak in radian. [25]

❖ **Scanning Electron Microscope (SEM):**

Scanning Electron Microscope (SEM) is one of the electron microscopy techniques which are used to find the size, shape and surface morphology of the nanoparticles. Nanoparticles solution is transformed into dry powder for the SEM process characterization. The dry powder is coated with conductive metals such as gold by using sputtering and then mounted it on a sample holder for further process. The whole sample was then analyzed by focussing a beam of electrons on it. The surface morphologies of the sample are determined by the secondary electrons emitted from the sample. [26]

❖ **Energy Dispersive X-Ray Analysis (EDX):**

Energy Dispersive X-Ray (EDX) provides the elemental composition of the sample at various positions by measuring near surface elements. EDX is combined with SEM for finding the elemental proportion of sample. X-ray is emitted from the sample when an electron beam of 10-20KeV energy strikes the sample surface. The examined sample material is responsible

for the energy of the emitted X-rays. Each element image in the sample is found by transferring the electron beam across the sample. There is low intensity of the X-rays so it requires long duration to acquire the image. [27]

❖ Fourier Transform Infrared Spectroscopy (FTIR):

Fourier Transfer Infrared Spectroscopy (FTIR) analysis identified organic, inorganic and polymeric materials by scanning the sample using infrared light. The characteristic patterns of absorption band give the material composition. FTIR identifies and detects contaminants in the sample, characterizes unknown materials, identifies decomposition and oxidation and finds additives. FTIR spectrometer consists of source, detector, sample cell, amplifier, analog to digital (A/D) converter, and computer. The Infrared Radiation is transferred from source to detector and then through interferometer. A/D converter and amplifier helped to amplify and convert the signal into digital signal and the signal is moved to computer where the Fourier Transform happens. Some part of the infrared radiation absorbed and some passed through the sample when infrared radiation of 1000-100 cm^{-1} is passed into it. The absorbed radiation by the sample is converted into vibration or rotational energy. [27]

❖ Ultraviolet-Visible Spectroscopy:

Ultraviolet-Visible Spectroscopy contains a deuterium or tungsten lamp, a detector, a monochromator, sample and reference cuvettes. Cuvettes are made up of glass, plastic, silica and quartz. Cuvettes hold sample. Cuvettes are kept inside the instrument and light is introduced to the sample. Quartz cuvettes absorb wavelength above 180nm so they are used for absorption measurement in the ultraviolet region. Reference beam is a beam travelled from source to detector without the interaction of sample whereas sample beam is a beam that interacts with the sample. This works on the principle called Beer-Lambert law that the absorbance of the sample is directly proportional to the concentration of the absorbing substance and length of the path at the particular wavelength and shown in the below equation (Eq. 1.2)

$$A = c\varepsilon l \quad \text{..... (1.2)}$$

where, A is the absorbance, c is the concentration, ε is absorptivity and l is the path length. Detector records the intensities ratio between the sample beam and reference beam. The maximum absorption level of the sample determines the wavelength. If the intensity of reference beam is higher than the sample beam then the wavelength have high absorbance. By passing the light beam through the sample, some part of the light is absorbed by the sample while the rest will be transmitted through the sample. Transmittance is defined as the ratio of light entering the sample to the light exiting the sample at given wavelength. Absorbance refers to the negative logarithm of transmittance. [27]

❖ **Atomic Absorption Spectroscopy (AAS) :**

Atomic Absorption Spectroscopy (AAS) is one of the techniques which are used for determining the particular element or absorbing species concentration in the analysed sample. AAS can be used in both quantitative and qualitative analysis. AAS depends on the principle of Beer-Lamberts law which needs standards of known metal concentration to set up relationship between the measured absorbance and the concentration of metal ions. There are two different types of AAS- Flame Atomic Absorption Spectroscopy (FAAS) and Graphite Furnace Atomic Absorption Spectroscopy (GFAAS). FAAS is most common methods to find the concentration of metals ion in a sample in parts per million (ppm) and parts per billion (ppb). In FAAS, the metal ions are condensed to their atoms by nebulising as a fine spray into high temperature flame which absorbs radiation from hollow cathode lamp of specific elements [60].

1.8. WATER POLLUTION

Water is said to be polluted when the quality of water and its composition gets affected due to human activities so that it makes unsuitable for human consumption. When harmful substances enter water bodies and contaminate these water bodies, lowering the quality of water and making it toxic to environment and human. Water pollution is a result of human activities [28]. Water pollution occurs from two sources and those are point sources and non-point sources. Point sources are those which have direct identified source and place. Point sources of pollution include wastages coming out from industries, discharge from factories, and oil spill. It also includes wastewater from sewage, municipal and industries. Nonpoint sources of pollution are those in which source of origin is not identified. There is a number of ways through which contaminants enter ground water and surface water from unidentified source. Nonpoint sources include agriculture runoff, urban waste runoff and acid rain. Water pollutants may be microbial, organic, inorganic and macroscopic water pollutants. Microbial pollutants include pathogens such as bacteria, virus and protozoa. Organic pollutants include insecticides, azo dyes, phenols, polyaromatic hydrocarbons, herbicides, detergents, disinfectants, petroleum, food processing wastes, and other chemicals. Inorganic pollutants include heavy metals such as arsenic, mercury, zinc, chromium; copper from acid mine, fertilizers from agriculture runoff which includes phosphates and nitrates, and ammonia. Macroscopic water pollutants include wood pieces, plastic and trash. [29]

The different causes of water pollution are agriculture, industries, sewage, oil spillage, thermal pollution, radioactive waste and acid rain pollution. Agriculture chemicals include fertilizers, pesticides, insecticides, herbicides which are used in fields to increase the productivity of crops. These chemicals lead to the contamination of water bodies because of

improper disposal and surface runoff after rain and which live in environment for longer duration. Most of the industries are located along the river banks such as textile, paper and steel industries for the requirement of huge amount of water in various processes. These industries produce wastes, containing dyes, acids, heavy metals and other chemicals which are dumped as effluents into rivers. Sea water gets polluted when oil accidently leaks from cargo tankers carrying petrol, diesel and their derivative. Pollution in water also causes due to investigation of oil from offshore. There is a formation of thin layer of oil in water. Human activities results in majority of the thermal pollution. Sources of thermal pollution are petroleum refineries, electrical power point, steel factories, and coal fire power plant. They release large quantity of heat into the water bodies which destroys its composition, result in high temperature of water bodies. When sulphur dioxide and nitrogen dioxide generated from natural sources such as volcanic eruption and man-made sources such as burning of fossil fuels react with atmosphere to form sulphuric acid and nitric acid. Acid rain occurs when these acids falls down onto the earth surface in the form of rain. [29]

There are adverse effects of water pollution in the environment, human health, and aquatic life. Sulphate, nitrate, chloride, phosphate and chromates make the water bodies acidic and also change the colour of water. Plants get seriously affected by the detergents from domestic and industrial wastes. Water containing phosphate can destruct plant growth, chlorophyll, roots and more. Pesticides, herbicides and insecticides result in change of pH rate of water and also reduce the photosynthesis rate of plants. Fly ash from industries may result in death of aquatic plants and animals. Oil spills reduces the oxygen content of water bodies. Thermal pollution adversely affects the aquatic life. Thermal pollution reduces the photosynthesis rates of aquatic plants. Euthrophication occurs in water bodies due to excess inorganic nutrients such as nitrogen and phosphorous. It also results in excessive growth of algae and plant in water bodies [29].

Heavy metals such as arsenic, fluoride, mercury, lead, cadmium, pesticides and other fertilizers have a toxic affect on human health. Presence of arsenic in water is very toxic and might come from insecticides, chemical factories and ceramic industries which results in skin problems, bladder and lungs cancer. Concentration of fluoride above 0.5 mg/l may result in fluorosis for 5-6years. Lead affects blood, central nervous systems and kidneys of human beings. Higher concentration of mercury causes chromosomal aberrations and neurological damage to human beings and results in death of humans. Cadmium is also toxic and also causes nephritis. Microorganisms in water causes cholera, typhoid fever, dysenteries and diarrhoea. [29]

There has been advancement in waterborne diseases because of irresponsible management and growth of water pollution. Water borne pathogen in various water bodies is a matter of serious concern. These water borne bacteria pose a serious threat on the health of people, animals and other living beings. Water borne pathogens are reckoned for approximately 5million death per year out of which half of them are accounted for children, based on the reports of UNICEF in 1995 (the state of World's children, Oxford University Press, Oxford). [51]

Figure 1.4. Sources of water pollution [58].

1.9. HEAVY METALS AND CADMIUM

Heavy metals are one of the most hazardous pollutants because of their toxic behaviour. These toxic heavy metals are arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni), silver (Ag), mercury (Hg), copper (Cu), and cobalt (Co), etc. The heavy metals entered into the water bodies from mining, agriculture, urbanisation and various industries like textile, painting, tanneries, batteries, fertilizers, pigments, paper, electroplating and metal plating industries. Industries have vast application of heavy metals so its effluent discharge contains a lot of heavy metals which needs to be treated. Heavy metals can live in environment for longer duration in different oxidation states. Heavy metals in urban pollution travel long distance in the environment emanating from road dust, sediment and polluted air [30]. The spreading of heavy metals in drinking water source is an area of immense concern. The other sources of heavy metals in water are agriculture runoff, rain water entering into drinking water sources and stormwater runoff. Heavy metals cause harmful effects to human being because of toxic and carcinogenic nature. Heavy metals are of particular concern because they are non-biodegradable and get accumulated in humans and other animals when they consumed the contaminated water. These metals are hazardous to human even at low concentration [31].

Cadmium is one of the toxic heavy metal which has adverse effects on human, animals and environment. Exposure to cadmium is toxic. The sources of cadmium are primary metal industries, manufacturing of certain batteries especially Ni-Cd batteries, electroplating industries, color pigments, used as stabilizer in PVC products and tobacco products.

Exposure to cadmium causes various types of cancer of breast, kidney, lung, prostate, and pancreas. Cadmium can be extremely harmful and leads to the dysfunction of kidney and liver, testicular damage, osteomalacia, and pulmonary damage. [32]

The permissible limit for cadmium in drinking water as per World Health Organisation guidelines is 0.003 mg/L. [33]

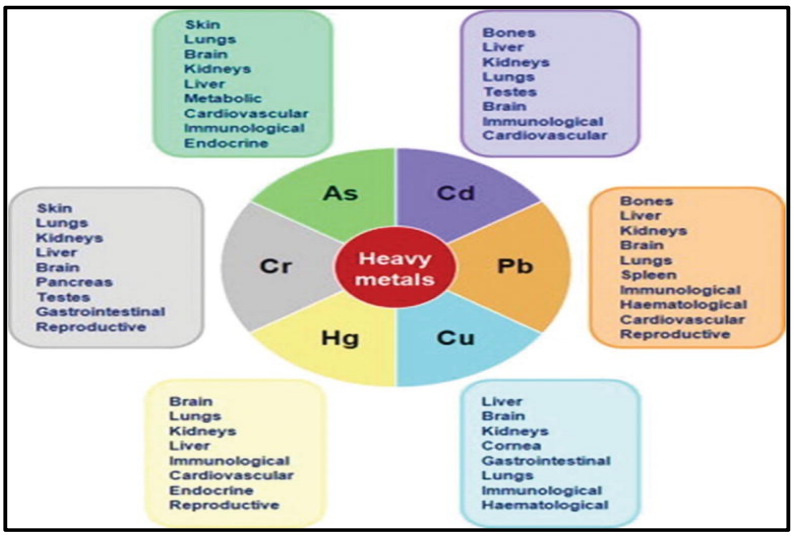

Figure 1.5. Heavy metals effect on humans [59].

1.10. NANOTECHNOLOGY APPROACH TO WATER PURIFICATION

There are several nanotechnology approaches to water purification which are currently in practices. Nanotechnology approach to water purification exploits nanomaterials such as carbon nanotube in filtration. It also makes use of nano size pores in zeolite membrane. The application of nanotechnology can be used for the removal of sediments, chemicals, charged particles, pathogens and other harmful substance. It is helpful in removing elements such as arsenic and liquid impurities such as oil. The main advantages of nanotechnology as compared to conventional methods are that requirement of less pressure to pass across filter, more efficient, and have large surface areas. For example, carbon nanotube can easily remove all types of contaminant. Nanofilters can be easily cleaned by back-flushing compared with conventional methods as they have large surface area. Nanotechnology based water purification does not cause any environmental issues and health problems [34]. The nanotechnology processes of water purification are highly efficient, modular and multifunctional in nature and provide great performance in wastewater treatment. These nanomaterials have high specific surface area that is high surface to volume ratio limit the interaction with contaminants. Nanotechnology is really advantageous in treating contaminated water because they help in obtaining purified water which leads to reduction in labour and time. The property of high surface area is good for adsorption. The property of

high reactivity is good for photocatalysis. The property for antimicrobial is used for disinfection. The superparamagnetic property is good for particle separation. They can also measure the quality of water by their sensing property [35].

1.11. NANOMATERIALS FOR CADMIUM REMOVAL

The different types of nanomaterials that can be used for removal of cadmium are:

- **Metal nanoparticles:**

Metal nanoparticles are silver, gold, palladium, iron etc particles. The size of nanoparticle is 10-200nm. Silver nanoparticles have strong antimicrobial properties which can be used as water disinfectant. Iron nanoparticles have large surface area due to their small size and can be used as excellent adsorption. Gold nanoparticles coated with palladium are used as effective catalyst in treatment of ground water. [36]

- **Metal oxide nanoparticles:**

Metal oxide nanoparticles are titanium oxide (TiO_2), zinc oxide (ZnO), magnesium oxide (MgO) and iron oxide. Titanium oxide nanoparticles are used in photocatalytic degradation method for the removal of contaminants as an effective catalyst. The catalyst oxidise contaminant and helps in degradation. Iron oxide nanoparticles are used as adsorbent and can remove heavy metals from water. Iron oxide nanosorbants can be easily recovered from the water because of their magnetic behaviour. Zinc oxide nanoparticles are also used as an effective photocatalysis catalyst and can be used as an adsorbent for removal of cadmium. [37]

- **Carbon Nanotubes (CNTs):**

Carbon nanotubes are cylindrical molecules consisting of rolled up of graphene sheets in a tube like structure. Carbon nanotubes are classified as Single walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs). Single walled carbon nanotubes are rolled up of single graphene sheet of diameter 4-10nm whereas Multiwalled carbon nanotubes are rolled up of multiple graphene sheets of diameter 10-100 nm. Carbon nanotubes have excellent adsorption capability because of their large surface area to volume ratio and controlled pore size. The adsorption capacity can be enhanced by functionalization of carbon nanotubes. [38]

❖ **Fullerene:**

Fullerene is carbon based nanoparticles of C60 molecules. It is also known as buckyball or buckminsterfullerene. Fullerene has high surface to volume ratio, surface defects (pentagons in hexagons) and hydrophobic character. Fullerenes along with nanoadsorbents are really useful for removal of heavy metals ions from water. Functionalization of fullerene is really easy, makes it suitable to be used in water disinfection. [39]

❖ **Quantum dots:**

Quantum dots are semiconductor crystals of very small size diameter. The diameter of Quantum dots are between 2-10 nm. Examples of quantum dots are cadmium selenide, zinc sulphide, zinc selenide, lead selenide, and cadmium telluride. Quantum dots have luminescence properties that mean by absorbing white light, they reemit colour depending on the band gap of material. They have improved mechanical, optical, electrical property. [40]

❖ **Zeolites:**

Zeolites are used as a media to exchange of ions for metal ions. Zeolites can be used affective sorbents. It can also remove heavy metals from wastewater easily. Zeolite nanoparticles are created by pulsed laser induced fragmentation using zeolites microparticles. [41]

1.12. METHODS APPLIED IN CADMIUM REMOVAL

Nanomaterials properties of high surface area can be used for adsorption, then high chemical reactivity has an advantage in photocatalytic reaction and antimicrobial property is useful for disinfection. The methods that can be used are:

❖ **Adsorption:**

Adsorption is a process in which adsorbate adsorbs to adsorbent. Adsorbent is used as separation media for the removal of contaminants from polluted water. Adsorbate is pollutants. Nanoparticles are effective adsorbents because of the unique properties they possess. Nanoparticles have large specific surface area and can be easily modified with functional group to remove particular contaminants. Nanoparticles have large specific surface area and can be easily modified with functional group to remove particular contaminants. [42] The nanoadsorbents are nanoparticle adsorbent and used inorganic and organic pollutant

from contaminated water. Some of the nanoadsorbents which are currently used in treatment of water are carbon-based nanoadsorbents (such as carbon nanotubes), metal based nanoadsorbents, polymeric nanoadsorbents (such as dendrimers), and zeolites. Functionalization of Carbon Nanotubes makes it suitable for the removal of heavy metal ions from contaminated water. Metal based nanoadsorbents such as iron oxide, alumina and zinc oxide are low cost material. The adsorption capacity is inversely proportional to the size of the nanoadsorbents. Magnetic nanoadsorbents are very useful in removing toxic elements from polluted water. [43]

- **Membrane Process:**

Membrane is thin layer porous materials which allows the flow of water through them but does not allow bacteria, virus, heavy metals and organic pollutant to pass through it. Membranes use pressure driven process or electrical techniques for the purification of water. Membrane separation process is one of the reliable methods for the treatment of heavy metals. Functional nanomaterials are incorporated into membrane really add on benefit to improve the membrane permeability, fouling resistance, mechanical and thermal stability [43]. Membrane can be nanofiber membrane, nanocomposite membrane, thin film nanocomposite membrane. Electrospinning is a low cost process to make nanofibers using ceramics; polymers and these nanofibers have large specific surface area and can be used as membrane for the removal of particles from wastewater. Nanocomposite membrane is the addition of metal oxide nanoparticles such as silica, alumna, titanium oxide and zeolite, antimicrobial nanoparticles such as carbon nanotubes and nanosilver into polymeric or inorganic membrane. This also increases the hydrophilicity of the membrane, permeability of water and prevents membrane bio fouling. Surface modification of thin film composite membrane by adding nanomaterials into it results in the development of thin film nanocomposite membrane. The permeability and selectivity of membrane depends on type, size and amount of nanomaterials is added [44].

- **Photocatalytic degradation:**

Photocatalytic degradation is a technique used for the treatment of water to degrade contaminants that are present in water by using active nanomaterials as a media. Photocatalysis is defined as a process in which there is a change in the rate of the reaction of a photocatalyst under the presence of ultraviolet light, visible and infrared radiation. Photocatalyst is a substance which absorbs light and generates an electron-hole pair. Photocatalyst is considered ideal if it has high photoactivity, stability, biological and chemical inertness. The examples of nanostructure semiconductor photocatalysts used are zinc oxide, titanium dioxide, ferric oxide, cadmium sulphide and zinc sulphide. The process is continuously used for the degradation of harmful pollutants into harmless byproducts such as carbon dioxide and water. Dyes from industries are released into the river is one of the main cause of water pollution but this pollutant can also be degraded by zinc oxide

nanoparticles. Solar energy can be an advantage for the photocatalytic degradation as it is abundantly available. It can also help in removing inorganic contaminants. [42]

The most widely used photocatalyst for the purification of water is titanium dioxide as it is low cost material, chemically stable and generates low amount of toxicity. The generated electron/hole pair may either migrate to the surface of catalyst, forming reactive oxygen species or recombine undesirably. [44]

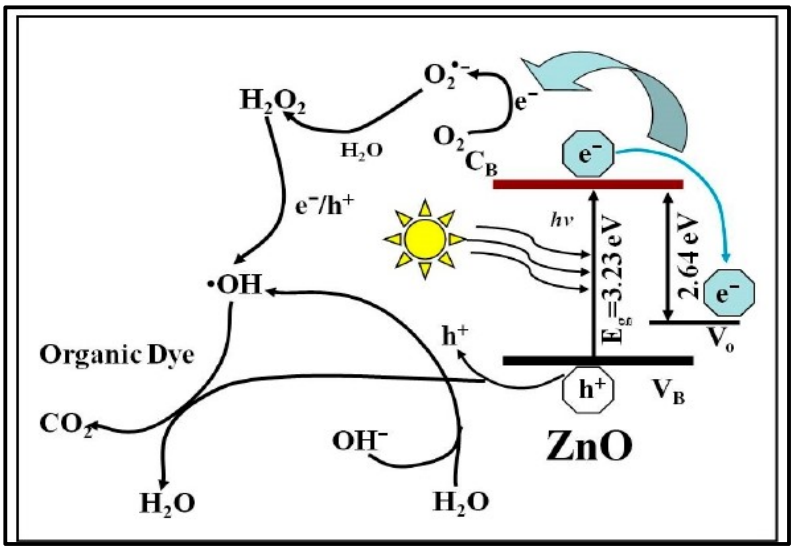

Figure 1.6. Photocatalytic degradation process of organic dye by ZnO nanoparticles [61].

❖ Filtration:

Filtration by nanomaterials is a pressure driven membrane separation process and consume low energy. Nanomaterials have better diffusivity; permeability and small pore size make it easier to remove any type of solute present in wastewater. Nanofilters can remove almost all types of organic and inorganic contaminants. The nanomaterials that can be used as Nanofilters are carbon nanotubes, metal oxides nanoparticles and zeolites. [42]

❖ Disinfection:

The conventional disinfectants such as chlorine and ozone produce toxic byproducts which can be really dangerous and harmful for the human health and environment. So some of the nanoparticles have antimicrobial properties, does not form toxic byproducts and can be easily disposable. The nanoparticles that can be used as disinfectants are silver nanoparticles, carbon nanotubes and fullerene. Silver nanoparticles have strong microbial activity and low toxic disinfectant byproducts. Carbon nanotubes can kill bacteria and other microbes. This could help in improving the quality of water. Zinc oxide and polymeric nanoparticles also have antimicrobial properties. [44]

1.13. ADSORPTION

Adsorption is the removal of molecules or ions from an aqueous solution onto the solid surfaces or adsorbent. Adsorption process can be efficiently used for the removal of multiple solutes in water treatment. The solid surfaces that can interact with solute in aqueous solution are actively heterogeneous. Adsorbent is the solid surface that provides surface for the process of adsorption. Adsorbate refers to the molecule species or ion that will be adsorbed on the adsorbent surface. Adsorbents should have great surface area because adsorption is a surface phenomenon. The adsorption theory consists of three parts are adsorption equilibrium, adsorption kinetics, and dynamics of adsorption. The dependency of the adsorbed amount on the concentration of adsorbate and temperature is defined as the adsorption equilibrium. So, adsorption isotherm describes the dependency of adsorbed amount on adsorbate concentration at particular temperature. Adsorption kinetics refers to the time dependency of the process that means the adsorbed amount depends on time. The information about adsorption equilibrium and adsorption kinetics is necessary to predict adsorption dynamics. [45]

Adsorption isotherm is defined as the interaction between the adsorbate and adsorbent. These interactions depends on various factors such as characteristic of adsorbent, adsorbate, solution, attractive or repulsive force between adsorbent surface and hydrophilic or hydrophobic group of the surfactant and lateral interaction among adsorbent surface [46]. Adsorption isotherm also depends on physical properties of the solution such as pH, ionic strength, temperature, adsorbate concentration and adsorbent mass. Based on the interaction between adsorbate and adsorbent surface, adsorption can be classified as physisorption process and chemisorption process. Physisorption process happens when weak electrostatic attraction forces such as London forces, dipole-dipole forces and van der Waals interactions between adsorbent and adsorbate and these bonds can be easily broken. Physisorption process is reversible. Chemisorption process occurs because of the chemical bond between adsorbate and adsorbent by sharing and transferring of electrons. Chemisorption is irreversible process. Based on the shape of adsorbate-adsorbate pairs, adsorption can be classified into six types. The various isotherm models are Henry, Langmuir, Freundlich and many more isotherms. [47]

- **Henry isotherm:**

This is one of the simplest adsorption isotherm in which partial pressure of the gas is proportional to the amount of adsorbate surface. All adsorbate species are undisturbed from their nearest neighbour so this isotherm model is suitable fit for the adsorption of adsorbate at low concentration. Therefore, the following expression (Eq. 1.3) can be used for equilibrium relation between adsorbate concentration of solution and adsorbed phase [48]:

$$q_e = K_{HE} C_e \text{..... (1.3)}$$

where, q_e is adsorbate amount at equilibrium in mg/g, K_{HE} is adsorption constant and C_e is equilibrium concentration of the adsorbate. [48]

❖ **Langmuir isotherm:**

Langmuir isotherm describes gas-solid phase which can be used to show the variation of adsorptive capacity of adsorbents. Langmuir isotherm assumes monolayer adsorption process and adsorption process is homogeneous. Langmuir isotherm is responsible for the surface coverage by maintaining equilibrium between adsorption and desorption rates. The linear form of Langmuir equation can be written as the following expression (Eq. 1.4) [48]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \text{..... (1.4)}$$

where, C_e is adsorbate concentration at equilibrium in mg/L, K_L is Langmuir constant which can be related with the surface area and porosity of the adsorbent. The larger surface area and pore volume of the adsorbent give rise to high adsorption capacity. Separation factor R_L is dimensionless constant which can be use to define the essential characteristics of Langmuir isotherm and can be expressed as the following equation (Eq. 1.5) [48]:

$$R_L = \frac{1}{1+K_L C_o} \text{..... (1.5)}$$

where, C_o is initial concentration of adsorbate in mg/l. R_L values indicate the adsorption nature. The adsorption is unfavourable when$R_L > 1$. It is linear when R_L=1. The adsorption is favourable when$0 < R_L < 1$. The adsorption is irreversible when R_L=0. [48]

❖ **Freundlich Isotherm:**

Freundlich isotherm is isotherm that occurs on the heterogeneous adsorbent surfaces. This isotherm gives the expression of the exponential distribution of active sites and their energies. This isotherm model defines the reversible and non-ideal adsorption process. Freundlich isotherm models are applicable to multilayer adsorption unlike the monolayer adsorption of Langmuir isotherm. The linear form of Freundlich isotherm can be expressed as the following equation (Eq. 1.6) [47]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \text{..... (1.6)}$$

Where, K_F and n are constant which depends on temperature. 1/n indicates adsorption intensity and adsorbate heterogeneity sites.

The adsorption is favourable when 0<1/n>1. The adsorption is unfavourable 1/n >1. The adsorption is irreversible when 1/n=1. [47]

Adsorption kinetic is the time required for the adsorption process. The adsorbate molecules from the solution phase enter into the adsorbent particle by external or internal diffusion or interaction at the surface. It is a curve plotted between adsorption capacity of adsorbent versus time and final concentration of adsorbate versus time. Adsorption kinetics can also be defined as a curve or line that explains retention rate of solute from aqueous solution to the boundary of solid at a fixed amount of adsorbent dose, given pH and temperature. Adsorption kinetics can be named as pseudo first order model, pseudo second order model, elovich model, intra-particle diffusion model and many more. [49]

❖ **Pseudo First Order Model:**

Pseudo First Order Model is also known as Lagergren model which describes the first order mechanism for the adsorption of adsorbate particle into adsorbent and can be expressed as the following equation (Eq. 1.7) [49]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \text{..... (1.7)}$$

The linear form that can be derived from the above equation (Eq. 1.8) [49] as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \text{..... (1.8)}$$

where, q_t is amount of adsorbate adsorbed onto adsorbent at time t and expressed as mg/g, k_1 is constant per min, and q_e is equilibrium adsorption capacity. The value of rate constant can be determined by plotting the graph of $\ln(q_e - q_t)$ versus t. [49]

❖ **Pseudo Second Order Model:**

The assumptions of this model are the solute adsorption rate is proportional to the available sites on the adsorbent and the reaction rate depends upon the solute amount on the adsorbent surface. The pseudo second order model can be expressed as the following Eq. 1.9 [49]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \text{..... (1.9)}$$

The linear form of pseudo second order model can be expressed as the following Eq. 1.10 [49]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \frac{t}{q_e} \text{..... (1.10)}$$

where, k_2 is pseudo second order rate constant. This rate constant can be found by plotting graph of $\frac{t}{q_t}$ versus t. Pseudo second order model is suitable for the low initial concentration of solute whereas pseudo first order model is suitable for high initial concentration of adsorbate. The model may be affected by various parameters such as pH of solution, adsorbent dose, size of the particle, temperature and adsorbate concentration. [49]

❖ **Intra-particle diffusion model:**

The solute adsorption of aqueous solution onto adsorbent includes film diffusion, pore diffusion and surface diffusion. Pore and surface diffusion occur simultaneously whereas film diffusion occurs independently. The linear equation (Eq. 1.11) for Intra-particle diffusion model as [49]:

$$q_t = K_d\sqrt{t} + C \quad \text{..... (1.11)}$$

Where, K_d is rate constant of the model and C is the thickness of boundary layer. [49] A linear plot function is obtained. The adsorbate transfer from the solution to the adsorbent can be described by four mechanisms. The first mechanism is known as mass transfer of adsorbate molecule into the adsorbent as soon as it is dropped into the solution. Film diffusion is the second mechanism which involves adsorbate movement from boundary layer to the surface of adsorbent. Third mechanism involves movement of adsorbate molecules from the surface to the pores of the adsorbent. The final mechanism includes rapid attachment of solute particle to active sites of adsorbent. [49]

1.14. ADSORBENTS

Adsorbents are the materials which are used for adsorption of heavy metals such as cadmium, chromium, lead, and other contaminants onto them. There are different types of materials which can be used for the treatment of water. Conventional materials include activated carbons, zeolites, clay minerals and biomaterials which can be used as adsorbents. These conventional materials suffer from low metal adsorption capacity. These materials also cannot provide higher removal efficiency for the heavy metal in treatment of water. There are other alternatives being found as a result of the costly production and regeneration of activated carbon. Nanomaterials are used as developing adsorbent for the removal of heavy metals or contaminants from wastewaters in recent years. These nanomaterials include carbon nanotubes, graphene, fullerene, metal oxide nanomaterials and others. These nanomaterials have high specific areas and large pore volume which can be used effectively for the adsorption process. They show various property such as high mechanical strength, thermal stability, electrical conductivity and non-corrosive property. [50]

Conventional materials like activated carbons are frequently used for the removal of odours, color, tastes, and impurities from contaminated water. The limitations for using activated carbon as adsorbent are adsorption efficiency gets reduced after regeneration and contaminants are not fully destroyed after regeneration. [50]

Metal oxide nanoparticles are also used as adsorbent for the removal of heavy metals because of the excellent adsorption performance, easily modification and economic value features. Metal oxides have enough number of active sites which can be used for the removal of contaminants even in low concentration. Metal oxide nanoparticles have large surface area and provide maximum adsorption capacity. The adsorption performance of metal oxide nanoparticle can be improved by its surface modification. [50]

1.15. WATERBORNE DISEASE AND HARMFUL EFFECTS

Waterborne diseases are the results of pathogens such as bacteria, virus, protozoa, and fungi in water bodies. The different types of bacteria are *Burkholderia pseudomallei, Escherichia coli, Pseudomonas aeruginosa, Salmonella typhi, Vibrio cholerae, Yersinia enterocolitica, and Enterococcus faecalis,* etc. The various types of virus are enteroviruses, astroviruses, hepatitis A viruses, hepatitis E viruses, adenovirus, rotavirus, sapoviruses and noroviruses. The different types of protozoa and fungi are *Acanthamoeba spp., Cyclospora cayetanensis, Entamoeba histolytica, Giardia intestinalis, Cryptosporidium, Balantidium coli, Isospora belli, Naegleria fowleri, Toxoplasma gondii, Dracunculus medinensis, Schistosoma spp., Rickettsia,* etc. The infections caused by these various types of pathogens are typhoid, cholera, intestinal infections, microcystins, conjunctivitis, throat sores, inflammation of abdomen, fever, rashes, respiratory disorders, gastroenteritis in human, inflammation in respiratory tracts and digestive systems. These types of pathogen proved to be fatal to human beings and a serious threat to aquatic life. [51]

There are adverse health effects such as neurological disorder, reproductive and fertility problems which causes from transmission of infective agents through water. When animal or human wastes are not treated properly and disposed into the water sources can result in waterborne diseases. Insects such as mosquitoes can transfer these waterborne diseases from one to other infected humans or animals. These harmful toxins can accumulate and causes harmful effects such as aquatic food webs, infections of fish, shore birds, marine mammals and other species. [52]

Waterborne diseases affect more than half of the population which is a matter of public health globally. According to World Health Organisation (WHO 2011) estimates, diarrheal diseases can cause 2.2million annual death which is a result of dependency of 1billion people on contaminated water sources. The waterborne diseases are a great challenge to the developing nations. In India, 10.87million every year are the number of cases of acute gastroenteritis which are caused by consuming polluted water and poor sanitation. These outbreaks are result of bacterial and viral pathogens. Pathogens have the ability to develop resistance

against particular drug and can also rearrange themselves as biofilms in water distribution pipelines for their survival and growth. Contaminated water is a result of faeces from infected people and animals and surface runoff from heavy rainfall and contamination of reservoirs, wells and groundwater. [53]

1.16. METHODS FOR EVALUATING ANTIBACTERIAL ACTIVITY

There are various types of methods for combating these bacteria resistance. The most common and well known techniques for evaluating antibacterial activity of any drug or nanoparticles are:

- **Agar disk-diffusion method**

The agar disk-diffusion testing method is approved by the Clinical and Laboratory Standard Institute (CLSI) for bacteria and yeast testing. The standardised inoculums of the testing bacteria inoculate agar plates. 6mm filter paper discs of the desired concentration of testing compound are placed on the surface of agar. Incubate the petri dish under required conditions. The antibacterial material diffuses into the agar plates and stops the tested microorganism growth. Measure the inhibition growth diameter. The advantages of the methods are simple procedures, low cost and results can be interpreted easily. [54]

- **Agar well diffusion method**

The agar is spread over the entire surface of petri dish plates and then inoculated with the bacterial inoculums over the agar surface. A hole of diameter 6-8mm is made on the agar surface by punching with a tip to form wells. Then the well is filled with 20-100microliters antibacterial particles of desired concentrations. Incubate the agar plates under suitable condition and then the tested antimicrobial particle diffuse into the agar plate which results in inhibiting the growth of bacteria strain. [54]

- **Broth dilution method**

The broth dilution method is basic method for evaluating the antibacterial activity of any testing agents such as zinc oxide nanoparticles. Prepare the two fold dilution of antimicrobial agents in liquid medium with small volume by using 96-well microtitration plate. Then inoculate each well with bacterial inoculums prepared in same liquid medium. The 96-well microtitration plate is incubated after well mixing under suitable conditions. [54]

❖ **Agar dilution method**

The desired concentrations of antibacterial agent are incorporated into molten agar medium plates by using two-fold serial dilution method. Then the defined microbial inoculums are inoculated onto the agar plate surface. The lowest concentration of antibacterial agents is recorded as MIC which completely inhibits the growth of microorganisms. [54]

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CHAPTER 2:

Literature Review

2. LITERATURE REVIEW

The comprehensive reviews about various topics such as the different types of methods can be used for the synthesis and characterization of zinc oxide nanoparticles are presented in this chapter. The previous works that has been done on adsorption of cadmium ions by zinc oxide nanoparticles and other nanomaterials and adsorption of heavy metals by various nanomaterials have also review in the chapter.

2.1. SYNTHESIS AND CHARACTERIZATION REVIEW OF ZINC OXIDE NANOPARTICLES

Shamhari et al. have synthesised zinc oxide nanoparticles by solvothermal process and use zinc acetate dihydrate and potassium hydroxide as a precursors and ethanol as solvent. The techniques which are used for characterization are X-Ray diffraction (XRD), transmission Electron microscopy (TEM), Fourier Transform Infrared (FT-IR) spectroscopy, Brunauer-Emmett-Teller (BET), ultraviolet-visible spectroscopy (UV-Vis), and energy dispersive X-ray spectroscopy (EDX). XRD data shows that the synthesised zinc oxide nanoparticles have a crystalline size of 10nm and the most intense diffraction is observed at (010). The presence of zinc oxide nanoparticle has been proved by UV-Vis absorption spectrum shown at 357nm. FTIR absorption spectrum shows a peak at 414cm^{-1} which indicates the presence of zinc oxide. [1]

Riyadh M. Alwan et al. have synthesised zinc oxide nanoparticles by sol-gel method and zinc acetate is used as precursor. The synthesised particle is characterized by XRD, FTIR analysis, Scanning Electron Microscopy (SEM) and UV-Vis spectroscopy. XRD data proves that the average size of Zinc oxide nanoparticle is 58.3nm and the most dominant peaks observed at (100) and (101) reflection. The spherical shape of zinc oxide nanoparticles with smooth surfaces is observed by SEM with 100-200nm in size. FTIR spectra shows absorption peaks at 417.52 cm^{-1} which shows absorption characteristics band of ZnO nanoparticles. [2]

K. Omri et al. have worked on zinc oxide nanoparticles under supercritical drying of ethyl alcohol at different temperatures by sol-gel method. The precursor has used for the synthesis of zinc oxide nanoparticles is zinc acetate dehydrate. The synthesised nanoparticles are characterized by XRD, TEM, UV-Vis spectroscopy and PL spectra. The sizes of nanoparticle are observed between 38 and 54nm by TEM. XRD indicates the structural properties of zinc oxide nanoparticles which show hexagonal wurtzite structure. UV-Vis spectrophotometer shows strong luminescence band around 384nm. The optical band gap of synthesised zinc oxide nanoparticles varies from 3.34 to 3.21 eV by increasing temperature. [3]

E. Janardhan et al. have synthesised zinc oxide nanoparticles by hydrothermal method and used sodium hydroxide and zinc acetate as precursors. The characterization techniques apply for are XRD, FTIR, and FESEM. XRD data indicates the formation of zinc oxide nanoparticles. FTIR spectrum shows absorption peak at 432.46 cm^{-1} which indicates the presence of zinc oxide nanoparticles. FE-SEM shows zinc oxide nanoparticles are spherical in shape with average particle size of 10nm. [4]

A. H. Moharram et al. use zinc acetate dihydrate and potassium hydroxide as a precursor for the synthesis of zinc oxide nanoparticles through direct precipitation method. The precursor is analysed by thermal gravimetric analysis (TGA) in order to find the temperature at which weight loss and thermal effects are effective. XRD, EDX, TEM and UV-Vis spectrophotometer are used for the characterization techniques of prepared zinc oxide nanoparticles. XRD data provides that the synthesised particles are crystalline in nature with hexagonal structure. The average crystallite size of the nanoparticle observed by XRD is in the range of 22.4 ± 0.6nm. TEM is used to confirm the structural properties of zinc oxide nanoparticles which are wurtzite in structure. EDX is used to confirm the purity of the prepared nanoparticle and results reveal that zinc and oxygen elements are present in the analysed sample in 1:1 ratio. The optical band gap of the prepared nanoparticle is found to be 3.52 eV. UV-Vis spectrophotometer shows the absorption peak of the manufacture ZnO nanoparticle is around 298nm. [5]

Satya Pal Singh et al. synthesise zinc oxide nanoparticles by sol gel method. Zinc acetate is used as precursor, methanol is used as solvent and sodium hydroxide is used as medium in this sol-gel method. The characterization methods used are SEM, XRD and UV-Vis spectrophotometer. SEM images show the spherical shape of zinc oxide nanoparticle with 15-25nm in size. XRD data analyses the average size of zinc oxide nanoparticle by using Scherrer equation is in the range of 81.28nm to 84.98nm. UV-Vis spectrum shows the maximum absorption peak at 235nm because of agglomeration and settling of nanoparticle. [6]

Umme Habiba et al. synthesise zinc oxide nanoparticles by sol gel technique and use zinc acetate dehydrate, triethanolamine, ammonium hydroxide and ethanol. The characterization techniques uses are XRD, environmental scanning electron microscope (ESEM), EDX, UV-Vis Spectroscopy, FTIR, thermo gravimetric analysis (TGA), and photoluminescence (PL) spectroscopy. XRD data reveals the hexagonal wurtzite structure of zinc oxide nanoparticle. The crystal size of the sample by XRD is 28nm. SEM shows the ball like uniform shaped of the prepared nanoparticle with fine agglomeration of the particle. The size of the nanoparticle found by SEM is 60nm. EDX spectra show the presence of zinc and oxygen in the prepared nanoparticle. FTIR spectrum shows absorption peaks around 514 to 442 cm^{-1} which indicates the presence of zinc oxide nanoparticles. UV-Vis reflectance obtains the optical band gap of value of 3.18 eV. The photoluminescence spectrum shows the strongest emission band at the wavelength of 375nm of the prepared zinc oxide nanoparticle. [7]

V. Ciupina et al. have synthesised zinc oxide nanoparticles by hydrothermal method. The characterization techniques used are XRD, TEM, SEM, FTIR, UV-Vis and EDX. XRD data indicates the hexagonal phase of prepared sample. EDX analysis reveals the presence of zinc and oxygen in the sample. UV-Vis absorption peak is obtained at the wavelength of 350nm. The average diameter of zinc oxide nanoparticles is 10nm obtained by XRD. TEM result reveals the uniform plate shape of the prepared nanoparticles. [8]

Aldbea et al. prepare zinc oxide nanopowder by sol-gel method and calcine the sample at different temperatures. The morphology and structure of the sample is obtained by characterization technique such as XRD, SEM and Raman Spectra. XRD confirms the hexagonal wurtzite structure of the prepared calcined sample at 600 and 700°C. The crystal sizes obtain by XRD of the sample at 600 and 700°C are 34 and 22nm. SEM results reveal the sample calcined at 700°C shows rod shaped particle with average diameter of 69nm. The

sharp and high intensity peak is obtained at 437 cm^{-1} related to E_2 mode is indicated by Raman Spectra. [9]

S.S. Alias et al. synthesise zinc oxide nanoparticles by sol-gel method at different pH. It is found that there is agglomeration of powder at pH of 6 and 7 but there is formation of fine powder at pH of 9. The samples have good structural properties and it has best properties at pH 9. The average particle size of ZnO nanoparticles is 48.31nm at pH 9 with spherical shaped particle. The optical properties are also changed by increasing the pH. [10]

M. Jay Chitra et al. have investigated the optical property of zinc oxide nanoparticles synthesised by chemical precipitation method. The synthesised sample is characterised by XRD, SEM, UV-VIS and PL spectrophotometer. The particle size is increased from 13.8nm to 33nm by increasing the pH of the solution from 6 to 13. SEM image shows the hexagonal shape of zinc oxide nanoparticles. The absorption peak is shown around 381nm by UV-Vis spectrophotometer. [11]

S. Preethi et al. have worked on the properties of zinc oxide nanoparticles and prepare by two different methods which are hydrothermal and sol-gel methods. The precursors use in the hydrothermal methods are zinc acetate, oxalic acid and zinc chloride, zinc nitrate and sodium hydroxide in sol-gel method. The synthesised ZnO nanoparticles is characterised by XRD, SEM, EDX, UV-Vis and PL spectrophotometer. XRD result provides the average crystal size of the sample is 20-30nm and high crystallinity, purity, composition and hexagonal phase of ZnO. The band gap of ZnO nanoparticle synthesised in hydrothermal method is 4.4-4.9eV and by sol-gel method is 3.5-3.9eV. There is no other element present in ZnO nanoparticle which is revealed by EDX. The morphology of ZnO nanoparticle given by SEM is near-spherical prismatic nanoparticles for hydrothermal method and nanoflakes for sol-gel method. [12]

R.C. Singh et al. have worked on the comparison between zinc oxide nanoparticles and nanorods in ethanol sensors. Chemical precipitation route is used to synthesise zinc oxide powder as nanoparticle and nanorods. The temperature of the reaction plays a significant role in synthesising different shaped zinc oxide nanostructure. The techniques used for characterization are XRD and SEM. By increasing the sintering temperature, the grain size increases therefore causes reduction in response of sensing. The sensing responses of Zinc Oxide nanoparticles are higher than that of Zinc Oxide nanorods. [13]

R. Wahab et al. have synthesised zinc oxide nanoparticle by solution method by varying the pH of the solution and use zinc acetate dihydrate and sodium hydroxide as precursors. Sodium hydroxide is added to increase the pH of the solution from 6 to 12. The diffraction patterns obtained from XRD of all pH value are matched with the standard data of JCPDS. The shape is sheet-like at pH 6 and rod-like at pH 10-12. HRTEM confirms crystallinity and nanostructure of all zinc oxide nanostructures. FTIR shows standard peak around 464cm^{-1} which represents the stretching vibration of Zinc Oxide. [14]

A. Vanaja et al. have synthesised zinc oxide nanopowder and Al doped zinc oxide nanopowder by sol-gel method. The structural properties of ZnO and Al doped ZnO nanopowders are characterized by XRD, SEM, FTIR, UV-Vis and PL. The average crystallite size obtains from XRD data pattern of pure ZnO and Al doped ZnO nanopowders are 36.448 and 62.83 nm. The band gap value is decreased by doping zinc oxide nanopowder with

aluminium. The prepared nanoparticle is applied in optoelectronic device indicated by PL studies. [15]

M. Kashif et al. have synthesised ZnO nanorods by varying the seed layer solution and used zinc acetate as a precursor. The chemicals use for the preparation of seed solutions are monoethanolamine in 2-methoxyethanol and potassium hydroxide in methanol. The spin coating of these two solutions on silica substrate is used for the synthesis of zinc oxide nanorods which lead to their hydrothermal growth. The ZnO nanorods are synthesised by monoethanolamine-based seed layer have better properties than by potassium hydroxide seed layer. The Zinc oxide nanorods are synthesised by potassium hydroxide seed layer have better conductivity which was explained by the current-voltage (I-V) characteristics. [16]

Agustinaa et al. have prepared zinc oxide nanoparticles by using sol-gel and calcinations method. The synthesis of zinc oxide has best condition at ultrasonication time of 60 minutes. Nehal A. Salahuddin synthesised zinc oxide nanotube by using zinc nitrate as a precursors in hydrothermal synthesis. [37]

Table 1: Synthesis and characterization of ZnO nanoparticles review.

Sl. No.	SYNTHESIS PROCESS	CHARACTERIZATION METHODS	Ref. No.
1.	A Khorsand Zak et al. have synthesised ZnO nanoparticles by solvothermal methods in triethanolamine and used zinc acetate as precursor	The peaks found by XRD are indexed to ZnO wurtzite structure. The crystalline size of the ZnO by XRD data is 33±2nm. SEM images show that the homogeneous shape and size of ZnO. The particle size is found to be 48±7nm. TEM shows that ZnO are in hexagonal shape. The absorption band by FTIR result is obtained at 375 cm^{-1} corresponds to the hexagonal ZnO.	[63]
2.	Madathil AN, Vanaja KA, Jayaraj MK have prepared ZnO nanoparticles by hydrothermal method and varied the precursors concentration and growth temperature.	XRD study confirms that the synthesised material is ZnO wurtzite phase with the entire diffraction peak agreed to standard ZnO phase. The average grain size is in the range of 7-24nm. TEM image shows the formation of ZnO nanoparticle with size 10nm. The band gap is found to be 3.42 eV by UV-Vis spectrophotometer.	[64]

3.	Dhanya et al. have manufactured zinc oxide nanoparticles by chemical precipitation methods by increasing batch volume of 200ml to 500mL, 1L, 2L and 5L. Zinc nitrate hexahydrate has been used as precursor.	XRD spectra of ZnO nanoparticles synthesised are highly crystalline. The average crystalline size of ZnO nanoparticle is 36.19± 3nm. SEM reveals that the particles are of spherical morphology. SEM image shows that the size of the particle is in the range of 20-40nm.	[65]
4.	Bekele B., L. T. Jule, and A. Saka have worked on the synthesis of ZnO nanoparticles by sol-gel method and the effects of annealing temperature on the particle shape, size, optical properties, chemical composition, and structure of nanoparticles. The precursor used for the synthesis is zinc oxide nanoparticles and sodium hydroxide is used as chelating agents.	The mean crystal sizes of ZnO nanoparticles annealed at temperature of 700°C, 800°C and 900°C obtained by XRD results are 33±20nm, 38±23nm, and 48±33nm. SEM result shows that the zinc oxide nanoparticles are uniformly distributed and spherical in shape. FT-IR data of synthesised ZnO nanoparticles indicates that three broadband frequency at wave number of 496, 1432, 3446cm^{-1}, 444, 1449, 3449cm^{-1} and 435, 1450 and 3425 cm^{-1} at 700°C, 800°C and 900°C of annealing temperature. The absorption peaks are observed at 370, 380 and 389nm from annealing temperature of 700°C, 800°C and 900°C.	[66]

2.2. ZINC OXIDE NANOPARTICLES APPICATION REVIEW

Wang et al. have reported the synthesis of zinc oxide nanoparticles with different morphologies by ethanolamine assisted hydrothermal process. The flowerlike zinc oxide nanoparticles have performed better photocatalytic than other morphologies structure of particles. Wojnarowicz et al. have investigated about the importance of water in the microwave for the synthesis of doped and un-doped zinc oxide nanoparticles by solvothermal process. The size of nanoparticle can be controlled by changing the content of water in the precursor solution of zinc acetate in ethylene glycol. Tonto et al. have found the synthesis of zinc oxide nanorods by using solvothermal esterification between zinc acetate and various alcohols. Inubushi et al. have investigated about the reaction mechanism of zinc acetylacetonate with sodium hydroxide in ethanol for the formation of nanocrystalline zinc oxide nanoparticles. [38]

Zinc oxide nanoparticle is used as superior photocatalyst in degrading pesticide, herbicide triclopyr, bleaching wastewater, phenol, 2-phenylphenol, acid red 14 and blue 19 because it effectively generates hydrogen peroxide, high rates of reaction and has more number of active sites. Zinc oxide is used in optoelectronic devices for its wide band gap. [39]

Zhu et al. have synthesised zinc oxide nanoparticles as photocatalyst with large number of oxygen defect by annealing them in a helium atmosphere at 240-260°C or in a hydrogen atmosphere. The catalyst shows high activity in the degradation of methylene blue under ultraviolet or visible radiation. Wang et al. have obtained zinc oxide nanoparticles with various vacancies of oxygen and can be efficiently used for catalytic degradation of 2, 4-dichlorophenol under visible light radiation. The generation of hydroxyl radical and holes present on the zinc oxide nanoparticles help in breaking down methylene blue dye. [40]

Chen et al. have synthesised gold doped zinc oxide photocatalyst which shows high photocatalytic activity because of huge separation of charge carriers in the presence of gold. Whang et al. have synthesised silver doped zinc oxide nanoparticles by laser induction method for the removal of methylene blue and it is found efficient with silver at pH 11. Divband et al. have found the charge separation and photocatalytic activity of zinc oxide nanoparticle is enhanced by the doping of silver. Platinum doped zinc oxide nanoparticle shows active photo-degradation of phenol by producing one intermediate is studied by Morales-Flores et al. [41]

Ghaffari Hadi et al. have assessed the antiviral activity of ZnO nanoparticles and PEGylated ZnO nanoparticles against H1N1Influenza virus. The cytotoxicity properties of the nanoparticles are evaluated by MTT (microtiter assay) and anti-influenza activity is calculated by TCID50 and quantitative Real-Time PCR assays. An indirect immunofluorosence assay is performed to study the inhibitory impact of nanoparticles. The inhibition rates of PEGylated zinc oxide nanoparticles and zinc oxide nanoparticles based on the viral loads are 94.6% and 52.2% respectively at its highest non-toxic concentrations. [60]

Lingling Zhang et al. have investigated the antibacterial behaviour of zinc oxide nanoparticle suspensions against *E. coli*. The antibacterial behaviour of nanoparticles is determined on the basis of particle size, concentration and dispersants use. The result shows that by increasing concentration of nanoparticles the antibacterial activity also increases and the antibacterial activity increases with decrease in particle size. The stability of zinc oxide nanoparticle suspensions is increased by using two different types of dispersants, Polyethylene glycol (PEG) and Polyvinylpyrolidone (PVP) which hardly affects the antibacterial activity of ZnO nanofluids. SEM images show the damage of the bacteria membrane wall with the help of ZnO nanoparticle. [61]

Hedaiat Moradpoor et al. have reviewed the application of Zinc Oxide nanoparticles in dentistry as restorative dentistry, endodontic, orthodontics, periodontal, implantology, and prosthodontics. In restorative dentistry, ZnO nanoparticle acts as adhesive between filler and dental tissues because of better mechanical properties. Endodontic treatment helps in removing the infections from root canal so ZnO is widely used as a root canal filling material because of its biocompatibility and antimicrobial properties. The quality of health care is significantly improved by dental prosthesis and denture used in prosthodontics. Polymethyl methacrylate (PMMA) used in dentistry and the mechanical properties are improved by loading the PMMA with zinc oxide nanoparticles. Nanoparticles are used on orthodontic appliances because of decrease in demineralization of enamel and microbial adhesion. [62]

2.3. ADSORPTION OF CADMIUM BY ZINC OXIDE NANOPARTICLES REVIEW

Salmani M.H. et al. use zinc oxide nanoparticles as an alternative for the treatment of Cd (II) from solution by adsorption process. Change in pH and ionic strength can affect cadmium removal efficiency. The pH of the solution increases from 4 to 7 by increasing cadmium removal efficiency. It is found that high ionic strength gives lower removal efficiency than the one having low ionic strength and the adsorption capacity is also affected by adsorption time. Pseudo second order equation is best defined for cadmium adsorption kinetics on zinc oxide nanoparticles. Langmuir isotherm is best defined for adsorption isotherm of cadmium ions. It is hence studied that zinc oxide nanoparticles are suitable adsorbent for removal of cadmium in wastewaters. [17]

L. Khezami et al. have synthesised magnetic (x)ZnO-(1-x)Fe_2O_3 nanocrystallines for the removal of cadmium and nickel ions. The characterization techniques uses for the prepared nanoparticles are N_2 adsorption, XRD and magnetization techniques. The parameters of the heavy metal ions adsorption on the ZnO nanoparticles are evaluated by batch mode experiments. The Langmuir isotherm is complied with the adsorption equilibrium data for Cd (II) ions while both Langmuir and Freundlich isotherm data are complied with adsorption equilibrium data for Ni (II) ions. It is found that magnetic nanoparticles remove 128 mg/L of cadmium and 83 mg/L of nickel at 328K. The kinetics model describes that the adsorption process is best fitted by the pseudo second order model. The thermodynamic study results show that the adsorption process is endothermic, spontaneous and physisorption process. The enhanced randomness at solid solution interface is suggested by the positive entropy obtained. The given adsorption mechanism suggests that the process supports intra-particle diffusion along with other kinetic model. [18]

K.Y. Kumar et al. have synthesised mesoporous hierarchical ZnO nanorods by hydrothermal method and use zinc nitrate, sodium hydroxide and Triton X-100 for the synthesis of ZnO nanoparticles. The techniques use for characterization methods are XRD, SEM, TEM, SAED, BET and EDX. The synthesised zinc oxide nanoparticles are further studied as an adsorbent for the Cd (II) and Ni (II) ions removal from aqueous solution. The parameters use for the batch study experiments are contact times, adsorbent dosages, adsorbate concentrations, temperature and pH. The maximum adsorption capacities are found to be 160.7 mg/g for Pb (II) and 147.25 mg/g for Cd (II) ions. Langmuir and Freundlich isotherm are best fitted for the adsorption equilibrium data. Pseudo second order model is best fitted with the experimental data obtain from the kinetic studies for the adsorption of lead and cadmium ions. The adsorption thermodynamics studies suggest that the adsorption process is endothermic and spontaneous. The effectiveness of ZnO for heavy metal ions adsorption remains unchanged after acid wash regeneration. ZnO nanoparticles are remained as a promising adsorbent for cleaning wastewaters because of the adsorption capacity of metal ions and its reusability. [19]

L. Khezami et al. have synthesised ZnO nanoparticle by a modified sol-gel method for the removal of cadmium ions. Batch mode experiments are conducted to perform the kinetics, thermodynamics, and equilibrium parameters of the cadmium ions adsorption on the zinc oxide nanomaterials. The Langmuir model is best fitted with the equilibrium adsorption data. Kinetics studies reveal that pseudo second order kinetics rate model is in good agreement

with the kinetic data for the removal of cadmium ions by zinc oxide nanoparticles. The determining factor for the cadmium ions removal is temperature. It is found from the positive value of enthalpy change of the adsorption reaction that temperature increases help in enhancing the adsorption rate. The endothermic process of the adsorption is indicated by increasing adsorption rate with temperature. The maximum adsorption capacity for cadmium removal is 217.4 mg/g at 328K. The positive value of entropy indicates that the increase in randomness at the solid solution interface. Diffusion and boundary layer effect are controlled by the adsorption mechanism. [20]

T. Sheela et al. have studied zinc oxide nanoparticles as an adsorbent for the Zn (II), Cd (II) and Hg (II) ions removal from aqueous solutions. The parameters which are evaluated for the adsorption process are temperature, pH effect, adsorption equilibrium and kinetics. It is found that the maximum adsorption capacity is 357, 387, and 714 mg/g for Zn (II), Cd (II) and Hg (II) ions at 303K. Langmuir isotherm is well suitable for the adsorption isotherm data with high correlation coefficient. Pseudo second order model is well fitted with the adsorption kinetics data. The best pH value for the above adsorption process is 5.5. [23]

Aigbe et al. have examined zinc oxide nanoparticles and carbonized sawdust composites for the removal of cadmium from wastewater. The synthesis process use for ZnO nanoparticles is precipitation method by using zinc nitrate tetrahydrate as precursor. SEM, EDX, FTIR, UV-Vis and XRD are the techniques used for the characterization techniques. The maximum adsorption capacities for the adsorption of Cd (II) ions by ZnO nanoparticle, carbonized saw dust and ZnO-CSD composite are 52.76, 57.27 and 63.57 mg/g. The ΔH° values are positive which indicates the process is endothermic. Pseudo second order model is best suitable for the adsorption process with high correlation coefficient values. [25]

V. Srivastava et al. have prepared zinc oxide nanoparticles by the simple solution based approaches, sol-gel method. The characterization techniques used for the prepared zinc oxide nanoparticles are XRD, TEM, SEM and FTIR. The crystallite size of the prepared zinc oxide nanoparticle is in the range of 18-31 nm which is confirmed by XRD and TEM. All the peaks from XRD data are matched with the hexagonal Zinc Oxide. SEM reveals formation of nanorods shape particle and forms agglomeration of nanoparticles. The prepared nanoparticle is used for the cadmium removal from aqueous solution. The maximum removal efficiency of cadmium is 92% with an initial concentration of 200 mg/l of cadmium. [26]

Mustafa Y. Hadid and Hamad F. Alharbi have described about the adsorption and tensile properties of electrospun polyacrylonitrile nanofiber (PAN) mat fill with different weight of zinc oxide nanoparticles (0.5, 1.0, 2.0 and 5.0 %). The addition of ZnO nanoparticles are resulted in surface roughness and diameter of the electrospun PAN nanofibers increase which was revealed by microscopic investigations. Adsorption data suggests that the increase in adsorption capacities of the fabricated PAN/ZnO (2%) for Cd (II) and Pd (II) ions as compared to the PAN nanofibers and the fabricated PAN/ZnO shows best adsorption performance of 261% and 167% for Pd (II) and Cd (II) ions. The adsorption isotherm study suggests that the adsorption process is better represented by Langmuir model and Pseudo Second Order Model describes best the adsorption kinetics process. 60 min duration is required to reach the equilibrium of adsorption. [59]

2.4. HEAVY METALS REVIEW

Jennings et al. have reported about lead gets accumulated with time and high concentration of lead in the body is harmful to kidney and central nervous system. Jarup et al. and Chen et al. have reported that exposure to cadmium can cause damage of renal tube. [27]

The spread of toxic pollutants such as toxic chemicals, and metals such as mercury, zinc, cadmium and lead which comes from untreated urban sewers and industrial drains, results in water pollution. Iron changes the colour of water to rust like colour. 60% of the total contaminants of sea, lakes and rivers are produced by factories. Conventional methods of water purification do not treat industrial pollutants, pesticides and inorganic contaminants. [28]

The heavy metals which arise from industries such as fertilizer, textile, paper, paints, iron, steel, chemicals, electrical, tanning, and electronics are toxic because of the chemical reactivity of these metals with the protein, enzymes, and membrane system of body. [29]

Schwarzenbach et al. have explained about contamination of fresh water is a major challenge. Qu et al. have reported about the conventional methods of wastewater treatment are unable to remove the contaminants completely and are inefficient to meet the quality of water. The conventional methods also have various drawbacks such as requirement of high energy, removal of pollutants and production of toxic sludge and by-products. Filtration process produces highly concentrated sludge which is not disposable and produce huge amount of toxic. [30]

Amin et al. have explained about the nanomaterials play a major role for removal of toxic contaminants from wastewater. Nanostructured materials such as carbon nanotubes, silica, titanium oxide, magnetic nanoparticles, zeolite, and silver nanoparticles are used to treat heavy metals, toxic chemicals, charged particles and other pathogen such as bacteria, fungi and other viruses are reported by Amin et al. and Chaturvedi et al. Ye et al. studies reveal that pH plays an important role for the removal of heavy metals contaminant by carbon nanotubes in wastewater. [31]

Van de Bruggen et al. describes about the removal of contaminants such as arsenic, nitrates, bacteria, and viruses from ground water and surface water by using nanoporous membrane. [32]

Lu et al. have demonstrated about the multi walled carbon nanotubes which can absorb chlorophenol and trihalomethane from the solution and carbon nanotubes also removes zinc from wastewater. Zhang have also explained that nanoscale zero-valent irons have large surface area and high surface energy and it can be used in water purification. Kaegi et al. has found about the behaviour of silver nanoparticles in a wastewater. Silver nanoparticles can be used as an antibacterial agent for the treatment of bacteria from wastewater. Poly (amidoamine) dendrimers are also used for the removal of copper ions from wastewater. [33]

2.5. NANOMATERIALS REVIEW

Lu et al. and li et al. studies have revealed that carbon nanotubes are better adsorbents than activated carbon for the removal of heavy metals and carbon nanotube has easily accessible adsorption sites so the kinetics of adsorption is fast on carbon nanotubes. Yean et al. demonstrate that the adsorption capacity of nano-magnetite particles increase with decrease in the size of particle. Li and Xia also explain about functional nanomaterials which can be easily doped for the fabrication of nanoparticle that infuse nanofibers. Nanomaterials such as nano-silver, nano-zinc oxide, carbon nanotubes and fullerene show antimicrobial properties with less oxidation and therefore, produce hardly any disinfection by product. [34]

A comparative study of a titanium oxide photocatalyst is done where titanium oxide nanocomposite photocatalyst are prepared by Yang et al. The detection of lead and sulphide ion can be done by using fluorescent molybdenum sulphide nanosheets is proposed by Wang et al. [35]

The sorption of lead on chitosan nanoparticles is evaluated by Qi and Su et al. Peng et al. synthesise an adsorbent cerium oxide-carbon nanotube for the effective removal of arsenic. The synthetic NaP1 zeolites (Na_6Al_6 $Si_{10}O_{32}.12H_2O$) is used for the removal of chromium, nickel, zinc, copper and cadmium from wastewater which is reported by Alvarez-Ayuso et al. Srivastava et al. have reported that the carbon nanotube filters are useful in removing bacteria and poliovirus Sabin 1 from the wastewater. [36]

Thess et al. have reported first vertically aligned carbon nanotubes (VACNTs). Ren and Huang have tried plasma-enhanced hot filament chemical vapour deposition by lowering the temperature below 666°C and alignment is produced by using electric field as an external force. Fan et al. report about growth of vertically aligned carbon nanotubes on silicon substrate and the detailed mechanism of alignment in carbon nanotubes. Lim et al. produce and modify carbon nanotubes by the application of plasma enhanced chemical vapour deposition. They grow single walled carbon nanotube at low temperature by using plasma enhanced chemical vapour deposition. Kim et al. have explained synthesis of carbon nanotubes at low temperature (480-612°C) on various metallic substrates by making use of diffusion plasma enhanced chemical vapour deposition. Vollebregt et al. prepare self aligned carbon nanotubes and carbon nanofibers by using palladium as catalyst material. They obtain high density self aligned carbon nanotubes by palladium as catalyst and atmospheric pressure chemical vapour deposition. Duy et al. have synthesised carbon nanotubes by coating silicon or nickel coated stainless steel substrate using direct current plasma enhanced chemical vapour deposition. The carbon nanotubes grown on the stainless substrate are uniform as compared to silicon substrate. Kim et al. have worked upon the growth of carbon nanotubes on an anodized aluminium oxide/silicon substrate. [42]

Bethune et al. have reported that single walled carbon nanotubes of small diameter are formed by the co-vaporising carbon and cobalt under helium atmosphere in an arc generator. Saito et al. study that for the production of single walled carbon nanotubes, nickel is found as an effective catalyst. Zhou et al. have reported about the growth phenomenon of carbon nanotubes without catalyst in arc discharge method. [43]

Stafiej and Pyrzynska have explained that the adsorption characteristics of carbon nanotubes affected by the pH and metal ion concentration in aqueous media. The surface features, ion exchange process and electrochemical potential govern the adsorption mechanisms. The

major adsorption mechanism is governed by the chemical interaction between heavy metal ions and carbon nanotubes functional groups. H.J. Wang et al. reveal that the adsorption capacity of multi walled carbon nanotube is increased when it is treated with concentrated nitric acid due to the presence of oxygen functional groups on the surface that can react with lead to form complexes. The equilibrium time of the adsorption for the acidified carbon nanotubes is found to be 20 minutes at the pH value of 2.0. The carbon nanotube composites are prepared with iron oxide, zirconium oxide and aluminium oxide. The adsorption capacity of the composites is from 10 to 31mg/g, depending on the pH and temperature. Luo et al. have experimented manganese oxide/iron oxide/ acidified multi walled carbon nanotubes nanocomposite for the removal of chromium. It is found that the maximum adsorption capacity of the nanocomposite to be 186.9 mg/g with the removal capacity of 85%. Zhao et al. and S.G. Wang et al. have found that carbon nanotubes based adsorbents using titanium oxide and manganese oxide is used for the removal of lead. The adsorption capacity is 137mg/g and 78.74 mg/g. The adsorption capacity for nickel and cobalt is increased by 10-30%. [44]

2.6. ADSORPTION OF CADMIUM IONS BY OTHER NANOPARTICLES REVIEW

H.K. Boparai et al. have used nano zerovalent iron (nZVI) as an effective adsorbent for the removal of cadmium ions from contaminated water sources. The kinetics and equilibrium data of adsorption of cadmium on nano zerovalent iron are determined by the temperature effect. The increase in cadmium adsorption rate is obtained from increase in temperature which concludes the endothermic reaction of the adsorption. Pseudo second order kinetic is the best fitted with the adsorption kinetics data. The adsorption process is found to be chemisorption which is indicated by the activation energy of 54.8 kJ mol^{-1}. Langmuir and Temkins both equations isotherm are used for describing the adsorption isotherm data which shows monolayer coverage of cadmium ions. The intraparticle diffusion model is used for the describing the rate limiting step which is surface adsorption. It is found to be the maximum adsorption capacity of nZVI for Cd^{2+} ions was 769.2 mg/g at 297K. The parameters of thermodynamic such as free energy changes, enthalpy and entropy are calculated for the adsorption process. Thermodynamic studies reveal that the adsorption process is endothermic and spontaneous. The presence of cadmium ions on the nZVI surface is indicated by EDX analysis. All the results indicate that the nZVI is used as an effective adsorbent for the removal of cadmium ions from contaminated water. [21]

M.F. Elkady et al. have prepared hydroxyapatite (HAP) by microwave process and use as an adsorbent for the removal of cadmium ions from the aqueous solution by using the batch technique. The diameter of prepared HAP is 40-70nm. The parameters studies for the cadmium ions adsorption process are adsorbent dose, speed of agitation, pH, temperature of the solution and initial cadmium ions concentration. The maximum cadmium adsorption is attained at 500 rpm agitation speed. The time required for attaining equilibrium is 240 min. Pseudo second order model is well fitted with the kinetics data. The endothermic and spontaneous nature of adsorption process is indicated by positive value of enthalpy change and negative value of free energy change. The activation energy is found to be 8.61kJ/mol. [22]

Lei et al. synthesise core shell iron oxide modified with polydopamine (Fe_3O_4@PDA) composite and efficiently use for the removal of cadmium ions from aqueous solution by

adsorption process. The maximum adsorption capacity of Cd (II) ions on Fe_3O_4@PDA obtain by Langmuir model is 21.58mg/g. The adsorption process is endothermic and spontaneous in nature which is revealed by thermodynamic studies. [45]

Ehrampoush et al. have synthesised iron oxide nanoparticles in the presence of tangerine peel extract of varying concentrations (2, 4, 6, 8 and 10%) by co-precipitation method and use it as an adsorbent for the removal of cadmium ions from contaminated solution. The average size of synthesised nanoparticle is decreased from 200-50 nm by increasing the concentration of tangerine peel extract. The maximum removal efficiency of Cd (II) ions obtained is 90% with an adsorbent dose of 0.4g/100ml and pH of 4. [46]

H.A. Aziz et al. have used low cost limestone, crushed bricks and gravel coarse media with particle size of 2.36-4.75 mm as an adsorbent for the removal of heavy metals such as cadmium, lead, zinc, nickel, copper and chromium. Limestone removes 90% of most heavy metals at pH 8.5 while crushed bricks and gravel remove 80% and 65% of the most heavy metals at pH 8.5. [50]

Amer et al. have used sodium polyphosphate modified kaolinite clay as an adsorbent for lead, zinc and cadmium ions removal from aqueous solution. The maximum removal efficiencies by sodium polyphosphate modified kaolinite clay are 92.10, 74.26 and 55.12 % for Pb (II), Zn (II), and Cd (II). The optimum pH selected for heavy metal removal is 5.0. The maximum adsorption capacity obtain is 40 mg/g for lead, 27.78 mg/g for zinc and 13.23mg/g for cadmium ions. Thermodynamics study shows that the endothermic reaction of adsorption process and enhances randomness at the solid solution interface. [53]

M.H. Dehghani et al. study the efficiency of poly urea formaldehyde as an adsorbent for the removal of cadmium ions from aqueous solution and synthesise poly urea formaldehyde. It is found that the maximum adsorption capacity from Langmuir isotherm is 76.3 mg/g of pH 5.5. Cadmium in water resources may cause a number of diseases such as itai-itai, kidney disorders, cancers, and kidney damages. [54]

B. Keochaiyom et al. have synthesised magnetic chorapatite nanoparticles (MNCAP) and utilize it as an adsorbent for the removal of zinc, cadmium and lead from aqueous solution. The size of MNCAP is 20nm with spherical shape. The maximum adsorption capacities for zinc, cadmium and lead by MNCAP adsorbent are 1.1769, 1.1022 and 1.1546mmol/g. Pseudo second order kinetic model is fitted well with adsorption kinetics data. The optimum amount of adsorbent used is 0.1g/L. [55]

M.F. Elkady et al. synthesize hydroxyapatite nanoparticle as an adsorbent for the removal of cadmium ions from aqueous solution. The process use for preparation of hydroxyapatite is microwave processing. The diameter of the nanoparticle is between 40 and 70nm. The maximum cadmium ions adsorption takes place at 500 rpm agitation rate. 240 min of contact time require for achieving the equilibrium of adsorption process. The activation energy is found to be 8.61kJ/mol which confirms that the process is diffusion controlled. Pseudo second order kinetic is matched well with the adsorption kinetics data. [56]

K. L. Wasewar et al. have studied the removal of cadmium from aqueous solution by using granular activated carbon (GAC) and activated clay (A-clay) as an adsorbent. The optimum pH value obtain is 6 with removal efficiency of 84% for GAC and 75.2% for A-clay. The

optimum adsorbent dosage is found 5g/L for GAC and 10g/L for A-clay. The optimum contact time is 5h for GAC and A-clay. [58]

2.7. ADSORPTION OF HEAVY METALS BY NANOMATERIALS

Y. Dehmani et al. synthesise nickel oxide by using nickel nitrate hexahydrate as precursor by precipitation method and have used nickel oxide as an adsorbent for the removal of phenol from aqueous solution. The techniques uses for characterization are FTIR, XRD, BET, SEM and thermal analysis. The maximum adsorption capacity is 5.29 mg/g. The adsorption process is endothermic revealed from thermodynamic studies. Kinetic studies reveal that the pseudo second order model is well suitable and activation energy is 34.77kJ/mol. Langmuir model is best fitted with the adsorption equilibrium data. Gibbs free energy change ($\Delta G°$) is negative, entropy change ($\Delta S°$) is 266 J/K/mol and enthalpy change ($\Delta H°$) is 60.41kJ/mol. [24]

N. Ballav et al. have prepared glycine doped polypyrrole (PPy-gly) by in situ polymerization of pyrrole (Py) monomer in glycine (gly) presence and use as an adsorbent for the removal of Chromium (Cr(VI)). The optimum pH found for the adsorption process is 2. It is found from the Langmuir isotherm model that the maximum adsorption capacity is 217.39-232.55 mg/g at 25-45℃ and pH 2. [47]

M T L Thi et al. have synthesised magnetic iron oxide/ graphene oxide nanocomposite (Fe_3O_4/GO) by coprecipitation method with 8:1, 4:1, 2:1 and 1:1 precursor ratio. The most suitable precursor ratio of Fe_3O_4/GO nanocomposite found for the adsorption of Cadmium ions is 4:1. The size of Fe_3O_4 nanoparticle which is decorated on graphene oxide nanosheets obtain from TEM images is 10-15 nm. It is found from the adsorption equilibrium data that the maximum adsorption capacity is 52.083 mg/g at pH 8. [48]

A. S. Poursani et al. have used titanium dioxide (TiO_2) nanoparticle as an adsorbent for the removal of lead from aqueous solution. Sol-gel method is used to prepare TiO_2 nanoparticles. The optimum conditions obtain for the adsorption of lead ions are of pH 6, adsorbent dose of 3g/l, time duration of 4hour and temperature of 25℃. The adsorption equilibrium data is fitted well with the Langmuir adsorption isotherm and the maximum adsorption capacity is 7.41mg/g. This has shown the good efficiency of TiO_2 nanoparticle for the removal of lead ions. [49]

Mehdinia et al. study the removal efficiency of lead, copper and zinc ions from aqueous solution by batch adsorption study and use magnetic amine-functionalized mesoporous silica nanoparticles as an adsorbent. The channels of magnetic mesoporous silica nanocomposites are grafted by amino groups. The maximum adsorption capacities are found from Langmuir model are 268mg/g for lead (II), 93mg/g for copper, 82mg/g for zinc ions. The applicability of the prepared nanoparticle is done on the natural sample and removal efficiency is found over 95%. [51]

P. Kajitvichyanukul and T. Sungkaratana have used titanium dioxide nanoparticles for the photocatalytic reduction of zinc in aqueous solution. The removal efficiency is dependent on

pH of solution, TiO_2 amount, types of reactor and hole scavenger species. The hole scavengers such as formate and acetate ions have also helped in reducing zinc ions from aqueous solution. The optimum conditions for the zinc ions removal are pH of 1.6, TiO_2 amount of 20g/L and formate ions of 1M. [52]

M. Adeli et al. synthesise sodium dodecyl sulphate-coated Fe3O4 nanoparticles (SDS-Fe_3O_4 NPs) by co-precipitation method and use as an adsorbent for the removal of Cu (II), Ni (II) and Zn (II) ions from water samples. There is a negative effect on the metal ion removal efficiency by the addition of salts. The contact time of 1min is found enough for the removal of metal ions. The maximum adsorption capacities obtain from Langmuir isotherm is 24.3 mg/g for Cu (II), 41.2 for Ni (II) and 59.2 mg/g for Zn (II). The optimum pH obtain from the experiments are 4 for Cu (II), 6 for Ni (II) and Zn (II). The recovery of adsorbent is possible which can be explained from regeneration and re-adsorption studies. [57]

M. Sharma et al. have prepared copper oxide/zinc oxide tetrapods nanocomposite (CuO/ZnO-T) by hydrothermal process for treatment of wastewater. The nanocomposite possess properties such as high porosity, large surface area make it suitable to use as an adsorbent for the removal of heavy metal ions such as chromium and lead ions and photocatalyst for the removal of dyes. Atomic absorption spectrophotometer is used to find the heavy metal ions concentration. The adsorption removal efficiency of CuO/ZnO-T nanocomposite is 99% for chromium (VI) ions and 97% for lead (II) ions. The maximum removal efficiency of chromium ions is observed at the pH 2 and adsorbent dosage of 0.5g/L. the maximum removal efficiency for lead ions is observed at pH of 10 and adsorbent dosage of 1g/L. [67]

2.8. ANTIBACTERIAL ACTIVITY OF ZINC OXIDE NANOPARTICLES REVIEW

Wang et al. have evaluated the antibacterial effects of zinc oxide nanoparticles in vitro. The pathogen bacteria chosen for this study is *Escherichia coli K88*. The disease caused by *Escherichia coli* is diarrhea in children. The characterization techniques use for the zinc oxide nanoparticles are atomic force microscopy and Zetasizer Nano-ZS90. The minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) are determined for evaluating antibacterial activities against *E. coli*. The effects on the optical density at 620nm values are also observed. Results show that by increasing the concentration of zinc oxide nanoparticle, the antibacterial activity is also increased. The MIC value is 0.1microgram/ml and the MBC value is 0.8microgram/ml. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) are used to observe the antibacterial activity of 0.8microgram/ml zinc oxide nanoparticles. Results indicate that cell membrane can be easily damaged which leads to the cytoplasm leakage and bacteria cells are killed. [68]

E. Hoseinzadeh et al. have synthesised zinc oxide nanoparticles via chemical method by using zinc sulphate and sodium hydroxide as precursors and evaluated the antibacterial properties of the prepared nanoparticles against four bacterial strains, *Escherichia coli ATCC* 25922 and *Pseudomonas aeruginosa ATCC 27853* as gram negative bacteria, *Staphylococcus epidermidis PTCC 1114* and *Staphylococcus aureus ATCC 25923* as gram positive bacteria. The prepared zinc oxide nanoparticles are characterized by UV-Vis spectroscopy, scanning

electron microscope (SEM) and XRD analysis. The average particle size found from SEM is 50nm. Minimum inhibitory concentration (MIC), minimum bactericidal concentration (MBC), time–kill studies and disk diffusion method as per CLSI recommendations are done to study the antibacterial activity. The MIC results show that with increase in nanoparticles suspension dose and treatment time, the efficiency also increases. The effectiveness of disk-diffusion method for *P. aeruginosa* is better. The results suggest that ZnO nanoparticles are an outstanding antibacterial material. [69]

L. S. Reddy et al. have investigated the antibacterial activity of synthesised zinc oxide nanoparticles against *Klebsiella pneumonia ATCC 70068*. The method used for the prepration of ZnO is precipitation method and characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD). The disk diffusion method is used to determine in-vitro susceptibility of *K. pneumonia*. The serial diution method is used to evaluate the minimum inhibitory concentration value (MIC). The crystallites size obtained by XRD is in the range of 20-40nm. The MIC vlue of zinc oxide nanoparticle is 40microgram/ml. ZnO nanoparticles inhibit the growth of *K. Pneumonia* after 4 hour which is revealed by the standard growth curve. It is found that there is a decrease in the optical density of ZnO nanoparticle in the presence of SDS within incubation of 30min. [70]

N. Jones et al. have investigated the antibacterial activity of metal oxide nanoparticles such as MgO, TiO2, Al2O3, CuO, CeO2, and ZnO. The bacterial strains used are *Staphylococcus epidermidis 1487 and RP62A strains, Streptococcus pyogenes NZ315, Enterococcus faecalis, Bacillus subtilis 168, Staphylococcus aureus* and Gram-negative *E. coli K12*. The growth analysis data suggests that zinc oxide nanoparticles show higher antibacterial effects than other nanoparticles on *Staphylococcus aureus*. [71]

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CHAPTER 3:

Objectives

Of

The

Work

3. OBECTIVES:

The objectives of the research work in details are given below as:

- To synthesize zinc oxide (ZnO) nanoparticles by a simple sol-gel process and characterize ZnO nanoparticles by using different techniques such as XRD, FTIR, FESEM and EDX for studying its various properties.

- To examine the efficiency of zinc oxide nanoparticles in removal of cadmium ions from real water sample analysis such as tap water and pond water by using Atomic Absorption Spectrophotometer (AAS).

- To investigate the efficiency of zinc oxide nanoparticles in removal of heavy metals, cadmium ions (Cd) from synthetic water by varying the pH and amount of ZnO nanoparticles using UV-Vis spectrophotometer.

- To study adsorption isotherm, adsorption kinetics and adsorption thermodynamics of adsorption process of ZnO nanoparticles for Cd (II) ions removal.

- To study the antibacterial properties of prepared ZnO nanoparticles by varying its concentration.

CHAPTER 4:

Materials

&

Methods

4. MATERIAL AND METHODS

This chapter discusses about the raw materials used for the synthesis of the zinc oxide (ZnO) nanoparticles and the description of the method use for the synthesis of zinc oxide nanoparticles. This chapter also includes the description of characterization techniques like XRD, FTIR, FESEM, EDX use to describe the physical properties and surface morphologies of the synthesised powder.

The batch mode method use for conducting the adsorption experiment by varying the different parameters such as pH, adsorbent (ZnO nanoparticles) dosages, time and temperatures and the equations use for calculating removal efficiency and adsorption capacity is also detailed in this chapter. The different types of adsorbate use and adsorbent for the experiment are also discussed. The antibacterial efficacy of zinc oxide nanoparticle is also tested on gram positive bacteria and gram negative bacteria by varying the concentration of synthesised nanoparticles.

4.1. CHEMICALS REQUIRED

- Zinc chloride ($ZnCl_2$) dry purified >95% purity, M=136.28g/mol, Merck Mumbai,
- Ammonium Hydroxide (NH_3), >25%, M=17.03 g/mol, Merck Mumbai,
- Double distilled water, prepare in the laboratory of School of Materials Science and Nanotechnology,
- Cadmium nitrate tetrahydrate purified [$Cd(NO_3)_2 \cdot 4H_2O$] >99%, M=308.47g/mol, Merck Mumbai,
- Conc. Nitric acid (HNO_3), 68-70%, M=63.01 g/mol, Merck Mumbai,
- Sodium hydroxide pellets (NaOH) >97% purity, M=40.00g/mol, Merck Mumbai.

4.2. SYNTHESIS OF ZINC OXIDE NANOPARTICLES

The zinc oxide nanoparticles are synthesised by the previous method published by V. Srivastava et al. [1]. The zinc oxide nanoparticles are synthesised by simple solution based approach of sol-gel method. Zinc chloride dry ($ZnCl_2$) is dissolved in distilled water to prepare 0.23M solution of zinc chloride. The solution is stirred continuously in a magnetic stirrer till zinc chloride gets dissolved completely. The experiment is performed at room temperature. Ammonium hydroxide solution is made by dissolving ammonia solution in distilled water. Ammonium hydroxide solution is added dropwise to the prepared zinc chloride solution till white bulky precipitate is formed. The pH of the solution is measured by pH paper which is high. This mixture is continuously stirred till white bulky precipitate settles down completely. After that, the precipitate is filtered. The formed precipitate is washed with distilled water many times to remove impurities and to decrease the pH value. Then, the precipitate is dried in hot air oven at 100°C till complete drying of the precipitate. The obtained dried precipitate is ground with the help of mortar and pestle in order to get fine powder. The obtained powder is calcined in a muffle furnace at 450°C by keeping the calcination temperature of 5°C/min for 2 hr [1]. Therefore, the final calcined powder is the zinc oxide nanoparticles formed and hence confirmed by the mentioned characterization techniques.

4.3. CHARACTERIZATION OF ZINC OXIDE NANOPARTICLES

The characterization techniques used for the synthesis of Zinc Oxide (ZnO) nanoparticles are X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscope (FESEM) and Energy Dispersive X-rays (EDX). All these techniques are used after calcination of the sample.

The Zinc Oxide (ZnO) nanoparticles sample is characterized by X-ray diffraction, (Bruker D8 Advance), supplied source of CuKα radiation with wavelength of 1.5418 Å, and voltage of 35 kV and current of 35 mA by powder diffraction method. The value of angle 2θ is taken in the range of 20° to 80° with an increment of 0.0153° at each step. XRD method is used to obtain crystal structure, crystal phase and crystallite size of the synthesised ZnO nanoparticles.

The zinc oxide nanoparticles are also analyzed by using Fourier Transform Infrared Spectroscopy, (Shimadzu, IR prestige-21) in the range of 400cm^{-1} to 4500cm^{-1} to find out the infrared spectrum of absorption of the sample. FTIR is used to identify the surface functional groups and vibrational spectra of the synthesised zinc oxide nanoparticles. In FTIR analysis, potassium bromide (KBr) is used for the initialization of background then background spectrum is collected. Samples are mixed with KBr to find the stretching vibrational bonds present in the synthesised ZnO nanoparticles.

The obtained powder is also characterized by field emission scanning electron microscope (FEI, INSPECT™ F50) with energy dispersive X-rays (BRUKER, Spectrum: Acquisition 2452). FESEM is used to find the surface morphology of nanoparticle at different magnification operated at 20kV. The powder form of the sample is inserted inside the chamber for FESEM analysis. EDX is used to find the constituents elements presents in ZnO nanoparticles.

4.4. ADSORBATE

Stock solution of 1000mg/L of cadmium is prepared by dissolving cadmium nitrate tetrahydrate [$Cd(NO_3)_2.4H_2O$] in double distilled water. The stock solution is further diluted to get the working solution of cadmium for the adsorption experiments. The pH of the solution is adjusted using 0.1M of nitric acid (HNO_3) and sodium hydroxide (NaOH).
For finding out the efficiency of the synthesised ZnO nanoparticles as an adsorbent, it is also applied in the analysis of real water. So, further in the study, tap water and pond water samples are also used as an adsorbate of the adsorption experiments.

4.5. ADSORBENT

The zinc oxide nanoparticles (ZnO) formed from the above synthesis experiment is used as an adsorbent for the removal of cadmium ions from prepared diluted cadmium aqueous solution. The ZnO nanoparticles are used for the batch study adsorption experiment. The ZnO nanoparticles are also used as an adsorbent for the real water samples analysis which is tap water and pond water.

4.6. ADSORPTION EXPERIMENT

Batch mode experiments are performed to study the adsorption of cadmium ions on zinc oxide nanoparticles at a constant temperature. For this experiment, a fixed amount of zinc oxide nanoparticles are added in prepared diluted cadmium solution of 50mL in a 100mL beaker at a fixed pH. Then, the solution is stirred for a definite amount of time at 200rpm in a magnetic stirrer. The nanoparticles were separated from the solution by filtration using Whatman™ filter paper after stirring has been done. The pH of the solution in adsorption process is adjusted by adding 0.1M nitric acid (HNO_3) and sodium hydroxide (NaOH). The batch mode study is carried out with different adsorbent mass, varying pH and different time at constant temperature. The absorbance value at cadmium wavelength in the solution before and after adsorption process is measured by using UV-Vis spectrophotometer (Shimadzu 3600) and the initial cadmium ions concentration and residual cadmium ions concentrations of the solution are calculated with the help of Beer-Lamberts law.

The removal percentage of cadmium (R %) in aqueous solution or removal efficiency is calculated as the given equation (Eq. 4.1) [1] :

$$R\,(\%) = \frac{C_i - C_e}{C_i} \times 100 \text{..... (4.1)}$$

where, C_i is initial concentration of cadmium ions of aqueous solution in mg/L and C_e is equilibrium concentration of Cd (II) ions of aqueous solution in mg/L [1].

The amount of cadmium ions adsorbed per unit adsorbent mass or adsorption capacity at equilibrium (mg/g) is calculated by the following equation (Eq. 4.2) [2]:

$$q_e = \frac{C_o - C_e}{m} \times V \text{..... (4.2)}$$

The amount of cadmium ions adsorbed per unit adsorbent mass or adsorption capacity (mg/g) at time t is calculated as the following expression (Eq. 4.3) [2]:

$$q_t = \frac{C_o - C_t}{m} \times V \text{..... (4.3)}$$

where, C_o is initial concentration of cadmium ions in mg/L, C_e is the residual concentration of cadmium ions of the solution in mg/L, C_t in mg/L is concentration of cadmium ion in solution at time t, t is time in minutes (min), V is volume of the solution in L and m is the mass of adsorbent in g [2].

The pH selected for adsorption batch study experiment are 4, 6 and 8 by making other parameter constant such as adsorbent dose as 0.1g, time of duration for stirring as 60min, temperature is kept at 30°C, and initial concentration of cadmium ions in aqueous solution as 200mg/L.

The variation of adsorbent mass is also studied in this study. The amount of zinc oxide nanoparticles are taken as 0.05g, 0.1g and 0.15g by keeping constant pH of 6, time of duration for stirring as 60 minutes, and temperature at 30°C.

The adsorption kinetics is also studied by varying time of 20, 40, 60 and 80min at three different temperature of 20, 30 and 40°C by keeping constant pH of 6 and adsorbent dose of 0.1g and initial concentration of cadmium ions constant.

The Energy Dispersive X-ray analysis (BRUKER, Spectrum: Acquisition 2452) is done on the residue powder obtained from the adsorption experiment in order to further prove adsorption of Cd (II) ion on ZnO nanoparticles.

Real water sample such as tap water and pond water is characterized by using Atomic Absorption Spectrophotometer (PerkinElmer, PinAAcle 900F and APHA 23rd Edition, 3111 B). The adsorption experiment as described above is performed on these two real water sample by keeping pH as 6, adsorbent dose as 0.1g, time of 60 minutes and temperature at 30°C. The cadmium concentration in real water sample is analysed by AAS before and after experiment.

4.7. BACTERIA CULTURE

The two water-borne bacteria which are used to test the antibacterial activity of zinc oxide nanoparticles are one gram positive bacteria, *Enterococcus faecalis (E. faecalis)* and one gram negative bacteria *Escherichia coli (E. coli)*.

4.8. ANTIBACTERIAL TEST OF ZINC OXIDE NANOPARTICLES

Antibacterial properties of synthesized zinc oxide nanoparticles samples are analysed by using broth micro-dilution method. The Zinc oxide nanoparticles suspensions of 5mg/ml are prepared by dissolving 10mg in 2ml of distilled water with the help of ultrasonication. The sonication of the sample is performed till nanoparticles are completely dissolved. From the above concentration, two different concentrations are prepared by half-dilution method which are 2.5mg/ml and 1.25 mg/ml.

100 microliters of nutrient broth is added to the wells of 96-well plate and 50 microliters of synthesised zinc oxide nanoparticle suspensions (three different concentrations) are added to it and then 10microliters of bacterial inoculums are added to it.

Wells with 100 microliters of nutrient broth and 10 microliters of bacteria suspensions are used as control. All the sets of experiment are performed in triplicate. The 96-well plate is then incubated at 37℃ for 6 hours. After the incubation, the 96-well plate is then read for the absorbance value using microplate reader (iMark Microplate Reader 595nm) to measure the efficacy of the synthesised zinc oxide nanoparticles over gram positive and gram negative bacteria with three different concentrations [3].

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3. Sukri, Siti Nur Amalina Mohamad, Kamyar Shameli, Magdelyn Mei-Theng Wong, Sin-Yeang Teow, Jactty Chew, and Nur Afini Ismail, Cytotoxicity and antibacterial activities of plant-mediated synthesized zinc oxide (ZnO) nanoparticles using Punica granatum (pomegranate) fruit peels extract, Journal of Molecular Structure, 1189, 2019, 57-65.

CHAPTER 5:

Results

&

Discussions

5. RESULTS AND DISCUSSION

The results obtained from the different characterization procedures of XRD, FTIR, FESEM and EDX which are used to study the synthesised zinc oxide nanoparticles have detailed in this chapter. The discussion in details about the adsorption of cadmium ions, Cd (II) by zinc oxide nanoparticles (ZnO) is also being included in this chapter. For the adsorption studies, removal efficiency of adsorption process and maximum adsorption capacity is calculated and plotted by varying the pH and adsorbent dose. The adsorption isotherm is also studied by taking into account of Langmuir and Freundlich isotherm. The adsorption kinetics is also studied by varying time duration at three different temperatures. The variation of adsorption capacity with different time at particular temperature is also plotted in this chapter. Pseudo first order model and pseudo second order model are also studied at three different temperatures. The activation energy of the adsorption process is also found in this chapter. The adsorption thermodynamics process is also explained in this chapter.

The adsorption process of Cd (II) ions by ZnO nanoparticles are also applied in real water samples of tap water and pond water. The analysis is done and removal efficiency is calculated. Therefore, the efficiency of synthesised ZnO nanoparticles is found.

5.1. CHARACTERIZATION OF ZNO NANOPARTICLE

5.1.1. X-RAY DIFFRACTION (XRD)

The X-Ray Diffraction (XRD) pattern of prepared ZnO nanoparticles is shown in figure Figure 5.1. The major diffraction peaks are obtained at 31.68°, 34.35°, 36.17°, 47.47°, 56.52°, 62.80°, 66.32°, 67.89°, 69.01°,71.81°, and 76.89° which can be assigned to crystalline planes of (100), (002), (101), (102), (110), (103), (200), (112), (201),(004), and (202) respectively. All the peaks obtained in the XRD pattern are matched well with the hexagonal structure of ZnO, which can be assigned according to the available Joint Committee on Powder Diffraction Standards, JCPDS card no. 36-1451 with lattice constant a=3.249Å and c=5.206Å. The maximum intensity peak is observed at 36.17° oriented in (101) plane. The peaks are of high intensity and narrow width that is represented by high crystallinity with low surface defects. The sample has good crystallinity which is indicated by sharp intensity of the XRD peak. There are no peaks of any other phase or impurities which confirms synthesis of pure zinc oxide nanoparticle [11].

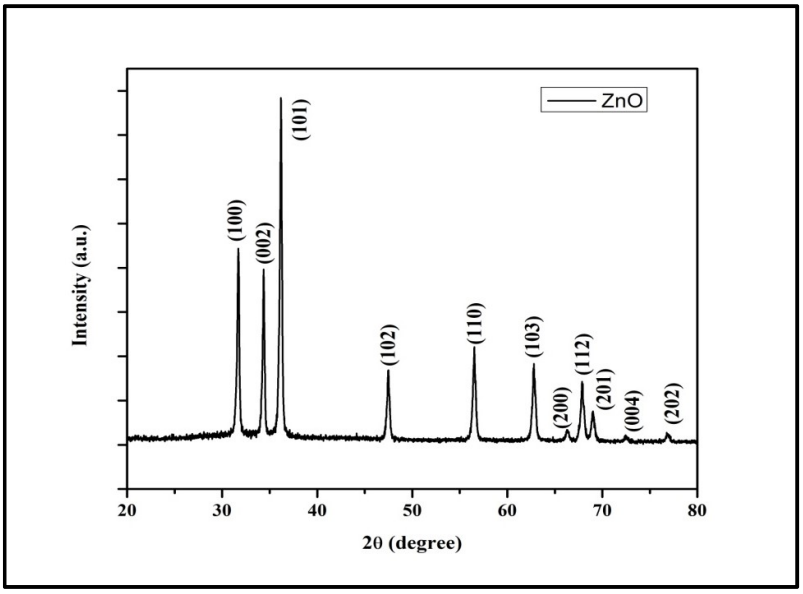

Figure 5.1. XRD of ZnO nanoparticles.

The size of zinc oxide nanoparticles which is determined by XRD and corresponding angles, (hkl) and Full Width Half Minima (FWHM) values are shown in Table 2 and are in the range of 19-28nm. The crystallite size of ZnO nanoparticles is determined from XRD pattern according to the following Scherer's equation (Eq. 5.1) [20]:

$$D = \frac{(k\lambda)}{(\beta \cos\theta)} \quad \text{..... (5.1)}$$

where, D is crystallite size of ZnO nanoparticles, k is a constant whose value is 0.89 [19], λ is wavelength of Cukα radiation, θ is Bragg diffraction angle and β is Full Width Half Maxima (FWHM) in radian. [20]

So, the average crystallite size of Zinc Oxide nanoparticles is 24nm.

Table 2: Details of ZnO nanoparticles from XRD.

Angle, 2Ɵ(degrees)	FWHM	(hkl)	Size(nm)
31.6855	0.29129	100	27.87
34.3508	0.28353	002	28.77
36.1742	0.30168	101	27.15
47.4743	0.33669	102	25.07
56.5225	0.38481	110	22.62
62.8041	0.4192	103	21.29
66.3202	0.45745	200	19.81
67.8910	0.46617	112	19.58
69.0107	0.45572	201	20.14
76.8911	0.42396	202	22.53

5.1.2. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Fourier Transfer Infrared Spectroscopy (**FTIR**) is used to study the functional groups of prepared ZnO nanoparticles. The FTIR spectrum of synthesized ZnO nanoparticles is represented by Figure 5.2. The FTIR spectrum shows strong absorption peak in the range of 400 cm^{-1} to 514 cm^{-1} with most dominant peak at 420 cm^{-1} which can be attributed to stretching vibrations of Zn-O bond in Zinc oxide nanoparticles. The weak peak near absorption band 1385 cm^{-1} can be corresponded to deformation of angular ammonium ion [1]. The absorption peak is observed at 690 cm^{-1} and 900 cm^{-1} which can be attributed to the Zn-OH functional groups. The weak absorption peak around the wavenumber of 1340 cm^{-1} can be assigned to the functional group of CO_2 which can be predicted from the outside air [17]. The broad absorption peak is observed at 3500 cm^{-1} which can be attributed to stretching vibrations mode of the hydroxyls (-OH) groups on the surface of zinc oxide nanoparticle and sharp peak is observed near 3450 cm^{-1} can be assigned to the free hydroxyl groups. The weak peak observed at 1590 cm^{-1} can be corresponded to the bending vibration mode of H-O-H water molecules. The other peaks may be due to some unresolved impurities [18].

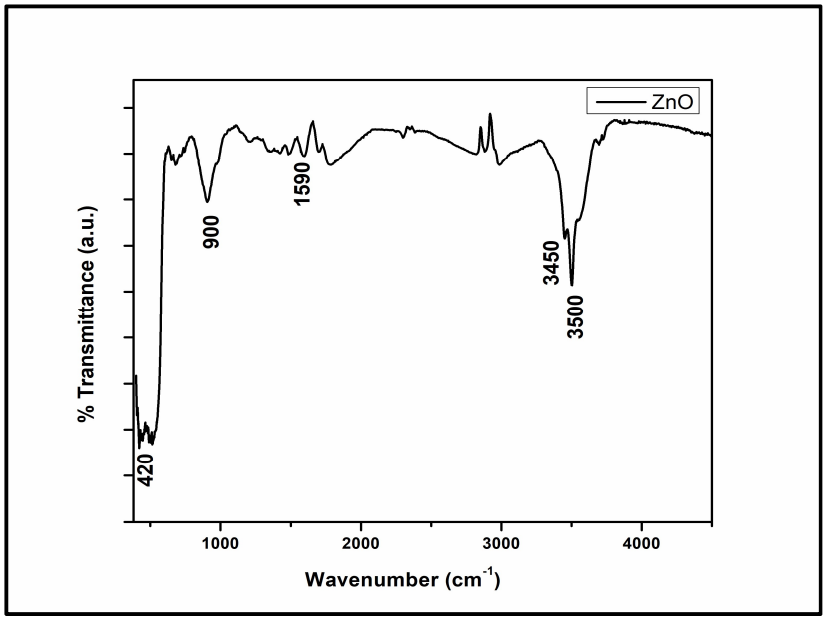

Figure 5.2. FTIR of ZnO nanoparticles.

5.1.3. FIELD EMISSION SCANNING ELECTRON MICROSCOPE (FESEM)

Field Emission Scanning Electron Microscope **(FESEM)** is used to find about the surface morphology of the synthesised nanoparticles. The FESEM micrograph of the synthesised zinc oxide nanoparticles sample at 40,000; 80,000 and 130,576 magnifications is represented by Figure 5.3, Figure 5.4 and Figure 5.5. The images show that large number of rod like shape of ZnO nanoparticles along with some of spherical shape particles and high agglomeration of powder is also resulted. The average diameter and average length of the rod shape is 60-100nm and 150-300nm. The average diameter of spherical shaped particle is 45-75nm. There are an agglomeration of zinc oxide nanoparticles because of high surface area and surface energy.

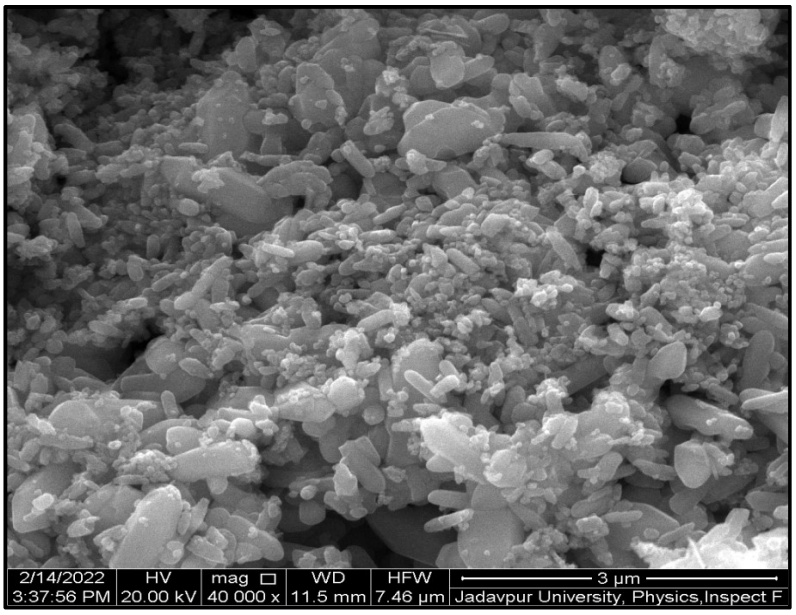

Figure 5.3. FESSEM image at 40,000 magnifications.

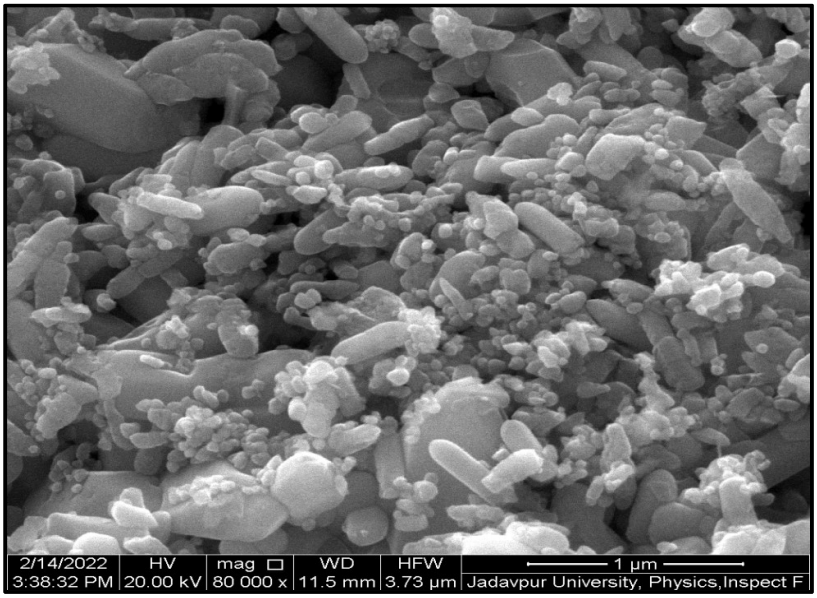

Figure 5.4. FESEM image at 80,000 magnifications.

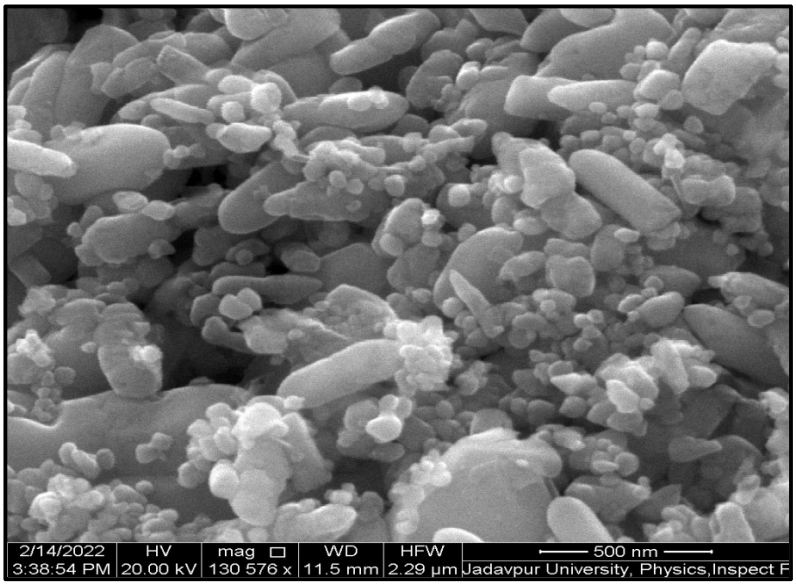

Figure 5.5. FESEM image at 130,576 magnifications.

5.1.4. ENERGY DISPERSIVE X-RAY (EDX)

The **EDX** determines the purity of Zinc Oxide nanoparticles. The element composition present in the sample is determined by EDX. EDX pattern of synthesized ZnO nanoparticles is represented by Figure 5.6. EDX data composes of two elements which are zinc (80.34%) and oxygen (19.66%) which is shown in Table 3. The high purity of Zinc oxide nanoparticles is confirmed by the EDX result. The binding energy at 1KeV and 0.5KeV show major emission energy which can be concluded for zinc and oxygen as suggested in the published paper by A.C. Janaki et al. [15].

Researchers have reported earlier in the published literature that the four peaks shown here in the Figure 5.6 can be identified as zinc and oxygen. [16]

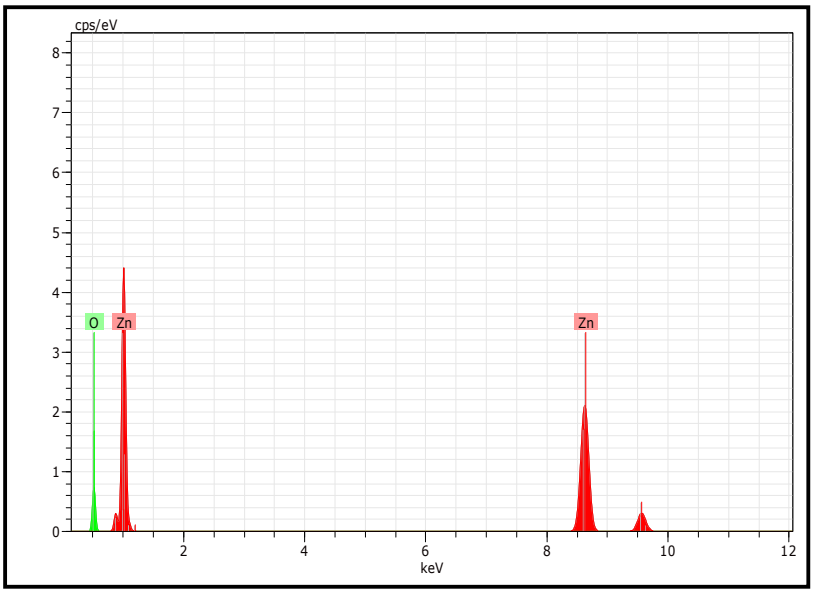

Figure 5.6. EDX of ZnO nanoparticles.

Table 3: EDX analysis of ZnO nanoparticles.

ELEMENT	Wt%	At%
Zinc	80.34	50.00
Oxygen	19.66	50.00

5.2. ADSORPTION STUDIES

5.2.1. EFFECT OF PH

Adsorption of cadmium ions [Cd (II)] can be significantly affected by the pH of the solution. So, the effect of pH is one of the significant factor. For pH study, the pH of the solution is varied from 4 to 8 by keeping the initial concentration of Cd (II) ions in the solution constant and adsorbent dose is taken as 0.1g. There may be precipitation of Cd (II) ions in the form of cadmium hydroxide at high pH of the solution. The variation of removal efficiency (R %) of Cd (II) ions with the solution pH is shown by Figure 5.7. Figure 5.8 shows the variation of adsorption capacity of Cd (II) ions (q mg/g) on ZnO nanoparticles with the solution pH. The observation derived from the figures that the adsorption capacity or removal efficiency of Cd (II) ions is maximum at pH 6. This pH effect of the solution on adsorption process can be explained by studying the zinc oxide nanoparticles surface charge and degree of speciation of Cd (II) ions. The adsorption of Cd (II) ions on zinc oxide nanoparticles is low in acidic medium or at pH 4 may be because of the competition between hydrogen and Cd (II) ions for the same surface sites of ZnO nanoparticles and this adsorbent have positive surface charges in the medium. The adsorbent surface, hydrous oxide surface (MOH) at lower pH will react with H^+ ions forming protonated surface (MOH^{2+}) [19]. The ZnO surface becomes more negative by increasing the solution pH. The hydroxide ion (OH^-) reacts with the hydrous oxide (MOH) forming deprotonated (MO^-) ion. There will be dissociation of hydroxyl group from the ZnO surface and forming low soluble Cd (II) ion species such as $CdOH^+$, $Cd(OH)_2$ which may be contributed to the maximum adsorption of cadmium [3]. At high pH, there is precipitation of Cd (II) ions which no more serves as an adsorbate for the active sites of ZnO surface. The maximum removal of Cd (II) ions obtained at pH 6 was 77% and the maximum adsorption capacity of Cd (II) ions by ZnO nanoparticle obtained is 75mg/g. So, pH 6 is selected for the further adsorption experiment.

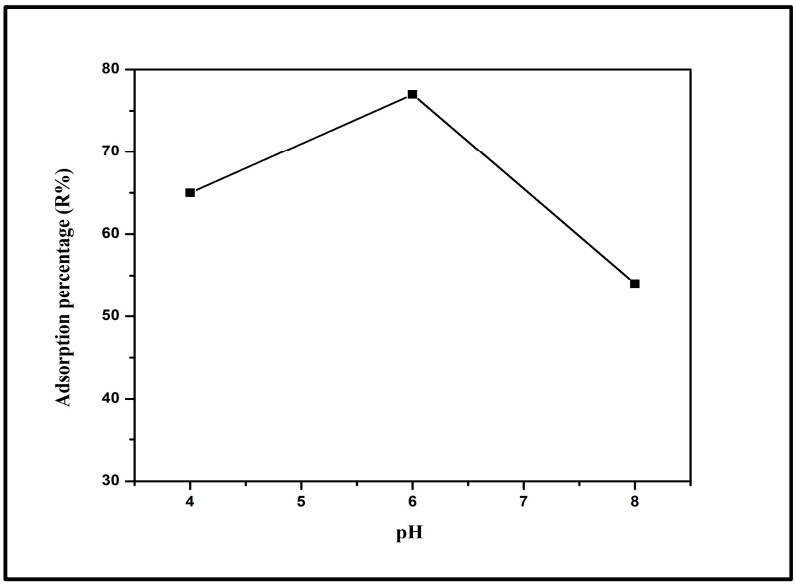

Figure 5.7. Effect of pH on adsorption percentage (R %) of Cd (II) ions by ZnO nanoparticles.

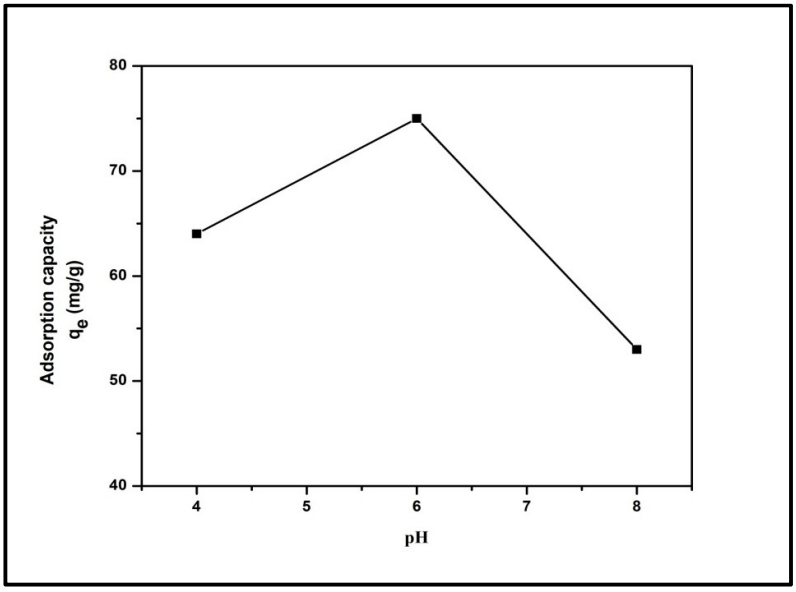

Figure 5.8. Variation of adsorption capacity, q_e (mg/g) with the solution pH.

5.2.2. EFFECT OF ADSORBENT DOSE

The amount of adsorbent taken for the adsorption studies are 0.05, 0.1 and 0.15g per 50ml of the solution by keeping the initial concentration of cadmium ions constant and consider pH as 6. The duration taken for the study is 60minutes and temperature is kept at 30ºC. The variation of adsorption capacity (mg/g) of Cd (II) ions on ZnO nanoparticles with adsorbent dose is shown in Figure 5.9. It is clear from the figure that the adsorption capacity is maximum at 0.05g and then the adsorption capacity decreases and nearly same. There is decrease in adsorption capacity by increasing the adsorbent dose may be because of the less number of Cd (II) ions for the increase in adsorption sites of zinc oxide nanoparticles or the agglomeration of nanoparticles in the solution. The reason for this decline may be equilibrium established between Cd (II) ion and zinc oxide nanoparticles in the solution [4].

Aigbe et al. have observed the removal of cadmium ions by using zinc oxide nanoparticles, carbonised saw dust and zinc oxide nanoparticles-carbonised saw dust composite shows same pattern of the effect of adsorbent dosage as the results studied in the Figure 5.9 of this work [25].

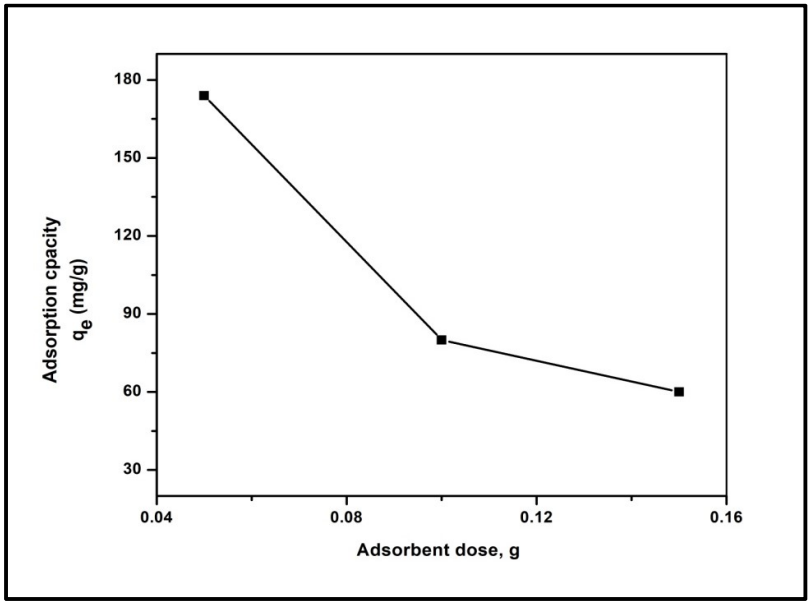

Figure 5.9. Variation of adsorption capacity with adsorbent dose.

5.3. ADSORPTION ISOTHERM

The equilibrium conditions of the adsorption process can be explained by studying the adsorption isotherm. The mechanism of the adsorption process can be understood from adsorption isotherm by determining the adsorbent capacity and other related adsorption parameters. There are several isotherms available. The Langmuir and Freundlich isotherm models are two most popular and important isotherm model to fit these experimental data values. These two models are used to describe the adsorption of cadmium ions by zinc oxide nanoparticles [6].

5.3.1. LANGMUIR ISOTHERM

The assumptions of Langmuir isotherm model are that the adsorption process happens at monolayer surface of adsorbent; each surface site can adsorb maximum one adsorbate species at a time and lack of interactions between near adsorbed species and all unoccupied adsorption sites [7]. The Langmuir isotherm can be expressed as following Eq. 5.2 [7]:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad \text{..... (5.2)}$$

and the linear form of Langmuir isotherm can be written as the following equation (Eq. 5.3) [7]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad \text{..... (5.3)}$$

Where q_e and q_{max} are adsorption capacities at equilibrium and maximum adsorption capacities in mg/g, C_e is the concentration of Cd (II) ions at equilibrium in mg/L and K_L is the Langmuir constant related to adsorption energy in (L/mg) [7].

R_L is a constant known as separation factor or equilibrium factor which is used as essential features of Langmuir isotherm for predicting the affinity between adsorbate and adsorbent and can be calculated as following equation (Eq. 5.4) [21]:

$$R_L = \frac{1}{1 + a_L C_o} \quad \text{..... (5.4)}$$

Where a_L is Langmuir constant and C_o is initial concentration in mg/L. R_L is the indication of isotherm shape which can be unfavorable if it is greater than1, linear if it is 1, favorable if it is in between 0 and 1 and irreversible if it is equal to 0 [21].

Figure 5.10 shows a plot of $\frac{C_e}{q_e}$ versus C_e with a slope of $1/q_{max}$ or $a_L/K_L$and intercept of $\frac{1}{q_{max}K_L}$ with R^2=0.76 which gives the maximum adsorption capacity is 86mg/g and K_L is 2.71L/mg. $R_L$is calculated as 0.2 which indicates the adsorption process is favorable.

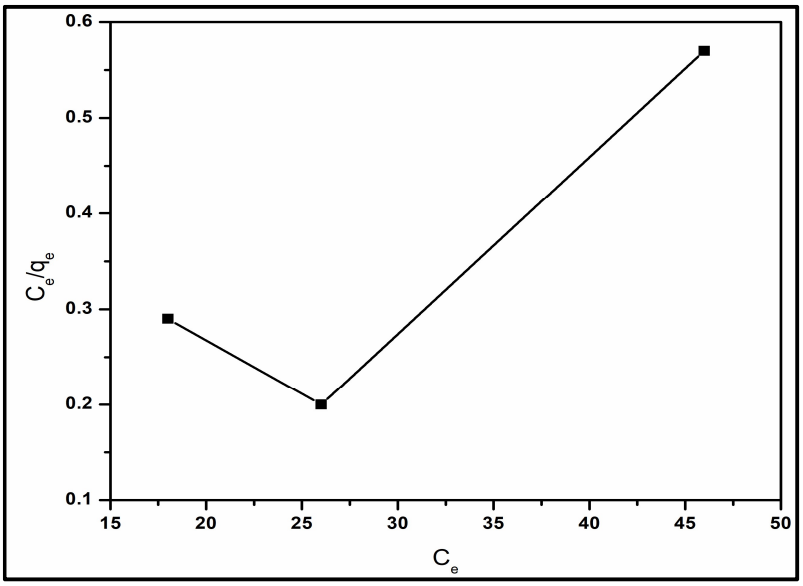

Figure 5.10. Langmuir isotherm of Cd (II) ions by ZnO nanoparticles.

5.3.2. FREUNDLICH ISOTHERM

Freundlich isotherm is often used to describe multilayer adsorption process onto heterogeneous surface sites. The linear form of Freundlich model can be written as the following Eq. 5.5 [3]:

$$\log q_e = \frac{1}{n}\log C_e + \log K_f \quad \text{..... (5.5)}$$

Where q_e is adsorption capacity at equilibrium in mg/g, C_e is concentration at equilibrium in mg/L, n and K_f are Freundlich constants related which represent adsorption capacity and intensity of the adsorption process [3].

Figure 5.11 shows a plot between log q_e versus log C_e which gives a slope (1/n) of 0.25 and intercept ($\log K_f$) of 1.55 from Eq. 5.5. 1/n is 0.25 which means it is in between 0 and 1 that indicates the favourability of adsorption process. The equilibrium parameters obtained from Langmuir and Freundlich model are mentioned in Table 4 . The correlation coefficient (R^2) of

Langmuir isotherm is 0.75 so adsorption data is fitted better with the Langmuir model indicating the cadmium ions adsorbed on the adsorbent surface by monolayer coverage.

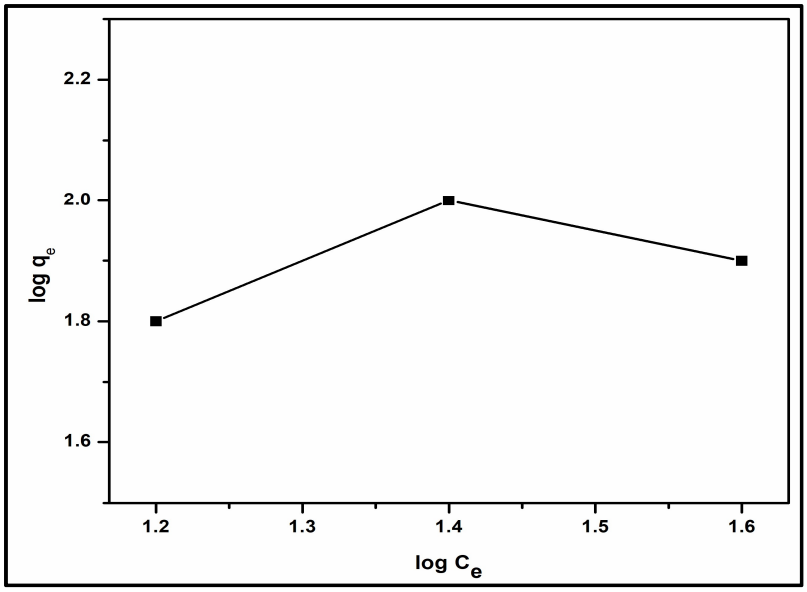

Figure 5.11. Freundlich isotherm model of Cd (II) ions by ZnO nanoparticles.

Table 4: Isotherm parameters for adsorption of Cd (II) ions on ZnO nanoparticles.

Langmuir			**Freundlich**		
q_{max} (mg/g)	K_L(L/mg)	R^2	K_f(mg/g)	1/n	R^2
86	2.7	0.75	35.48	0.25	0.25

5.4. ADSORPTION KINETICS

Adsorption kinetic models are used to determine the mechanism and steps of rate controlling for the adsorption of cadmium ions on zinc oxide nanoparticles. For kinetics study, 0.1g of zinc oxide nanoparticles is taken in 50 ml of solution by keeping initial concentration of Cd (II) ions fixed in aqueous solution and pH as 6. The time durations taken for this study are 20, 40, 60 and 80 minutes at three different temperatures of 20 ºC, 30 ºC and 40ºC. Temperature is one of the significant factors for the study of adsorption kinetics process. The temperature may affect the adsorption of Cd (II) ions by ZnO nanoparticles. Figure 5.12 shows adsorption capacity (q_t) in mg/g with time t in minutes at temperature 20°, 30°, and 40ºC. The kinetic parameters provide significant information about the rate of adsorption which can be used for designing the process of adsorption. The pseudo first order, pseudo second order and intraparticle diffusion model are kinetics models which are used to evaluate the kinetics of the adsorption process and explain the experimental data values [8].

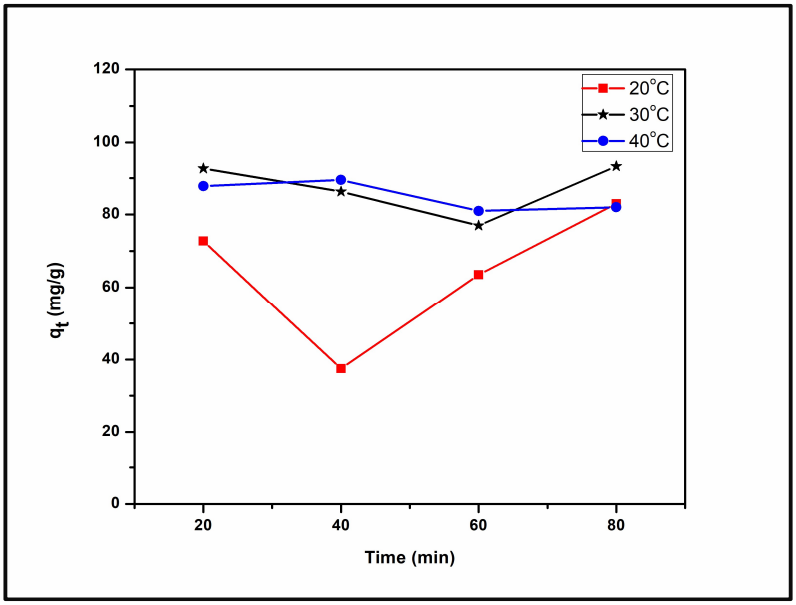

Figure 5.12. Variation of adsorption capacity with time for 20 ºC, 30 ºC and 40°C.

5.4.1. PSEUDO FIRST ORDER MODEL

The pseudo first order equation is also known as lagergren's equation. This model is based on the adsorption capacity of solid in solid liquid system. The linear form of pseudo first order model equation (Eq. 5.6) can be written as the following expression [9]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{..... (5.6)}$$

where q_e is adsorption capacity at equilibrium in mg/g and q_t is adsorption capacity at time t in mg/g, time required for adsorption is t in minutes and k_1 is pseudo first order rate constant in min^{-1}. The rate constant can be found from the linear plot between $\ln(q_e - q_t)$ versus t [9].

Figure 5.13 shows the plot of $\ln(q_e - q_t)$ versus t for temperature 20°C, 30°C and 40°C from which pseudo first order rate constant at different temperature can be found by slope and intercept. The correlation coefficient (R^2) values obtained by applying the pseudo first order model results are not high for the cadmium adsorption on zinc oxide nanoparticles. (Table 5)

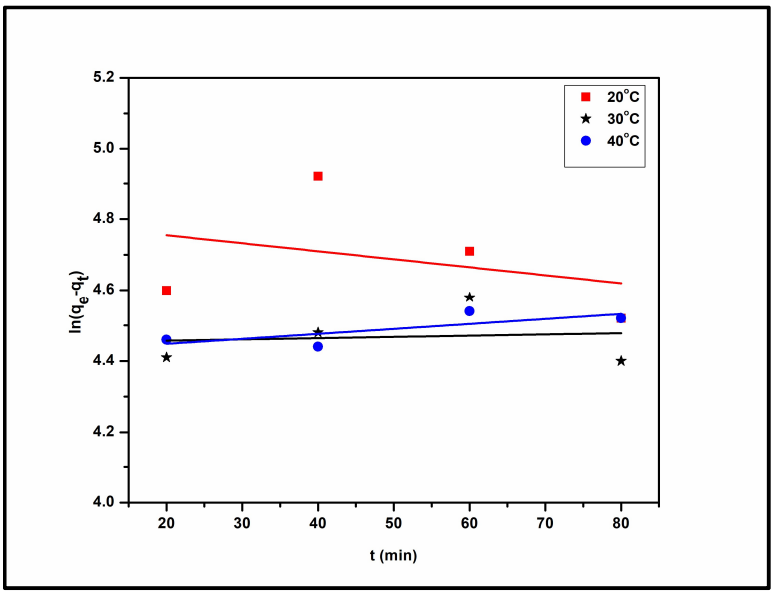

Figure 5.13. Pseudo First Order kinetic model for Cd (II) ions adsorption on ZnO nanoparticles at temperature 20°C, 30°C and 40°C.

5.4.2. PSEUDO SECOND ORDER MODEL

The important factor in the system of adsorption is finding the adsorption rate values. The pseudo second order model is also known as Ho and Col equation. The linear form of pseudo second order rate model is expressed by the following equation (Eq. 5.7) [17]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 {q_e}^2}\right) + \frac{t}{q_e} \quad \text{..... (5.7)}$$

where, q_t is the adsorption capacity at time t in mg/g, t is time in minutes, q_e is calculated adsorption capacity in mg/g and k_2 is the pseudo second order rate constant (min^{-1}). [17]

The adsorption pseudo second order rate model parameter q_e and k_2 can be calculated from the slope and intercept of t/q_t versus t graph. Figure 5.14 shows pseudo second order kinetic

model for cadmium ions adsorption on zinc oxide nanoparticles at temperature 20°C, 30°C and 40°C which is linear plot between t/q_t versus t.

Table 5 shows the parameters found from the pseudo second order rate model at temperature 20°C, 30°C and 40°C. The correlation coefficient (R^2) of the pseudo second order rate model is high and better than pseudo first order model. So, the experimental kinetic data of the adsorption system can be more appropriately represented by pseudo second order rate model.

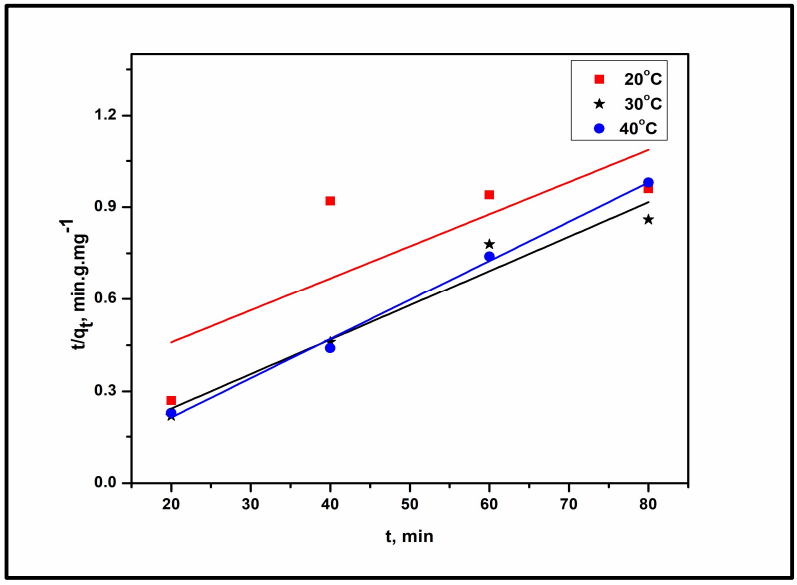

Figure 5.14. Pseudo Second Order Kinetic model fit for Cd (II) ions adsorption on ZnO nanoparticles at temperature 20°C, 30°C and 40°C.

Table 5: Adsorption kinetic model rate parameters for cadmium ions adsorption on zinc oxide nanoparticles at 20°C, 30°C and 40°C.

T°C	Pseudo First Order Model			Pseudo Second Order Model		
	$k_1 \times 10^{-3}$ (min^{-1})	q_e (mg/g)	R^2	$k_2 \times 10^{-3}$ ($g.mg.min^{-1}$)	q_e (mg/g)	R^2
20	2.25	121.51	0.11	0.44	95.69	0.65
30	0.35	85.62	0.012	5.9	91.09	0.956
40	14	83.1	0.58	4.06	78.43	0.995

5.4.3. INTRAPARTICLE DIFFUSION MODEL

The adsorption process can be studied by intraparticle diffusion model is proposed by Weber and Morris model which is written by the following equation (Eq. 5.8) as [22]:

$$q_t = k_{id}t^{1/2} + C \text{..... (5.8)}$$

where, q_t is adsorption capacity in mg/g at time t, t is time in minutes, k_{id} is intraparticle diffusion rate constant in mg g^{-1} min^{-1} and C is the intercept. [22]

The stages that involve the adsorption of adsorbate molecules onto the surfaces of adsorbent are all adsorbate molecules get transferred across the boundary of adsorbent, metal ions diffusion into adsorbent surface via boundary layer and intraparticle diffusion of metal ions from adsorbent surface to its pores. The adsorptions of metal ions are dominant either by intraparticle pores diffusion or film diffusion that is the transportation rate of metal ions into adsorbent [11].The intraparticle diffusion rate constant can be determined by plotting the graph of q_t versus t. The slope of the graph gives the value of intraparticle diffusion rate constant. Figure 5.15 shows intraparticle diffusion model for cadmium adsorption on ZnO nanoparticle at three different temperatures of 20°, 30° and 40°C. The data obtain from the experiment as shown in Figure 5.15 clearly gives the idea that the straight line fit does not pass through origin which implies the difference between mass rate transfer in the first and last stages of the adsorption process.

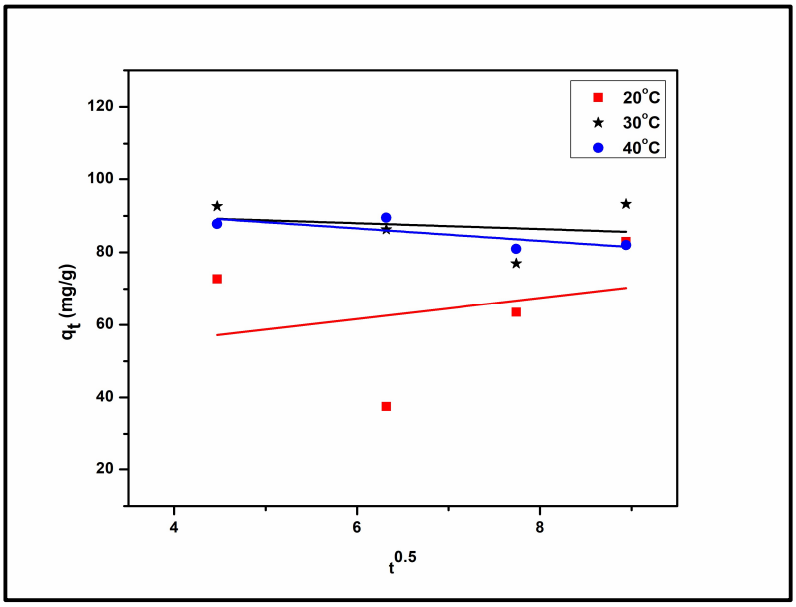

Figure 5.15. Intraparticle Diffusion Model of Cd (II) ions adsorption on ZnO nanoparticles at 20°, 30° and 40°C.

5.5. ACTIVATION ENERGY OF ADSORPTION PROCESS

The kinetics data is used for the calculation of adsorption activation energy of Cd (II) ions on ZnO nanoparticles at temperature 20°C, 30°C and 40°C. Activation energy can possibly be calculated from the pseudo second order rate constants values which are given in Table 5 by using the Arrhenius linear relation. The Arrhenius linear equation for calculating activation energy E_a can be expressed by the following Eq. 5.9 [12]:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad \text{..... (5.9)}$$

where, k_2 is pseudo second order rate constant in $g \cdot mg^{-1} \cdot min^{-1}$, E_a is activation energy in $kJ \cdot mol^{-1}$, A is frequency factor or pre-exponential factor in min^{-1}, T is temperature of adsorption in K and R is gas constant whose value is given as 8.314 $J \cdot mol^{-1} \cdot K^{-1}$ [12].

Physical adsorption and chemical adsorption process can be distinguished by using the magnitude of activation energy. The range of activation energy required for physical adsorption process is 5-40 kJ/mol because this adsorption processes are reversible and time required for attaining equilibrium is very fast. The range of activation energy required for chemical adsorption process is 40-800 kJ/mol because these adsorption processes require strong chemical forces [13]. The slope of $\ln k_2$ versus 1/T graph gives the value of activation energy (E_a) and intercept of the graph gives the value of Arrhenius frequency factor (A). Figure 5.16 shows the linear plot of $\ln k_2$ versus 1/T graph with correlation coefficient (R^2) value as 0.683. The activation energy found from the graph for cadmium ions adsorption onto zinc oxide nanoparticles is 84.195kJ/mol which implies that the chemical adsorption process takes place and cadmium ions are chemically adsorbed on the zinc oxide nanoparticles surface.

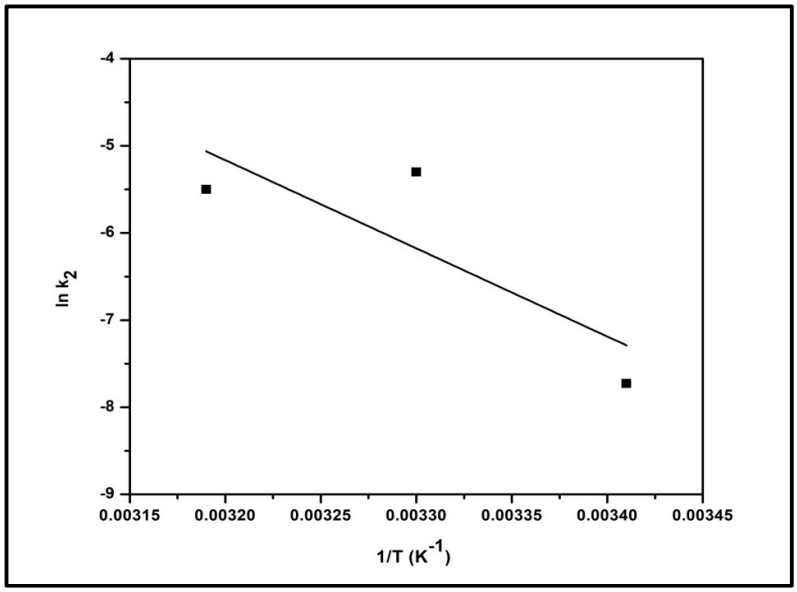

Figure 5.16. Plot of $\ln k_2$ with 1/T.

5.6. ADSORPTION THERMODYNAMICS

Adsorption thermodynamics studies are helpful in explaining any type of reaction. The temperatures taken for the adsorption of cadmium ions on zinc oxide nanoparticles are 293K, 303K and 313K by keeping adsorbent mass as 0.1g, time duration is taken as 60minutes and pH as 6. Thermodynamics studies parameter such as enthalpy change (ΔH°), entropy change (ΔS°) and Gibb's free energy change (ΔG°) are found at different temperatures. The following expression use for calculating the Gibb's free energy change (ΔG°) is written as Eq. 5.10[5]:

$$\Delta G^\circ = -RT \ln k_c \text{.....} \quad (5.10)$$

where, T is temperature in K, R is gas constant whose magnitude is given as 8.314 $J \cdot mol^{-1} \cdot K^{-1}$, [5] and k_c is thermodynamic constant which is calculated by the following expression as Eq. 5.11 [5]:

$$k_c = \frac{C}{C_e} \text{.....} \quad (5.11)$$

where, C is the concentration of cadmium ions adsorbed onto zinc oxide nanoparticles and C_e is the final concentration of cadmium ions at equilibrium.
The other thermodynamic parameters can be found from the given Van't Hoff expression as Eq. 5.12 [5]:

$$\ln k_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \text{.....} \quad (5.12)$$

The slope and intercept of the linear plot of $\ln k_c$ versus 1/T gives the value of enthalpy change (ΔH°) and entropy change (ΔS°) [5].

Figure 5.17 shows the straight line plot between $\ln k_c$ versus 1/T with correlation coefficient (R^2) value of 0.974. This high R^2 value shows the better fit of the straight line plot.

Table 6 shows all the values of thermodynamic parameters of cadmium ions adsorption on ZnO nanoparticles. The positive values of enthalpy change (ΔH° = 128.88 KJ mol^{-1}) suggests the endothermic nature of the reaction. The endothermic nature of the adsorption process is also represented by increasing k_c values with increase in temperature as given in Table 6. The electrostatic attraction between cadmium ions and zinc oxide nanoparticles in an adsorption process is suggested by enthalpy change (ΔH°). An overall endothermic adsorption process is a result of the energy required for the metal ions to get attached on the surface of adsorbent. The positive value of entropy change ($\Delta S^\circ = 0.45594$ KJ mol^{-1} K^{-1}) suggests that the spontaneous process of adsorption which is thermodynamically favorable. The entropy change values are positive for Cd (II) ions adsorption suggests increase in randomness at the interface of solid/solution. The values of Gibb's free energy change (ΔG°) decrease with increase in temperature as shown in Table 6 gives the idea that the adsorption

of cadmium ions on zinc oxide nanoparticles increase with increase in temperature. The negative value of enthalpy change suggests the feasibility and the spontaneity of the adsorption process. The decrease in Gibb's free energy change with increase in temperature suggests that the adsorption is favourable at high temperature. [14]

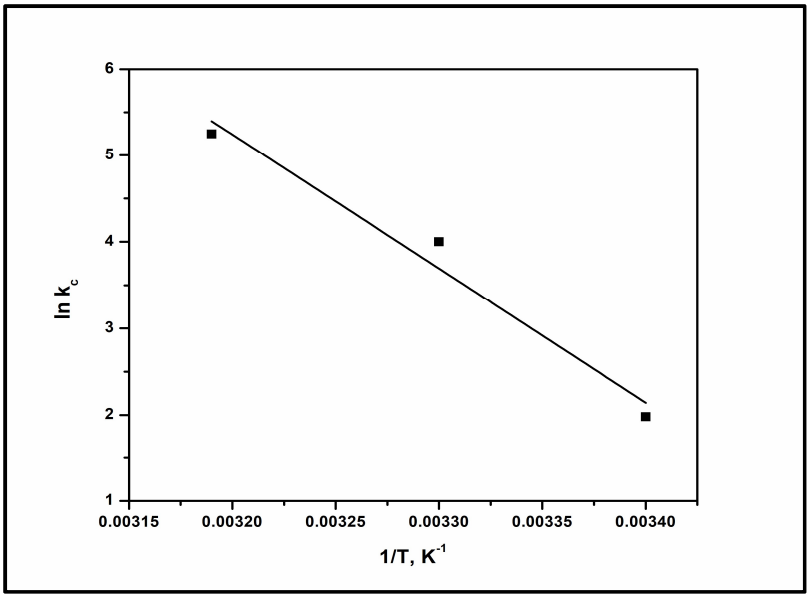

Figure 5.17. Plot of $\ln k_c$ versus 1/T for cadmium ions adsorption on zinc oxide nanoparticles.

Table 6: Thermodynamic parameters for Cd (II) ions adsorption on ZnO nanoparticles.

T (K)	k_c	ΔG° (kJ.mol⁻¹)	ΔH° (kJ.mol⁻¹)	ΔS° (kJ.K⁻¹.mol⁻¹)	R²
293	0.69	-1.68	128.88	0.45594	0.974
303	1.38	-3.48			
313	1.66	-4.32			

5.7. EDX ANAYSIS

The adsorption of Cadmium ions [Cd (II)] on Zinc Oxide (ZnO) nanoparticles is further confirmed by energy dispersive X-ray analysis (EDX) analysis. The residue powder which is obtained from adsorption experiment is dried at room temperature and analysed by EDX (BRUKER, Spectrum: Acquisition 2452) to prove the adsorption of Cd (II) ions.

The EDX pattern of Cd (II) ions on ZnO nanoparticles is confirmed by Figure 5.18. Figure 5.18 shows the presence of Cd (II) signals along with zinc and oxygen signals of ZnO nanoparticles. Hence it proves the adsorption of Cd (II) ions on ZnO nanoparticles.

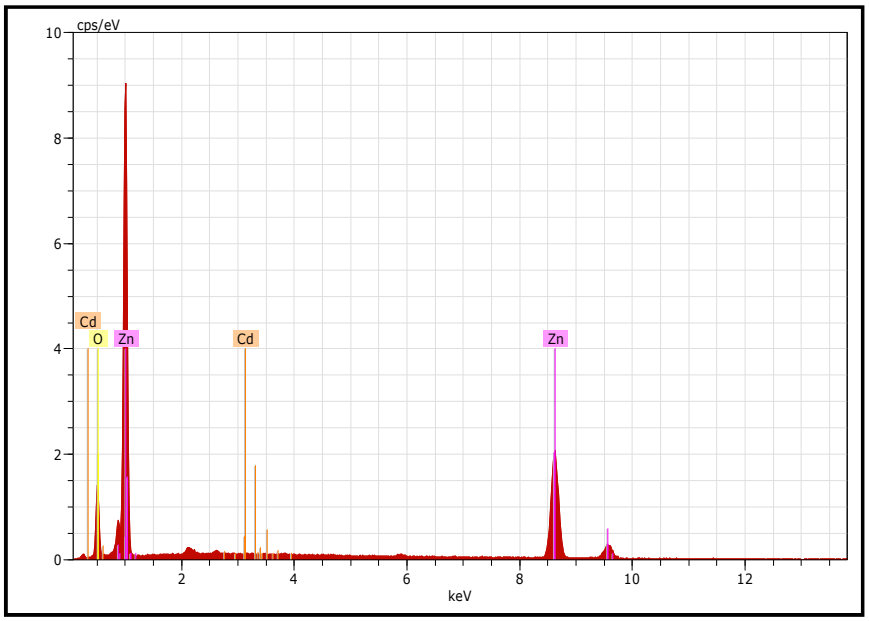

Figure 5.18. EDX pattern of Cd (II) ions on ZnO nanoparticles.

5.8. REAL WATER SAMPLE ANALYSIS

Real water samples are used in this work to analyse the efficiency of synthesised zinc oxide nanoparticles in removing cadmium ions from the samples by conducting the adsorption experiments (as defined previously in Materials & Methods of 4.6) on the samples. Real water samples used in this study are tap water and pond water.

For real water sample analysis, the tap water is collected from the tap, Laboratory of School of Materials Science and Nanotechnology, Jadavpur University. The collected tap water is analysed for the concentration of Cd (II) ions by using Atomic Absorption Spectrophotometer (PerkinElmer, Atomic Absorption Spectrometer PinAAcle 900F). The initial Cd (II) ions concentration of tap water is found to be 0.022mg/L. Then, the adsorption experiment is performed on the 50ml of collected tap water sample by taking the amount of zinc oxide nanoparticles as 0.1g, time of duration for stirring as 60minutes and temperature at 30℃. The 50mL pond water solution is stirred for one hour with 0.1g zinc oxide nanoparticles by using magnetic stirrer. After one hour, the nanoparticles are separated by using filtration methods. After the adsorption experiments, the residual cadmium ions concentration of treated tap water is measured by using Atomic Absorption Spectrophotometer (APHA 23rd Edition, 3111 B) and the value is found to be less than 0.02mg/L. The removal efficiency (R %) of adsorption of Cd (II) ions by zinc oxide nanoparticle for tap water is calculated to be 68.18%.

For analysis of real water sample, the pond water is collected from the pond of Anandnagar, Belur, Howrah. The collected pond water is analysed for the concentration of Cd (II) ions by using Atomic Absorption Spectrophotometer (PerkinElmer, Atomic Absorption Spectrometer PinAAcle 900F). The initial Cd (II) ions concentration of pond water is found to be 0.007mg/L. Then, the adsorption experiment is performed on the 50ml of collected pond water sample by taking the amount of zinc oxide nanoparticle as 0.1g, time of duration for stirring as 60minutes and temperature at 30℃. The 50mL pond water solution is stirred for one hour with 0.1g zinc oxide nanoparticles by using magnetic stirrer. After one hour, the nanoparticles are separated by using filtration methods. After the adsorption experiments, the residual Cd (II) ions concentration of treated pond water is measured by using Atomic Absorption Spectrophotometer (APHA 23rd Edition, 3111 B) and the value is found to be less than 0.02mg/L (nil). The removal efficiency (R %) of adsorption of Cd (II) ions by zinc oxide nanoparticle for pond water is calculated to be 100%.

Table 7: Results from Different Types of Water.

Types of Water	pH	Adsorbent Dose (g)	Time (min)	Adsorption capacity, q_e, (mg/g)	Removal efficiency, R (%)
1. Synthetic Water	6	0.1	60	77	78
2. Tap water	6	0.1	60	0.075	68
3. Pond water	6	0.1	60	0.035	100

5.9. ANTIBACTERIAL RESULTS

The antibacterial activities of Zinc Oxide (ZnO) nanoparticles against *Escherichia coli (E. coli)* bacteria and *Enterococcus faecalis (E. faecalis)* bacteria are shown in Figure 5.19 and Figure 5.20. The figure shows the relation between the absorbance values and three different concentrations of ZnO nanoparticles (5mg/ml, 2.5mg/ml and 1.25mg/ml) along with control (Bacterial growth without any treatment). The bacterial growth is measured by absorbance values which indicate that light being absorbed is more with increase in number of bacteria [23]. It is observed from the figure that ZnO nanoparticles minimize the growth of bacteria at 5 mg/ml concentration. The mechanism behind antibacterial activity may be explained by liberating of zinc (Zn^{2+}) antimicrobial ions from the zinc oxide nanoparticles which can result in destruction of bacterial cell when come in direct contact with cell wall. These Zn^{2+} ions stop the bacteria functions by binding it with biomolecules such as proteins and carbohydrates with the help of electrostatic forces [24].

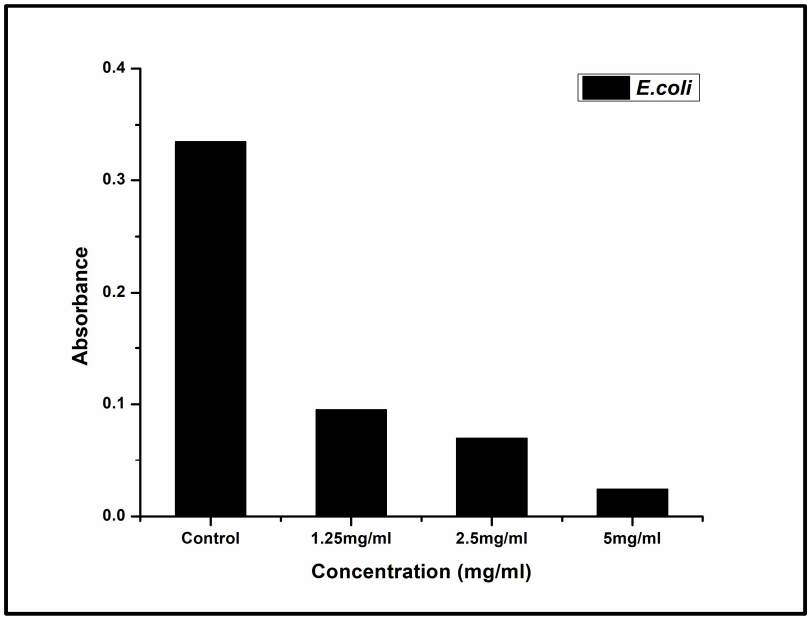

Figure 5.19. Antibacterial activity of ZnO nanoparticles against *E. coli.*

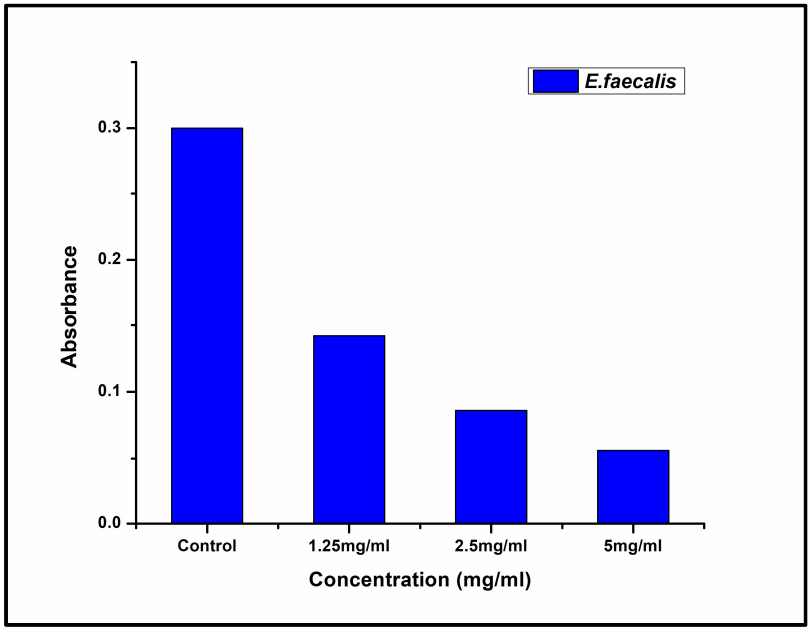

Figure 5.20. Antibacterial activity of ZnO nanoparticles against *E. faecalis.*

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CHAPTER 6:

Conclusions

CONCLUSIONS

A brief description of synthesis procedure of zinc oxide (ZnO) nanoparticles, its characterization techniques and its application in water purification are mentioned in the previous chapter. From the literature survey, it is clear that the ZnO nanoparticles can be used for the removal of various heavy metals and cadmium ions and can also be utilized in every prospects of water purification. In the research studies, the ZnO nanoparticles are synthesised by sol-gel method. The synthesised nanoparticles have been characterized by different techniques such as XRD, FTIR, FESEM and EDX. Batch adsorption experiment has performed for the removal of cadmium Cd (II) ions from aqueous solution. The removal efficiency and adsorption capacity is calculated from the measured data. From the results, the following conclusion has been derived:

- The ZnO nanoparticles are successfully synthesised and characterized by XRD, FTIR, FESEM and EDX. XRD results indicate that the most of the peaks are matched well with hexagonal structure of ZnO and the average crystal size of ZnO nanoparticles is 24nm. FTIR analysis shows that the strong absorption peak is obtained in the range of 400cm^{-1} to 514 cm^{-1} with most dominant peak at wavenumber of 420 cm^{-1} which can be assigned to Zn-O bond. FESEM images show rod shaped ZnO nanoparticles along with spherical shaped particles and the agglomeration is also observed. EDX data proves that the sample contains only zinc and oxygen as its constituents.

- The adsorption studies are performed by varying pH and adsorbent dose. It is found that the maximum removal efficiency of Cd (II) from aqueous solution is observed at pH 6 of 77%. The maximum adsorption capacity of Cd (II) ions on ZnO nanoparticles is observed at an adsorbent dose of 0.05g.

- The adsorption isotherm model is used to explain the equilibrium of the process. Langmuir and Freundlich isotherm model are used to explain the adsorption isotherm processes. The Langmuir model best describes the adsorption of Cd (II) ions because of

higher correlation coefficient (R^2) as compared to Freundlich model with the maximum adsorption capacity of 86mg/g. The low value of R_L (=0.2) and 1/n (=0.25) indicates the favourability of the adsorption process.

- Adsorption kinetics is performed with four duration of time period at three different temperatures. Pseudo first order model, pseudo second order model and intraparticle diffusion model is used to study the adsorption kinetics of the process. The kinetics data follows pseudo second order rate model with high correlation coefficient. The process is found to be chemical adsorption process as the activation energy required for the process is 84.195kJ/mol.

- Thermodynamics studies reveal that the Gibb's free energy ($\Delta G°$) change values decrease with increase in temperature which suggests favourability of adsorption process. The positive values of enthalpy change (=128.88 kJ/mol) indicates the endothermic nature of the adsorption process. The positive value of entropy change suggests the spontaneous nature of the process.

- The removal efficiency (R%) of adsorption of cadmium ions by zinc oxide nanoparticle for tap water and pond water is calculated as 68.18% and 100%.

- Antibacterial activities suggest that the ZnO nanoparticles minimize the growth of bacteria, *E. coli* and *E. faecalis*, at the concentration of 5mg/ml. It is also observed that with increase in concentration of nanoparticles, bacterial growth decreases.