SYNTHESIS, CHARACTERIZATION OF ZnO NANO PHOTOCATALYSTS AND THEIR APPLICATION IN PHOTOREMEDIATION OF WASTE WATER

BY

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DECLARATION

Declaration by the Student

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This thesis has been submitted for examination with our approval as university supervisors.

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DEDICATION

To my children Meshack, Abeland Faith, May you live to realize your dreams and aspirations and inherit the peace, love andprosperity that the world has to offer.

ABSTRACT

Water scarcity and its contamination with toxic metal ions and organic dyes represent a serious worldwide problem in the 21stcentury. Today's world faces alarming challenges in the rising demand for drinking water and conditions are particularly bad in developing countries with the rapid escalation of industrialization towards a developed society. The waste products generated from the textiles, chemicals, mining and metallurgical industries are mainly responsible for contaminating the water. This contaminated water contains non-biodegradable effluents such as heavy metal ions (Copper, Nickel, Cadmium, Arsenic etc.) and organic materials such as dyes that are carcinogenic to human beings and harmful to the environment because of their bioaccumulation, non-biodegradable property and toxicity even at low concentrations. In an effort to reduce the environmental effects of heavy metals and dyes, various techniques have been employed. However, these techniques are expensive and ineffective resulting in an intensively coloured discharge and high concentration of heavy metals from the treatment facilities. Nanotechnology is a promising field in waste water treatment. This study aimed at assessing the efficiency of synthesized ZnO nanoparticles in photodegradation of synthetic dyes and adsorption of heavy metal ions from waste water. The objectives of this study were to synthesizeZnO nanoparticles, characterize and apply it in adsorption of heavy metals and photodegradation of methyl orange dye. Methyl orange was used as a model dye and the heavy metal determined wereNi^{2+}, Cd^{2+} and Cu^{2+}. Precipitation technique was used to synthesize ZnO nanoparticles. Two samples L_1 and L_2 were synthesized. They were characterized using PXRD (Power X-ray Diffraction), FTIR (Fourier Transform Infra-Red), SEM (Scanning Electron Microscopy) and EDX (Energy Dispersive X-ray Spectroscopy), methods of analysis. Photodegradation studies were carried out using solar and fluorescent light energy. The EDX results showed elemental composition of ZnO nanoparticles which showed 54.00% Zn, 44.07% O and 1.93% Mn impurities for $L_1$and 55.34% Zn, 42.3% O and 2.37%Mn impurities for L_2. The PXRD results showed diffraction peaks which were indexed to ZnO reference as per JCPDS file 80-0075. The average size of ZnO nanoparticles was found to be 26 nm. FTIR spectra showed a broad band at around 430 cm^{-1} with shoulder shape, characteristics of Zn-O bond. The images obtained by SEM showed rod shaped clusters of nanoparticles. They were distributed well within a range of 100 nm which is a favorable property to exhibit better photo catalytic activity. The results of heavy metal ions adsorption showed an increase in percentage removal with increase in adsorbent dose and contact time. There was a decrease with increase in heavy metal concentration (ppm). For photodegradation, the results indicated an increase in colour removal with increase in photocatalyst dose and contact time and a decrease with increase in concentration of methyl orange. In conclusion, ZnO nanoparticles used as an adsorbent and a photocatalyst is efficient and a promising technique for treatment of waste water from textile, paper and dyeing industry and metallurgical industries. It can act as an adsorbent for heavy metal ions and aphotocatalyst for degradation of synthetic dyes. Future studies could focus on possibilities of improving and commercializing this material through designing a treatment facility that incorporates it, with the aim of being used on large scale waste water treatment.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
AFM	Atomic Force Microscopy
AOP	Advanced Oxidation Processes
BDH	Burrell Durrant Hifle
BET	Brunauer–Emmett–Teller
eCB	electron conduction band
ED	Energy Dispersive
EDX	Energy Dispersive X-ray Spectroscopy
EHT	Extra High Tension
EXAFS	Extended X-ray Absorption Fine Structure
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width at Half Maximum
FWHM	Full-Width Half-Maximum
hVB	hole valence band
IBM	International Business Machines

ICRAF	International Center for Research in Agroforestry
IR	Infra Red
JCPDS	Joint Committee on Powder Diffraction Standards
MBE	Molecular Beam Epitaxy
OD	Optical Density
PXRD	Powder X-ray Diffraction
PZC	Point of Zero Charge
QSAR	Quantitative Structure–Activity Relationship
SDD	Silicon Drift Detectors
SDD	Silicon Drift Detectors
SEM	Scanning Electron Microscope
SPM	Scanning Probe Microscopy
SSA	Specific Surface Area
STM	Scanning Tunneling Microscope
TEM	Transmission Electron Microscopy

USEPA	US Environmental Protection Agency
UV-VIS	UV-Visible Spectroscopy
WDS	Wavelength-dispersive spectroscopy
WDS	Wireless Distribution System
WHO	World Health Organization
XRD	X-Ray Diffraction

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CHAPTER ONE

INTRODUCTION

1.1 Background Information

Dyes are an important class of synthetic organic compounds used in textile industry,paper,dyeing and plastic industries as colour for dyeing their products.Ahuge amount of water is used which results in production of dye containing water.These industries use approximately 10,000 dyes and pigments(Baouer *et al*., 2001). Metal processing waste water often contains species of heavy metals for example Cr (IV),etc which are toxic and could act as carcinogens,terratogens and mutagens in biological systems.Industries are supposed to reduce the chromium in their effluents to around 0.1mg/L, before discharging it into the sewer system (Ayuso *et al*., 2003).

"Nano "is derived from the Greek word for dwarf. A nanometer is one billionth of a meter(10^{-9}) and might be represented by the length of ten hydrogen atoms lined up in a row. It emerged billions of years ago at the point where molecules began to arrange in complex forms and structures that launched life on earth. Throughevolution, mutations and adaptations; plants were able to carry out photosynthesis (Roco, 1999).Another example of a natural nanotechnology is "chemical catalysis "through catalysts called enzymes which sometimes are considered as indispensable for completion of some chemical reactions (Akoh*et al.,* 2007).Nanostructure science and technology is a broad

research area that encompasses the creation of new materials from nanosized building blocks (Hu and Shaw,1998).

Nanotechnology was first proposed, by the Nobel Prize winning physicist Richard Feynman, who suggested that someday it would be possible to put the entire 24 volume EncyclopediaBritannica on the head of a pin(Feynman, 1959). Feynman proposed that tiny robots might be able to build chemical substances. He noted that they could be used to create nano-machines. He had also pointed out that a new class of miniaturized instruments would be needed to manipulate and measure the properties of the small "nano" structures.

In the 1980's these instruments were invented, they could begin to do what Feynman talked about. However, little happened until researcher Drexler, the name that is most widely seen innano-technological circles, released his book Engines of Creation (Drexler, 1986). This book enginesof creation, created a sensation for its depiction of magnificent control over matter. The bookalso describes self-replicatingnano-machines that could produce virtually any materialgood, while reversing the global warming, curing disease and dramatically extending the lifespan. He has also authored a number of technical journal articles and books on the subjectincluding and inbounding the future, the nanotechnology revolution (Keiper, 2003).In both books, Drexler proposed a number of potential benefits of this new technology. Hehas also pointed out the potential hazards of molecular manipulation, some of which areunpredictable. His books emerged as the main

driving force among the researchcommunities. For instance, the following is one of the examples of technique demonstratedby IBM researchers.The technique of manipulation of atoms was firstdemonstrated, when in April 1990, a team in the IBMresearch division placed thirty-five xenon atoms in aprecise pattern and spelled out the letters "IBM. The logo is 60 billionths of an inch wide, or 13 millionths of the diameter of a humanhair (IBM Corporation, 2001).

1.1.1Environmental Potentials of Nano Technology

According to research communities agenda and some of which as described by Drexler in his books, nanotechnology promises to show major advances in the fieldsof materials and manufacturing, environmental and energy, electronics and computers,medical and health, and space and aircraft. In research community there are statements that nanotechnology is still not well defined (Maynard, 2007). Some define it on the basis of physical dimension of structures ranging from 0.1 nm to 100 nm; the meaning is different for different disciplines of people, definitions of nanotechnology are as diverse as its applications.

Water purification and desalinization are some of the focus areas of preventive defense and environmental security since they can meet future water demands. Nanotechnology based devices for water desalinization have been designed to desalt sea water, like the use of carbon nanotubes. Carbon nanotubes enhances waterpurification technologies to the point where they can far out compete reverse osmosis ordistillation processes using at least 10 times less energy than reverse osmosis and at least 100 times less energy than

distillation (Ellis, 2004).The other source of water, ground water is traditionally treated through iron treatment walls to reduce the organic and inorganic environmental contaminants, which currently involves granular or “micro-scale” iron (>50,000 nm). The same process under nano technology uses nano-sized iron, which can enhance the reaction, as it is more reactive and effective than macro-scale iron. Its smaller size also makes it more flexible to penetrate (Wenzhon *et al*., 2008).

ZnO-based materials have size and morphology dependent physicaland chemical properties at the nanoscale which could offertremendous opportunities for advanced technologies. Forexample, nanostructured ZnO is being actively explored in lightemitting diodes, laser diodes, sensors, piezo-electronics, solar cells, UV-blocking components, photo-catalysis, and transparent conductive glass coatings. Various kinds of ZnOnanostructures have been reported ranging from uniform nanobelts, nano-tubes to nano wires. Uniquestructures could introduce additional tunable properties (Wenzhon *et al*., 2008).

In the context of semiconductor photo catalysts for water treatment, ZnO nanostructures could offer various advantages. Non-biodegradable dyes widely used in textile,paper and other industrial application pose severe threats to aqueousenvironments when released without treatment. The eliminationof harmful components (including dyes) from wastewater is animportant goal for environmental control in industrial settings.Adsorption and chemical coagulation are traditionally used for the treatment of

such wastewater. However, the traditionalmethods transfer dyes, and the solid waste containing dyes ishard to handle. On the other hand, semiconductor photo-catalystssuch as ZnO utilizing photo-induced oxidation processcould decompose the dyes effectively. Both powder and thin film forms of ZnO have been exploredto date for environmental applications. Powder-form ZnOsemiconductor photo-catalysts normally show higher photo-efficiencydue to the increased active surface area. However, the powder form photo-catalysts used in suspension state in waterhave certain limitations due to particle aggregation and technicalchallenges in photo-catalyst separation and recovery. Incomparison, thin film ZnO can be easily recovered, yet its surfacearea is low leading to poor overall efficiency (Shipra, 2008).

1.2 Problem Statement

Recently quality drinking water has become a major concern worldwide due to the increasing population and decreasing energy resources. Therefore, the efficient treatment of waste waters has become of immediate importance among scientific communities around the globe as there is a growing need to come out with the state – of – the- art technologies that are capable to solve the problems. Ideally an effective waste water treatment is to mineralize completely all the toxic contaminants in waste water without leaving anyhazardous residues. In addition the waste water treatment process should be cost effective and feasible for large scale applications.

Water bodies are increasingly choking with wastes ranging from uncollected garbage, industrial wastes inform of heavy metals and synthetic dyes among the many. There are many known sources of heavy metals that find their way to water bodies. The wastes have accumulated in the river sediments and in water to a level which pose precarious effects to human health, aquatic life and the environment. The common polluting heavy metals are lead, calcium, copper, chromium, selenium and mercury.

Large scale production and extensive application of synthetic dyes cause considerable environmental pollution. Dyes are difficult to decompose biologically and chemically. Colour removal in textile and effluents from paper industries remains a serious challenge and the cause of serious effects in water bodies as it reduces light penetration and hence death of aquatic life.

In an effort to reduce the environmental effects of the above (heavy metals and dyes) various techniques have been employed. These techniques include coagulation and sedimentation in which sediments again create disposal problems. Other techniques include the use of constructed wetlands but are expensive to construct, require more space and minimal chances of success as the ecological conditions may not favor particular plant species that are known to remove heavy metals.Nano technology is a promising field in waste water treatment. The aim of this study was to assess the use of synthesized ZnO nanoparticles in photo degradation of dyes and heavy metals adsorption from waste water.

1.3 Justification

Toxic dyes are very important in the view point of environmental protection, because they produce toxic aromatic amines and have other harmful environmental effects. They are widely used and have low degradation rates by aerobic treatment processes. Many of dye molecules are resistant to biological degradation (Baouer*et al.,* 2001). Dying industries use approximately 10,000 dyes and pigments, which are manufactured 7×10^5 tons per year, 50% of them are hazardous (Zhu *et al.,* 2000).Approximately 15% of synthetic toxic are discharged into waste waters.

The existing methods for industrial effluents treatment such as flocculation and sedimentation cause disposal problems, while constructed wetlands for heavy metals removal are expensive. The use of ZnO nanoparticles in photo catalytic colour removal and adsorption of heavy metals is cheaper in cost and does not pose disposal challenge, also the technology uses small amount of energy. The use of nanomaterials like ZnO nanoparticles offers a promising technology for reduction of global environmental pollutants. This semi-conductor catalyst has been preferred because of its wide energy band gap, high photo sensitivity, stability and low cost.

Methyl orange was used as a model dye since it's an organic dye similar to that used in the textile and paper industries. The metal species (Ni^{2+}, Cd^{2+}, and Cu^{2+}) were selected because of their known toxicological effects on humans and high levels of exposure (Giller*et al.,* 1998).

1.4Objectives

1.4.1 General Objective

The general objective of this study was to synthesize ZnO nanoparticlesand use it as an adsorbent and a photo-catalyst in remediation of waste water.

1.4.2Specific Objectives

The study was guided by the following specific objectives;

1. To synthesize ZnO nanoparticlesby precipitation method
2. To characterize the synthesizedZnO nanoparticlesusing PXRD,FTIR, SEM and EDX instrumental methods.
3. To determine the extent of removal of Ni, Cd and Cu usingZnO nanoparticles.
4. To determine percentage removal of the methyl orange usingZnO nanoparticles

1.5 Research questions

This research was guided by the following questions

1. Can ZnO nanoparticles be synthesized using precipitation method?
2. What is the size, morphology and distribution of ZnO nanoparticles?
3. What is the extent of removal of Ni, Cu and Cd when treated with ZnO nanoparticles?
4. What is the percentage removal of the methyl orange using ZnO nanoparticles?

CHAPTER TWO

LITERATURE REVIEW

2.1 Synthesis of ZnO nanoparticles

Synthesis of nanoparticles is most commonly done based on three strategies; liquid-phase synthesis, gas-phase synthesis,vapor-phase synthesis. Under liquid phase synthesis the techniques used for synthesis are: precipitation,sol-gel processing, micro-emulsions, hydrothermal/solvo-thermal Synthesis, microwave synthesis, sono-chemical synthesis and template synthesis (Jagadish and Pearton,2006). The method of synthesis of nanoparticles depends upon the desired physical and chemicalproperties such as size, size disparity, shape,surface state, crystal structure, organization onto a support, and dispensability. The current study adopted precipitation technique. This involves precipitating zinc oxide using zinc acetate ($Zn(CH_3COO)_2{\cdot}H_2O$) and ammonium carbonate $(NH_4)2CO_3$ (Lanje*et al.,* 2013).

2.2 Structural Characterization of Nanoparticles

Characterization is the act of describing distinctive characteristics or essential features or qualities of a chemical substance in order to get exact information about the crystal structure, surface morphology, and particle size among others (Dann, 2000). The following characterization techniques are applied; XRD (X-ray diffraction), SEM (scanning electron microscope), transmission electron microscope (TEM),andFourier

transform infrared spectroscopy (FTIR). In this study, characterization was done using PXRD and FTIR, EDX and SEM.

2.2.1 XRD (X-ray diffraction)

Widely used for precise determination of the position of action in molecules and solids (inorganic)X–rays interact with electrons in matter. When a beam of X–rays impinges on a material it is scattered in various directions by the electron clouds of the atoms.A beam of electrons striking a metal target will eject electrons from energy levels close to the nucleus some of metal atoms. Once vaccines have been created, electrons from higher energy levels fall down into these orbitals; the difference will be emitted as an X-ray of precise energy.

The electrons are created by heating tungsten filaments in a vacuum and then accelerated by a high voltage towards a metal target. Core electrons are knocked out of the metal target and X–rays characteristics of the metal target are produced by decay. Single X–rays must be selected from the tube to carry out the X-ray experiment. Once a single X–ray has been selected, the beam is collimated by passing it through a slit to remove wavelengths other than the desired one before interaction with the sample and finally detection of scattered X–rays (Dann, 2000).

2.2.2 Powder diffraction

A powdered sample contains an enormous number of very small crystals which randomly adopts the whole range of possible orientations.When an X-ray beamstrikes a powdered

sample, it is diffracted in all possible directions as governed by Braggs equation. Each lattice space can rise to a cone of diffraction. These join to form a continuous cone.To analyze the data, the positions of the cones need to be measured using photographic film or by a detector.The actual pattern resulting from powdered sample is similar to the single crystal experiment in which the data are generated from the particular arrangement of atoms within the unit cell.Factors affecting intensity of peaks are; latticetype, symmetry, unit cell parameters, distribution and typeof atoms in the unit cell.All crystalline solids have a unique powder X-ray diffraction in terms of positions and intensities as the observed reflections(Dann, 2000).

Up to 1895 the study of matter at the atomic level was a difficult task but the discovery of electromagnetic radiation with 1 Å (10^{-10} m) wavelength, appearing at the region between gamma-rays and ultraviolet, makes it possible. As the atomic distance in matter is comparable with the wavelength of X-rays, the phenomenon of diffraction finds its way through it and gives many promisingresults related to the crystalline structure. The unit cell and lattices which are distributed in a regular three-dimensional way in space forms the base for diffraction pattern to occur. These lattices form a series of parallel planes with its own specific d-spacing and with different orientations exist. The reflection of incident monochromatic X-ray planes of crystal lattices when the difference between the planes is of complete number n of wavelengths leads to famous Bragg's law:

$n\lambda=2d\sin\theta$ ---------- 1

Where *n* is an integer 1, 2, 3…..$\lambda$is wavelength in angstroms (1.54 Å for copper), d is interatomic spacing in angstroms, and θ is the diffraction angle in degrees (Kacher*et al.,* 2009). Figure 2.1 shows Reflection of incident monochromatic X-ray from successive planes of crystal lattices.

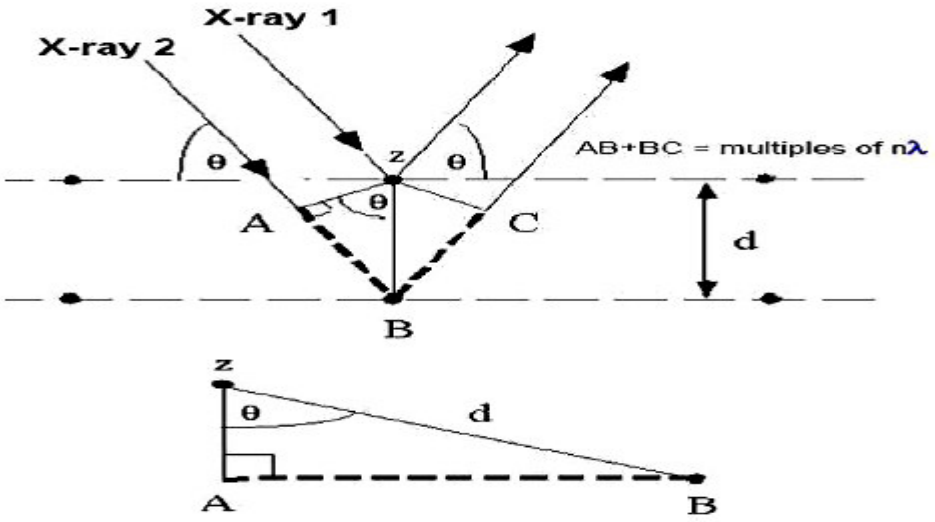


Figure 2.1: Reflection of incident monochromatic X-ray from successive planes of crystal lattices (Source: Authier, 2006)

Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. The fingerprint characterization of crystalline materials and the determination of their structure are the two fields where XRD has been mostly used. Unique characteristic X-ray diffraction pattern of each crystalline solid gives the designation of "fingerprint technique" to XRD for its identification. XRD may be used to determine its structure, that is, how the atoms pack

together in the crystalline state and what the inter-atomic distance and angle are to name a few. From these points it can be concluded that X-ray diffraction has become a very important and powerful tool for structural characterization (Özgür*et al*., 2005).

2.2.3Fourier Transform Infrared Spectroscopy (FTIR)

In the region of longer wavelength or low frequency the identification of different types of chemicals is possible by this technique of infrared spectroscopy and the instrument requires for its execution is Fourier transform infrared (FTIR) spectrometer. The spectroscopy merely based on the fact that molecules absorb specific frequencies that are characteristic of their structure termed as resonant frequencies that is the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. And the detection of energy is done on the basis of shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling. Sometimes the help of approximation techniques like Born–Oppenheimer and harmonic approximations are also taken (Worth& Cederbaum, 2004). As each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present(Howe andMacintosh,

1991). FTIR can be used to analyze a wide range of materials in bulk or thin films, liquids, solids, pastes, powders, fibers, and other forms. FTIR analysis can give not only qualitative (identification) analysis of materials, but with relevant standards, can be used for quantitative (amount) analysis. FTIR can be used to analyze samples up to ~11 millimeters in diameter, and either measure in bulk or the top ~1 micrometer layer.FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint"(Flemming*et al.*, 1991).

2.2.4 Energy dispersive X-ray Spectroscopy (EDX)

EDX makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements ($Z < 10$). Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. Quantitative analysis (determination of the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration standards of known composition (Goldstein,2003).

By scanning the beam in a television-like raster and displaying the intensity of a selected X-ray line, element distribution images or 'maps' can be produced. Also, images produced by electrons collected from the sample reveal surface topography or mean atomic number differences according to the mode selected.

The EDX spectrum is displayed in digitized form with the x-axis representing X-ray energy(usually in channels 10 or 20 eV wide) and the y-axis representing the number of counts per channel. An X-ray line (consisting of effectively mono-energetic photons) isbroadened by the response of the system, producing a Gaussian profile. Energy resolution isdefined as the full width of the peak at half maximum height (FWHM). Conventionally, this isspecified for the Mn Kα peak at 5.89 keV. For Si(Li) and SDD detectors, values of 130-150 eVare typical (Ge detectors can achieve 115eV). The resolution of an EDX is about an order ofmagnitude worse than that of a WDS, but is good enough to separate the K lines of neighboringelements (Scott and Love, 1994).

The object of qualitative analysis is to find what elements are present in an 'unknown' specimen by identifying the lines in the X-ray spectrum using tables of energies or wavelengths. Ambiguities are rare and can invariably be resolved by taking into account additional lines as well as the main one. The ED spectrometer is especially useful for qualitative analysis because a complete spectrum can be obtained very quickly. Aids to identification are provided, such as facilities for superimposing the positions of the lines of a given element for comparison with the recorded spectrum(Scott and Love, 1994).

2.2.5 Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that

contain information about the sample's surface topography and composition (Soltaninezhad and Amrnifar, 2011). The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, in wet conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures (Joshi and Shrivastava, 2012).

The most common mode of detection is by secondary electrons emitted by atoms excited by the electron beam. On a flat surface, the plume of secondary electrons is mostly contained by the sample, but on a tilted surface, the plume is partially exposed and more electrons are emitted. By scanning the sample and detecting the secondary electrons, an image displaying the topography of the surface is created (Lynch and Dawson, 2008).

2.3Nano-Materials and their Environmental Applications

In 1864, James Clerk Maxwell was the first to mention some of the nano-concepts in nanotechnology through a proposed experiment on a tiny entity known as Maxwell's Demon able to handle individual molecules. In the early 20^{th} century, the first observations and size measurements of nano-particles using an ultra-microscope were made possible in a study of gold sols and other nano-materials with sizes down to 10 nm and less (Zsigmondy, 1914). Zsigmondy was the first to characterize particle sizes using the term nanometer and he developed the first system of classification based on particle size in the nanometer range. Several advances in the field of nanomaterial

characterization were possible with Langmuir in 1920s introduced the monolayer concept, and Derjaguinin 1950s conducted the first measurement of surface forces (Derjaguin, 1954). Feynman (1959) at an American Physical Society meeting at Caltech described a proposed process to manipulate individual atoms and molecules by using one set of precise tools (Gribbin, 1997).

Since then, several advances were made in the study of nanoscale structures, but the term nanotechnology was first defined by Taniguchi (1974) as "nanotechnology mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or one molecule". The tools and methods for nanotechnology involve imaging, measuring, modeling, and manipulating matter at the nano-scale. In 1980s, nanotechnology and nanoscience got a boost with two major developments: the birth of cluster science and the invention of the Scanning Tunneling Microscope (STM). Major current tools for nanotechnology measuring include many devices such as STM, Scanning Probe Microscopes (SPMs), Atomic Force Microscopy (AFM) and Molecular Beam Epitaxy (MBE) (Roco, 1999).

Diagnosis of particles at the nano-scale level contributed extensively to the production, modification and shaping of structures that were used in different industrial, health and environmental application. Nanostructure science and technology is a broad research area that encompasses the creation of new materials and devices from nanosized building blocks (Hu and Shaw, 1998). Building blocks are used to make molecules that are arranged in nanostructures and nanomaterials with dimensions of 1 to 100 nm. This

process is known as a "bottom up" approach where building blocks are arranged and then assembled to form larger size materials. The formation of powder components (structural composite material) through aerosol techniques is a main example of this approach (Wu *et al*., 1993). Many other approaches are being used to synthesize and assemble nanostructures but the critical point remains in the control of the size and composition of nanocluster components and in the control of interfaces and the distribution of nano-components within the fully formed materials (Hu and Shaw, 1998).

Many potential benefits of nanotechnology have already been identified by many researchers in the environmental and water sector, medicine, and in several industrial applications but the future nanotechnology might bring innovations that can answer many existing scientific questions (Fleischer and Grunwald, 2008). Hence, nanotechnology is going to play an important role in addressing fundamental issues on health, energy and water (Binks, 2007).

Major potential environmental benefits of nanotechnology were reported in the draft nano-materials research strategy by (Savage and Wentsel, 2008), including: early environmental treatment and remediation, stronger and lighter nano materials, smaller, more accurate and more sensitive sensing and monitoring devices.Additional benefits lay in the cost-effective use of renewable energy, low energy requirement and low waste generation devices, early disease detectors for preventive treatment, pollution control, and the prevention and remediation using improved systems.For the purpose of

improving the above listed treatment processes, the use of nano-materials is being researched to fabricate separation and reactive media which is of high quality in terms of reactivity and performance (Bellona and Drewes, 2007).

Additionally, the use of nano-materials and nanoparticles to bio-remediate and disinfect wastewater is gaining popularity (Mohan and Pittman, 2007). For instance, metal oxide nano-materials such as TiO_2 are among the promising nano-catalysts that were tested successfully for their antimicrobial activity. Moreover, fullerenes (C_{60}) as pollution tracers are being used to provide contaminant-fate information to assist in developing water remediation strategies. Magnetic nanoparticles are being developed to adsorb metals and organic compounds; and nano-catalysts are being explored to reduce pollution of oxidized contaminants (Hillie and Munasinghe, 2006). Metal processing wastewater often contains hexavalent chromium species, Cr (VI), which are toxic and can act as carcinogens, mutagens and teratogens in biological systems (Dupont and Guillon, 2003).

Metal industries are required to reduce the amount of chromium in their effluent to around 0.1 mg/L (Ayuso*et al*., 2003) before discharging it into the sewer system. Maghemite nanoparticles were studied for their potential in removing and recovering chromium from wastewater. Hu *et al*. (2005) developed a new method by combining the adsorption ability of nanoparticles and the magnetic separation technique. The method was space-saving, cost-effective, simple, and environmental-friendly. Additionally, chromium was successfully removed from the wastewater and the nano-scale maghemite

retained the original metal removing capacity after six adsorption-desorption cycles. The adsorption was pH dependent with optimal adsorption at pH 2.5.

2.4 Application of Nanotechnology in Water and Wastewater Treatment

Nanotechnology is being applied in the production of water purification membranes. Recently, Theron*et al*. (2008) reported the following water filtration membranes produced from nano-materials: nanostructured membranes from nano-materials such as carbon nanotubes, nanoparticlesand nano-reactive membranes from metal nanoparticles and other nano-materials. On the other hand, adsorption is considered as an effective, efficient and economic method to remove water contaminants (Jiuhui, 2008). Effective adsorbents include: activated carbon, clay minerals and silicas, zeolites, metal oxides, and modified composites (Zhang *et al*., 2005). The decomposition of organic compounds in water as well as the disinfection of water under UV light using TiO_2mediated photo-catalyst is gaining popularity as the effectiveness of the photo-catalysts has been demonstrated by many scientific studies (Kumar *et al*., 2008).

Nanotechnology for water remediation will play a crucial role in water security and consequently the food security of the world. The applications of nanotechnology in the cleanup of contaminated water could be summarized (Smith, 2006):nano-scale filtration techniques, adsorption of pollutants on nanoparticles andbreakdown of contaminants by nanoparticle catalysts.

2.5Photo-catalytic Degradation of Dyes

Paper, dyeing, plastic, and textile industries use colour for dyeing their products and thus use a huge amount of water, which results in the production of a dye-containing wastewater withhazardous effects on the environment (Sreedhar and Kotaiha, 2006). At present, 100,000 different types of dyes with annual production rate of 7.0×10^5 ton, are produced. Among them textile industries consume about 36,000 ton/year dye, 10 to 20 percent of which remains in wastewater (Gregorio, 2006). Degradation of organic materials existing in the environment which occurs according to the above process with radiation of ultraviolet light on the surface of zinc oxide is called photo-catalytic reaction of ZnO (Vijay *et al.,* 2009). Basis of ZnO/UV photo-catalytic process is the semi-conduct optical stimulation of ZnOas a result of electromagnetic ray absorption. ZnOhas an energy band of 3.2 eV which can be activated by radiation of UV in the wavelength of 387.5 nm. On the earth's surface, sunlight begins in the wavelength of 300 nm and only 4-5 percent of solar radiation may be used by ZnO.

Surface area and number of active places used by the catalyst for absorbing pollutants, play an important role in degradation level, among known catalysts like ZrO_2, ZnO and TiO_2. High efficiency of ZnOhas been approved and confirmed in many studies, ZnOis not poisonous and has high stability and very good performance and is also cheaper (Awitor *et al.,* 2008).An advantage of photo-catalytic method includes low temperature, low expenses and also radically low level of energy consumption in this method. These

factors have caused the photo-catalysts to be used in commercial scales.(Rajeswari and Kanmani, 2009).A significantly great number of researches and articles have been published regarding removal of dangerous and poisonous compounds from water, wastewater and air, using photo-catalytic methods (Zhang *et al.,* 2010).

2.6Dye Photo-catalytic degradation Mechanism

Advanced oxidation processes (AOPs) are alternative techniques of destruction of dyes and many other organic in waste water and effluents. These processes generally involve UV/H_2O or UV/O_3 for the oxidative degradation of contaminants. Semiconductor photocatalysis is a newly developed AOP which can be conveniently applied to dye pollutants for their degradation. AOPs produce $OH^{\cdot}$Radicals which are powerful oxidizing agents and completely degrade most organic pollutants.Photocatalytic process is the semiconductor optical stimulation of ZnO as a result of electromagnetic ray absorption. ZnO has an energy band of 3.2 eV which can be activated by radiation of inUV wavelength of 387.5nm (Daneshvar*et al.,* 2004).

On the earth's surface, sunlight begins in the wavelength of 300nm and only 4 – 5% of solar radiation may be used by ZnO. Surface area and number of active sites used by the catalyst for absorbing pollutants plays an important role in degradation level (Awitor *et al.,* 2008). Upon irradiation valence band electrons are promoted to the conduction band leavingholes behind. These electron hole pairs caneither recombineor can interact separately with other molecules. The holes may react either with electron donors in the

solution or with hydroxide ions to produce powerful oxidizing agents like$OH^{\cdot}$(Oxidation potential 2.8V) or superoxide radicals(O_2^-) (Tang and Huren, 1995).

Nanosized ZnO semiconductoracts as a sensitizer for light – induced redox processesdue to the electronic structure of the metal atoms in chemical combination which is characterized by a filled valence band and an empty conduction band (Hoffman, 1995).The relevant reactions at the semiconductor surface causing degradation of dyes can be expressed as;-

$ZnO + h(UV) \longrightarrow ZnO(eCB^- + hVB^+)$……..…..2

$ZnO(hVB^+) + H_2O \longrightarrow ZnO(hVB^+) + H^+ + OH^-$ ……..……..3

$ZnO(hVB^+) + OH^- \longrightarrow ZnO + OH^{\cdot}$…….…….....….4

$ZnO(eCB^-) + O_2 \longrightarrow ZnO + O_2^{\cdot -}$ …….…….…… 5

$O_2^{\cdot -} + H^+ \longrightarrow HO_2^{\cdot}$……..……..…..…6

$Dye + OH^{\cdot} \longrightarrow$ Degradation products…….……7

The resulting $OH^{\cdot}$radical, being a very strong oxidizing agent (standard redox potential +2.8 V) can oxidize most of methyl orange dye particles (Hoffman, 1995).The scheme below illustrates photo degradation process.

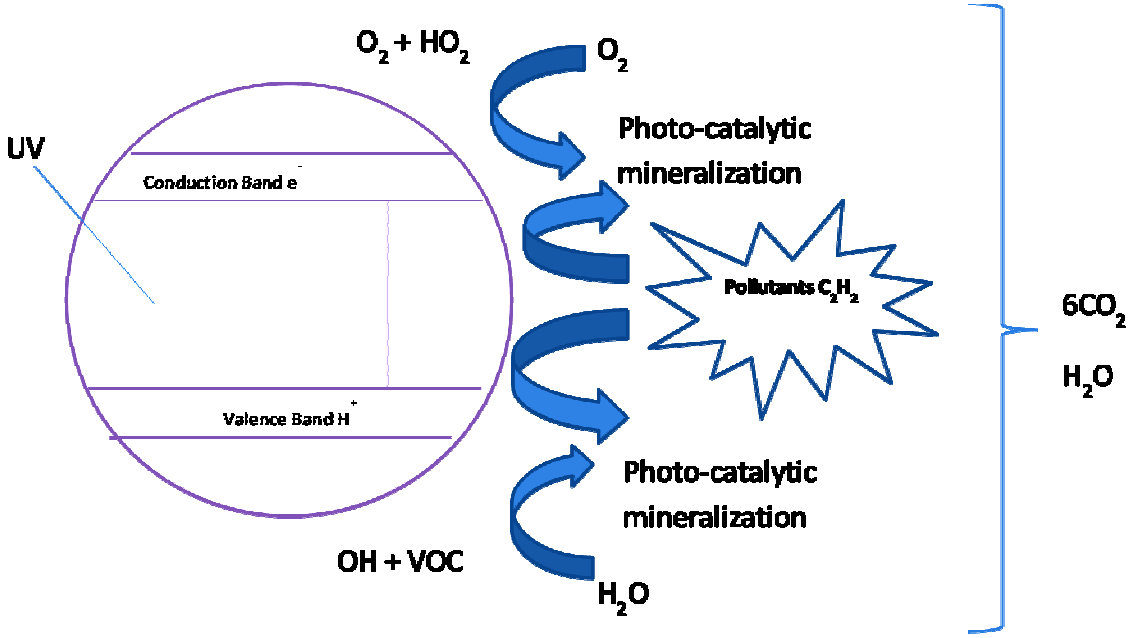


Figure 2.2: Summary of photo-catalytic degradation of dyes (Sampa and Biney, 2004)

The quantum efficiency of ZnO powder is significantly larger than other semiconductors and higher catalytic efficiencies have also been reported. The biggest advantage of ZnO is that it absorbs over a larger fraction of solar spectrum and for this reason, ZnO photo catalyst is the most suitable for photocatalytic degradation in presence of sunlight (Sampa and Biney, 2004).

2.7 Health Effects of heavy metals

According to the WHO (2006) the limit of the toxicity value for nickel is 130 μgL^{-1}, assuming a 60 kg adult drinking two litres of water per day. However, the presence of nickel at higher levels in the human body can cause serious lung and kidney problems as well as gastrointestinal distress, pulmonary fibrosis and skin dermatitis. A further

neurotoxin is mercury, which can cause damage to the central nervous system, and its concentration within the range of 0.12–4.83 mgL^{-1} may cause the impairment of pulmonary and kidney function,chest pain and dyspnea (Authier, 2006).

As per the USEPA(2005), cadmium is aplausible human carcinogen, and its presence potentially damages human physiology and other biological systems when the tolerance levels are exceeded. High levels of cadmium exposure (1 mgm^{-3}) may result in several complications leading to death.

Manahan (2000) described Cd to be very similar to zinc, and may replace zinc in some enzymes, there by altering stereo- structure and impairing its catalytic activity. Duffus (2002) stated that, in small doses Cd causes vomiting, diarrhea, and colitis. Continuous exposure to Cd causes hypertension, enlargement of heart, and premature death. There is evidence that, Cd causes chromosomal abnormalities and may exert carcinogenic effects on lungs.

WHO (2006) indicates that, acute Cu poisoning in humans is very rare, and it usually results from contamination of food stuff or beverages by Cu containers or from accidental ingestion of gram quantities of Cu salt, symptoms of acute Cu poisoning include; salivation, epigastria pains, nausea, vomiting, and diarrhea all of which are probably due to irritant effect of Cu on the Castro- intestinal mucosa.

Cd and Ni are widely dispersed in the environment, these elements have no beneficial effects in humans, and there is no known homeostasis mechanism for them (Vieira *et al*.,

2011). They are generally considered the most toxic to humans and animals; the adverse human health effects associated with exposure to them, even at low concentrations, are diverse and include; neurotoxic and carcinogenic actions (Tokar *et al.,* 2011).

2.8The use of metal oxides nanoparticle as heavy metals adsorbent in waste water

Nanoparticles have two key properties that make them particularly attractive as sorbents. On a mass basis, they have much larger surface areas than bulk particles. Nanoparticles can also be functionalized with various chemical groups to increase their affinity towards target compounds. It has been found that the unique property of nanoparticles isto develop high capacity and selective sorbents for metal ions and anions. Photo-catalytic nanomaterials allow ultraviolet light also used to destroy pesticides, industrial solvents and germs (Yantasee*et al*., 2007).

Zinc oxide nanoparticles have been used to remove arsenic from water, even though bulk zinc oxide cannot absorb arsenic. Some adsorption processes for wastewater treatment have utilized ferrites and a variety of iron containing minerals, such as akaganeite, feroxyhyte, ferrihydrite, goethite, hematite, lepidocrocite, magnetite and magnetite. Adsorption of organics to the nanoparticle media was extremely rapid (Apiratikul and Pavasan, 2008).

More than 90% of the organics is adsorbed within 30 minutes. The isotherm studies indicated that, on a surface area basis, the adsorption capacities of the nanoparticle media were significantly (>2 folds) higher than the ferric oxide media typically used in water

treatment (Pitcher*et al*., 2004). The smaller size of magnetic nanoparticles, which are 2-3 orders of magnitude smaller than a bacterium, provides extra benefits compared to magnetic beads. When their surface is appropriately elaborated, magnetic nanoparticles can also provide efficient binding to the bacteria because their high surface/volume ratio simply offers more contact area.

Iron (Fe) nanoparticles, nanodots or nanopowder are spherical or faceted high surface area metal nanostructure particles. Nanoscale iron particles are typically 20-40 nanometers (nm) with specific surface area (SSA) in the 30-50 m^2 g^{-1}range(Bhattacharyya and Gupta, 2008) .

The use of iron ferrite and magnetite inwastewater treatment has a number of advantages over conventional flocculent precipitation techniques for metal ion removal. The high surface area to mass ratios of nanoparticles can greatly enhance the adsorption capacities of sorbent materials. In addition to having high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites and disordered surface regions (Wu*et al*., 2009).

2.9Adsorption mechanism

In order to understand the mechanism of the adsorptionof metal ions by nanoparticles, a number of efforts havebeen undertaken in investigating the influence of theadsorption process using different techniques, such as infrared (IR) spectroscopy , X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and extended

Xrayabsorptionfinestructure(EXAFS)spectroscopy . The basis of discussion includesphysical adsorption, surfacecomplexation, ionexchange, electrostatic interaction and hard/softacid-base interaction.In general, the negatively-surface-charged nanoparticles form a complex with metal ions above their point(Singh,*et al*., 2011).

The enhanced complex tendency ofadsorbent at higher pH is expected, as at lowerpH the active sites are occupied withH^+ and are releasedat a higher pH, thereby originating the desired complex formation.Also, at lower pH, H^+ ions are adsorbed onto thesurface of nanoparticles, leading to a net positive charge.A certain amount of metal ions can still be adsorbed by nanoparticles at pH < pHpzc. This is perhaps due to the fact that ion exchange takes place atpH < pHpzc. Since the affinity of metal ions to nano ZnO ishigher than that of H^+ ions, metal ions can replace theadsorbed H^+ ions from the ZnO surface by an ionexchange mechanism . The adsorption of metal ions by ionexchange is relatively slow when compared to surfacecomplexation, since the organic molecules present on thesurface of the nanoparticles may cause steric hindrancetowards the adsorption of metal ions(Kansal*et al*., 2006).

2.10Toxicological Effects of Nano Materials

Knowledge of the potential toxicity of nanoparticles is limited but growing rapidly. Most of the work that has been done so far addresses primarily the occupational hazards associated with the manufacture and handling of nanostructured materials. There is a body of review papers available (Lynch and Dawson, 2008) that suggest that, owing to

their increased specific surface area and potentially altered bio-kinetics, nanoparticles may have a toxicity profile that deviates from that of their bulk equivalents. The toxicity of the nanomaterial, however, may be less than, greater than or similar to that of the bulk material, depending on the characteristics both of the material of which it is composed and of the particle itself (USEPA, 2005).

The relationship between the nanomaterial and the bulk material may depend on the dose metrics used in the comparison.There are only a limited number of published oral toxicity studies on some classes of nanomaterials, with those on solid particulates largely limited to insoluble metals and metal oxides. The quality of many of these studies is questionable, severely limiting the use of this information for risk assessment purposes. Common limitations include: use of a single size of nanomaterials, poor characterization and its administration at unrealistically high doses, study of only a narrow range of biological parameters, or omission of an appropriate larger particle of the same composition and a soluble form of the parent material as comparators to allow distinction between the effects of particle sizes and those of release of particle surface material into solution(Oberdorster*et al.*, 2007). This leads to the conclusion that the current state of knowledge does not permit reliable prediction of the toxicological characteristics of any givennanomaterials.

The capacity to predict computationally (such as using Quantitative Structure–Activity Relationship (QSAR)) the toxicological properties of conventional materials, however,

although considerably greater than for nanomaterials, is nonetheless limited and of variable reliability. It does not only trigger biological effects, but may absorb or bind proteins or other compounds on their surfaces (Lynch and Dawson, 2008). This selective binding and carrier potential has been termed a “Trojan horse” effect. The use of a nano-carrier to increase the bioavailability of bioactive compounds raises similar issues. The suggestion is that these carrier systems might impact the absorption of molecules, for example by introducing unintended molecules such as undigested or un-metabolized compounds across the gastro intestinal tract, leading to unintended effects. For example, chitosan can adsorb fat, including fat soluble micronutrients, and thereby prevent their absorption in the gastro intestinal tract. These issues, and the potential to disrupt the gastro intestinal barrier, will need to be addressed during the safety assessment of nanomaterials that have this potential, and in particular will require a careful consideration of the bio-kinetics and binding characteristics of the nanomaterials under consideration (USEPA, 2005).

2.11Stabilizing agents

Most organic stabilizers for semiconductor nanoparticles used such as organic thiols,oleic acids,urea,oxalic acids and others are water soluble.ZnO nanoparticles give significant stability under any type of stabilizer (Herrmann and Helmoltz, 2010).Oxalic acid is an organic compound which is used during synthesis of ZnOnanoparticles.It is used as a chemical capping in which it is used to passivate the surface of particles so that that they

do not agglomerate or ripen to form larger particles. This ensures that the nanoparticles synthesized yields stable product with uniform size distribution (Zaidi and Pant, 2008).

The capping agent provides protective organic shell to particles to prevent the nanoparticles from aggregating in solution. It also promotes formation of fewer,largernuclei and thus nanocrystal particle sizes (Gnanasangeetha and Sarala, 2013).Stabilizers enable the nanoparticles to be resistant to deactivation and thus its performance which depends on the nature and concentration of the stabilizing agent used.The difference in performance is due to electrical conductivity of stabilizers,the morphology and interface roughness and stabilizer particle interaction (Hu *et al.,* 2003).

The crystal structure of nano ZnO without as well as with oxalic acid has no effect on ZnO's wurzite structure as revealed by X-ray diffraction.SEM reveals different nature of surfaces and microstructures for nano ZnO obtained with and without stabilizers (Rajesh and Raychaudhuri, 2013).

2.12 Related studies

Shanthi and Muthuselvi (2012) studied morphology of synthesized nano ZnO using PXRD, FTIR and SEM. The PXRD results indicated particle size of 12nm, 16nm and 18nm for the three samples, all of which fall within the nano scale range of below100 nm. Rashed and El-Amin (2007) conducted a study on photo catalytic degradation of methyl orange in aqueous ZnO nanoparticles under different solar radiation sources. The results

revealed that; the degradation rate increases with the increase of dye concentration to a certain concentration, and further increase leads to a decrease in dye degradation rate.

The FTIR analysis showed a broad band between 430-419 cm^{-1}.The spectra showed bands at 3250 and 3500 cm^{-1} which they assigned to OH stretching vibrations of adsorbed water or residual $Zn(OH)_2$present in the bond.The images obtained from SEM for the samples showed sphere and cube like nanoparticles distributed well within the range of ~ 100 nm.On the effects of irradiation sources; the study revealed that decolourization efficiency of 98.92%was observed at 90 minutes irradiation time under solar light whereas in presence of UV radiation, for the same duration, only 50% decolourization efficiency was recorded(Rashed and El-Amin, 2007).

Singh *et al*. (2011) reported on the removal of various toxic metal ions, such as Co^{2+}, Ni^{2+}, Cu^{2+} Cd^{2+}, Pb^{2+}, Hg^{2+} and As^{3+} from wastewater by ZnO nano-particles. It was reported that Hg^{2+}, Pb^{2+} and As^{3+} have a stronger attraction towards ZnO nano-particles due to their high electro-negativity and, hence, that they exhibit better removal efficiency (63.5% Hg^{2+}, 100% Pb^{2+} and 100% As^{3+}).

Kumar *et al.* (2013) demonstrated the removal of Pb(II) and Cd(II) under different adsorbate concentrations, contact times, adsorbent dosages, pH and temperature conditions, from aqueous solutions usingZnO nano-particles. They observed the maximum adsorption capacities of Pb(II) and Cd(II) to be 160.7 and147.25 mg per g, respectively. Sheela *et al*. (2012) used ZnO nanoparticles of size 25 nm for the removal

of Cd(II) and Hg(II) ions from an aqueous solution. They found a maximum adsorption capacity of 387 and 714 mg per g for Cd(II) and Hg(II) ions, respectively.

Zinc oxide has received a great deal of attention in relation to the photo catalytic degradation of organic contaminants. It has been reported that different morphologies of ZnO exhibit different degrees of photo catalytic activity. Ma *et al*. (2011) andZhai *et al*. (2012) have reported on the photo catalyticactivity of ZnO nano-particles in decomposing methyl orange (MO) in water under UV irradiation, they noted high catalytic efficiency.

2.13Adsorption Isotherms for the photocatalytic degradation of dye

Photocatalytic degradation of dye is commonly expressed using two major adsorption isotherms: Langmuir and Freundlich (Romanchuk*et al.,* 2013).

Langmuir adsorption isotherm is the most commonly used due to its simplicity and its ability to fit a variety of adsorption data. It is based on four assumptions:

1. All of the adsorption sites are equivalent and each site can only accommodate one molecule.
2. The surface is energetically homogeneous and adsorbed molecules do not interact.
3. There are no phase transitions.
4. At the maximum adsorption, only a monolayer is formed. Adsorption only occurs on localized sites on the surface, not with other adsorbates.

These four assumptions are seldom all true: there are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the mechanism is clearly not the same for the very first molecules to adsorb to a surface as for the last (Kyzas, Lazaridis& Bikiaris, 2013). The fourth condition is the most troublesome, as frequently more molecules will adsorb to the monolayer; this problem is addressed by the Brunauer–Emmett–Teller (BET) isotherm for relatively flat (non-microporous) surfaces. The Langmuir isotherm is nonetheless the first choice for most models of adsorption, and has many applications in surface kinetics and thermodynamics (Senthamarai*et al.,* 2013).

The theory can be represented by the following equation:

$\frac{C_e}{Q_e} = \frac{1}{b}Q_0 + \frac{C_e}{Q_0}$ ----------8

Where q_e is the amount of methyl orange adsorbed per unit mass of adsorbent (mg/g^{-1}) and C_e is the equilibrium concentration of methyl orange, Q_o and b are Langmuir constant related to the capacity and energy of adsorption, respectively.

The Frendlich isotherm is not commonly used. The empirical Freundlich isotherm equation is:

$Q_e = K \text{ x } C_e^{(1/n)}$……..…9

in logarithmic form (linear)

$logQ_e = logK\ x\ \frac{1}{n}logC_e$……..…...10

where k is related to adsorption capacity, and n is related to intensity of adsorption.

CHAPTER THREE

MATERIALS AND METHODS

3.1Research approach

This project achieved its scientific objectives through laboratory experiments that allowed precisely controlled processes. Although laboratory based, the overall research plan was designed to ensure that the results will be used to achieve the project objectives. Experiments were conducted using methyl orange which was used as a model dye. Its mode of removal is similar to synthetic dyes. Stock solutions of Cd^{2+}, $Cu^{2+}$and Ni^{2+} were prepared and analysis was done using AAS (AA-7000).The experimental plan was carefully constructed to ensure that each objective was addressed by procedures and experiments that yielded the desired outcomes.

3.2Materials and Reagents

Methyl orange dye(ACS reagent, Dye content, 85%) was obtained from Indo lab chemicals in Eldoret while $ZnSO_4$(0.1 M, 99% Purity)and NaOH (0.1 M, 99% Purity) were purchased from Rimoi chemicals, Eldoret. All the reagents were prepared using double distilled water and in glass apparatus.All the materials required for synthesis, adsorption and photo degradation studies was obtained at University of Eldoret.

3.3Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized using precipitation method. In this method, ZnO nanoparticles were prepared in two ways. In the first set, 100ml of 1M $ZnSO_4$ solution was added to 100ml of 2M NaOH solution in drops. When the addition was complete, the mixture was kept at room temperature under constant stirring using magnetic stirrer for a period of 2-4 hours.

The constant stirring using magnetic stirrer makes the precipitation homogeneous and minimal particles which reduce the specific surface free energy of crystal nucleus which inhibit agglomeration and growth of the crystal nucleus so the particle size of the product is reduced (Zhang*et al*., 2010).

The resultant precipitate obtained was filtered using a filter paper then rinsed with distilled water. The formed white precipitate of $Zn(OH)_2$was allowed to settle, filtered using filter paper of pore size 0.4µm in a suction pump, washed with distilled water several times and dried in hot oven at 150^0C for 45 minutes. The synthesized ZnO nanoparticles were further irradiated at 180 W with microwave radiation in a microwave oven for 30 minutes. This was named as sample L_1. The above procedure was followed to synthesize ZnO nanoparticles in different experimental conditions. $ZnSO_4$, NaOH and oxalic acid were used as stabilizing agent. Thus one more sample was obtained and referred to as L_2.

The precipitation reaction was represented as

$ZnSO_{4(aq)} + 2NaOH_{(aq)} \longrightarrow Zn(OH)_{2(s)} + Na_2SO_{4(aq)}$----------11

$Zn(OH)_{2(s)Heat} \longrightarrow ZnO_{(s)} + H_2O_{(1)}$----------12

The resultant ZnO nanoparticles particles after irradiation were collected and stored in brown bottles.

3.4 Characterization of ZnO nanoparticles particles

The synthesized ZnO nanoparticles were subjected to (PXRD), (FTIR), at ICRAF Nairobi, (SEM) and (EDX), at The University of western Cape (South Africa) in order to confirm the nanostructure.

3.5Heavy metal analysis

Atomic absorption spectrometer (AAS) was used to analyze samples for levels of heavy metal species; Cd^{2+}, Cu^{2+} and Ni^{2+} before and after treatment with ZnO nanoparticles. During analysis, the following parameters were varied; heavy metals concentrations, dose of the adsorbent and the pH of solutions.

3.5.1 Optimizing operating conditions

The instrument's operating conditions were optimized before the actual analysis. The fixed parameters were automatically set upon selection of the element to be analyzed. These parameters included; wavelength, lamp current, slit width and extra heat tension (EHT) (Table 3.1). The other parameters were set according to the manufacturers

specifications in the manual (Fang, 1995). The acetylene and oxygen flow rate was set to attain maximum transparency of the flame. The optimized conditions for the AAS instrument during analysis are shown in table 3.1 below.

Table 3.1: Optimized conditions for AAS

Element	Wavelength λ (nm)	Lamp Current (mA)	Slit Width (nm)	Acetylene flow rate (L/min)	Oxidant flow rate (L/min)	BH (mm)	EHT (v)
Cu	324.8	4	0.5	2	13.5	13.5	494
Cd	228.8	4	0.5	2	13.5	13.5	562
Ni	352.4	4	0.5	2	13.5	13.5	582

Key**:** BH - Burner height, EHT - Extra Heat Tension

(Source: Manahan, 2000)

3.5.2 Calibration Curves

Sensitivity and detection limit checks were carried out to ensure that they were in agreement with the operating parameters by running the stock solution before the actual analysis. Calibration curve for each element were prepared using the standard working solutions. The curves had absorbance in the y – axis and concentrations in the x – axis.This plot was used as standard graph for estimation of metal ion concentration by interpolation technique.

3.5.3Laboratory-based heavy metals analysis

The concentrations of the adsorbed metals were analyzed using Spectra AA-200 Atomic Absorption Spectrophotometer. A reagent blank sample was taken through the method, analyzed and subtracted from the samples to correct for reagent impurities and other

sources of errors from the environment. The concentrations of the metals were determined in triplicates to ensure accuracy and precision of the analytical procedure.

After adsorption, the concentration of these metal ions wasanalyzed. The extent of removal in terms of percentage was calculated using the following relationship.

$$\% \text{ Removal} = \frac{C_1 - C_2}{C_2} \, x \, 100 \text{ ----------13}$$

Where C_1 = Initial concentration

C_2 = Final concentration

The effect of various experimental parameters on adsorption of heavy metals in the aqueous suspension by ZnO nanoparticles were studied by varying the experimental conditions; concentration of the heavy metals, amount of the sample (L_1 and L_2) and pH.

3.6Photo-catalytic degradation studies

3.6.1 Preparation of dye solution

Methyl orange (MeO) is an organic dye with a chemical formula of $C_{14}H_{14}N_3SO_3Na$ and characterized by sulphonic groups, which are responsible for high solubility of these dyes in water.The stock solution (1,000ppm) was prepared and stored in brown bottles. The stock solution was diluted to get different required initial concentrations of the dye used. Dye concentration was determined by using absorbance measured before and after the treatment using UV-VISspectrometer.

3.6.2 Measurement of concentration of dye solution

The stock solution was diluted to different initial concentrations10, 20, 30, 40 and 50 ppm for methyl orange in standard measuring flasks by making necessary dilutions with required volume of distilled water. The optical density of each dye solution was measured using UV-VIS spectro photometer (model – No-SL-150 Elico) at maximum wavelength value for MeO dye. A plot of optical density versus initial concentration was drawn. This plot was used as standard graph for estimation of dye by interpolation technique. The values of optical density for dye solutions before and after removal of dye were obtained by using UV-VIS spectrophotometer. Using these optical densities the corresponding dye concentration was obtained from the graph.

3.6.3 Determination of extent of removal of the dye

Stock solution of MeO dye (1,000ppm) was suitably diluted to get the required initial concentration from 15 – 45ppm. A 10ml of the dye solution of known initial concentration (C_1) wastransferredto 50ml beaker. Required amount of the photo-catalyst (L_1 and L_2) was exactly weighed and then transferred to the dye solution with different C_1. The beaker wasthen exposed to fluorescent light and direct sunlight for a fixed period of contact time.

After bleaching, the optical density (OD) of these solutions was measured using UV-Vis spectrophotometer and the final concentrations (C_2) obtained from the standard graph.

The extent of removal of the dye in terms of percentage removal was calculated using the following relationship.

$$\text{Percentage removal} = \frac{100(C_1 - C_2)}{C_1} \text{----------14}$$

Where

C_1 = initial concentration of dye (ppm)

C_2 = final concentration of dye (ppm)

3.7 Factors that govern degradation process

The effect of various experimental parameters on degradation of MeO dye in the aqueous suspension by ZnO nanoparticles were studied by varying the experimental conditions; concentration of the dye, amount of the sample (L_1 and L_2) and contact time. Eadch test was done in triplicate to ensure accuracy and repeatability.

3.7.1 Effect of variation of initial concentration of MeO dye

Keeping all other factors constant, the concentration of the dye was changed from 15ppm to 45 ppm then exposed to sunlight and fluorescent light energy and its effect on the rate of bleaching was studied.

3.7.2 Effect of variation of dose of photo catalyst on photo degradation ofMeO

The initial concentration of the dyes pHand contact time in all beakers were kept constant and the dose of photo-catalyst was varied from 0 $mgL^{-1}$to 400mgL^{-1}. The removal of the

dye at optimum initial concentration, 3hrs contact time and pH (6.8)was carried out following the general procedure.

3.7.3 Effect of variation of contact time on the photo-degradation of MeO

In order to study the effect of variation of contact time on the removal of MeO dye by exposure to sunlight and fluorescent light, experiments were carried out with optimum initial concentration of dye solution, pH (6.8)and optimum dose of photo-catalyst in the beakers containing required optimum initial concentration and pH was recorded. Then the optimum dose of photo-catalyst was added and immediately subjected to light energy. A stop watch to note the time was started simultaneously. The beakers were removed at different time intervals1,2,3,4, and 5 hours and then the solutionsanalyzed for dye content.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Characterization of ZnO nanoparticles particles

The synthesized ZnO nanoparticle samples were taken for instrumental analysis in International Center for Research in Agro forestry (ICRAF) laboratories in Nairobi. ZnO nanoparticle samples were subjected to powder X-ray diffraction (PXRD) and Fourier Transform Infrared (FTIR) studies to determinethe particle size andfunctional groups present respectively.The EDX and SEM analysis were also carried out in University of Western Cape,South Africa to determine elemental composition and morphology respectively.

4.2 Powder X-Ray Diffraction (PXRD)

The X-ray diffraction study of the samples was done by Philips X'pert model No. PW 3040/60 using Cu K αradiation (λ=1.5060A^0).The X-ray diffraction pattern of ZnO nano photocatalysts was recorded at 2Ɵ angle.Figure 4.1 and 4.2 show the XRD patterns of the synthesized Zinc oxide nanoparticles and the standard JCPDS file 80-0075, respectively.

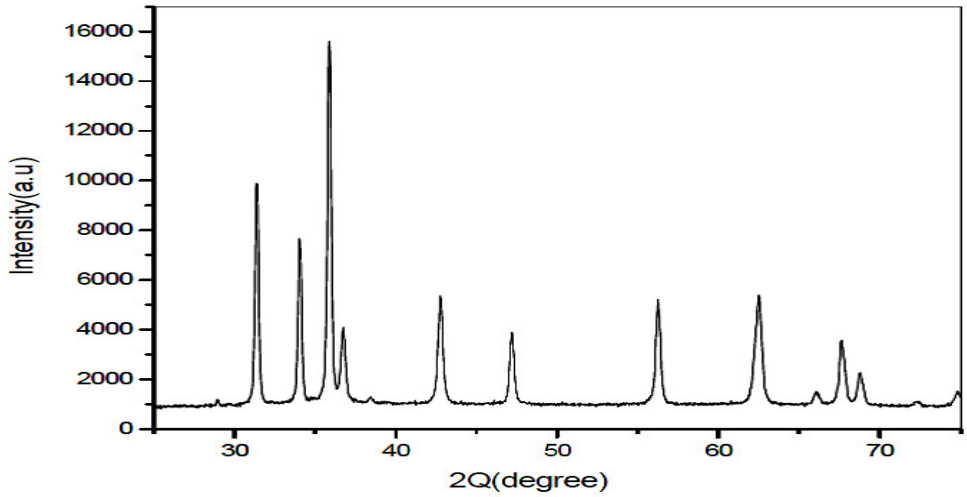
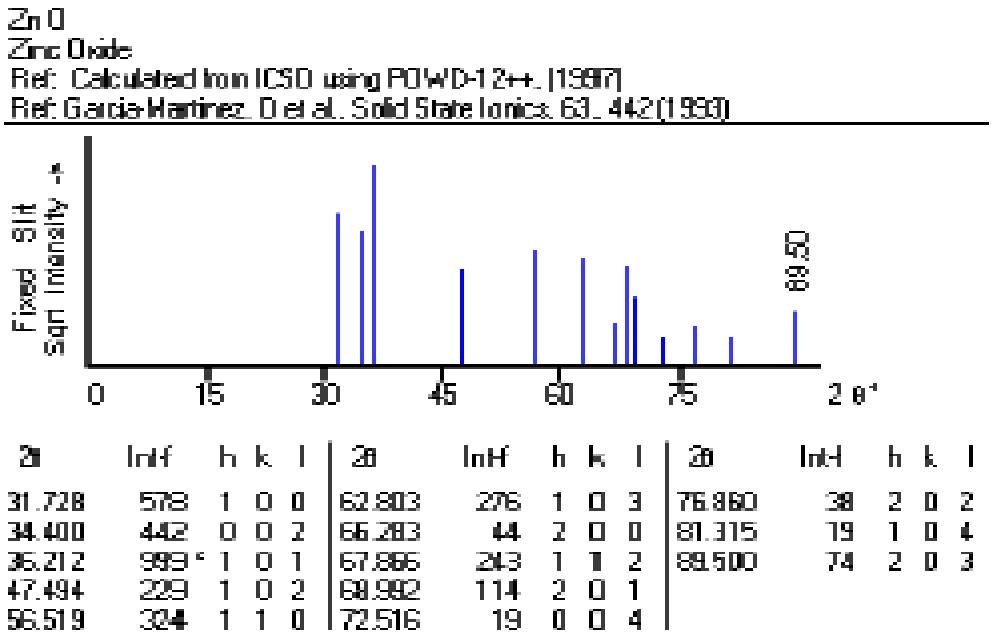


Figure 4.1: Observed Powder XRD pattern



2θ	Int-f	h	k	l	2θ	Int-f	h	k	l	2θ	Int-f	h	k	l
31.728	578	1	0	0	62.803	276	1	0	3	76.860	38	2	0	2
34.400	442	0	0	2	66.283	44	2	0	0	81.315	19	1	0	4
36.212	999	1	0	1	67.866	243	1	1	2	88.500	74	2	0	3
47.494	229	1	0	2	68.982	114	2	0	1					
56.519	324	1	1	0	72.516	19	0	0	4					

Figure 4.2: Reference JCPDS file 80-0075 for Wurzite ZnO

From figure 4.2, the diffraction peaks at 31.7, 34.4, 36.2, 47.4, 56.4, 62.5, 67.6, and 68.7 can be indexed to ZnO as per the JCPDS file 80-0075 as shown in Figure 4.1(b).Powder diffraction patterns are characteristic of a particular substance. It is its “fingerprint”and can be used to identify a compound.Powder diffraction data from known compounds have been compiled into a database by theJCPDS.The synthesized sample can be confirmed to be ZnO nanoparticle. Figure 4.1 (b) shows the reference JCPDS file that was used to visually compare (indexed) with XRD patterns obtained from the samples.Clear crystallinity of the ZnOnanoparticles was observed.The samples had

similar patterns.This suggests that the oxalic acid added as stabilizing agent had no effect on the wurzite structure of ZnO(Herrmann and Helmoltz, 2010).

Similar results were obtained by Gu *et al*. (2004) who obtained XRD peaks at scattering angles (2θ) of 31.3670, 34.0270, 35. 8596, 47.1635, 56.2572, 62.5384, 67.6356, and 68.7978, corresponding to reflection from 100, 002, 101, 102, 110, 103, 200 and 112 crystals. They indexed the XRD patterns to ZnO nanoparticles reference JCPDS file 80-0075 as well.

The average crystallite size of ZnO nanoparticles was estimated according to the diffraction reflection by using Debye-Scherrer equation

$$T = \frac{0.9\lambda}{\beta cos\theta} \text{----------} 15$$

Where

λ -is the wavelength of incident X- ray (1.5406A^0)

β- Is the full width for half maximum (FWHM),

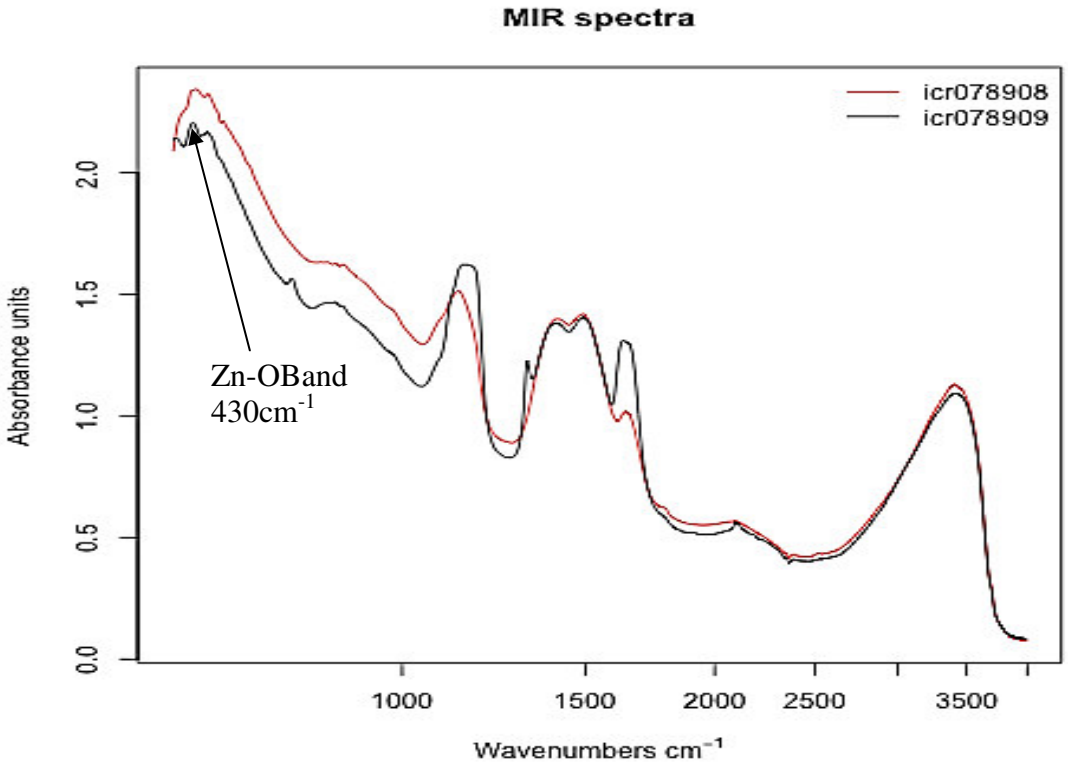
Θ -is the Bragg's angle for the peak

β- Can be calculated using the equation$\beta = (2\theta_2 - 2\theta_1)$, obtained to be 0.2755 radians. The average crystallite sizes of synthesized ZnO nanoparticles were found to be around26 nm.Similar results were obtained also by Shanthi and Muthuselvi (2012), who characterized synthesized nano-ZnO using PXRD.For their three samples prepared. The

sizes obtained were about18nm,16nm and 12nm.

4.2 The FTIR analysis

Figure.4.3 shows the FTIR spectrum of the synthesized ZnO nanoparticles synthesized by precipitation method, which was acquired in the range of 400-4000 cm^{-1}.



icr078908 – Sample 1
icr078909 – Sample 2

Figure 4.3: Observed FTIR pattern

FTIR of the ZnO nanocatalyst indicates the presence of water molecule adsorbed on the surface due to bands at around 3400 which may be assigned to OH stretching vibration of

adsorbed H_2Oor due to residual $Zn(OH)_2$ present in the powder (Shanthi and Muthuselvi, 2012).The absorption band at 430cm^{-1}correlated to metal oxide bond (Zn-O).

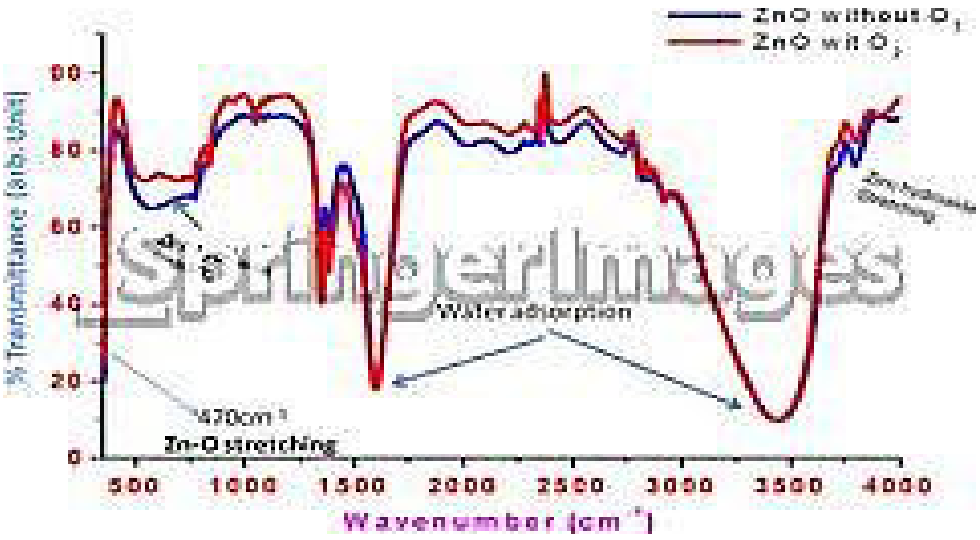


Figure 4.4: Reference ZnO Spectra

Kant and Kumar (2012) carried out similar study, FTIR spectra of ZnO obtained showed absorption band at 432.0 cm^{-1} which they attributed to (Zn-O) stretching frequency. Likewise peaks at 3401.3 cm^{-1} represent (O-H) stretching mode.Shanthi and Muthuselvi (2012) also carried out a similar study and their analysis showed a broad band between 419-430cm^{-1}.The spectra showed bands at(3250 and3500cm^{-1})which was assigned toO-Hstretching vibrations.

4.3 SEM Analysis

Figure 4.5 and Figure 4.6 shows the SEM diagram for sample $L_1$and L_2at high magnification respectively.

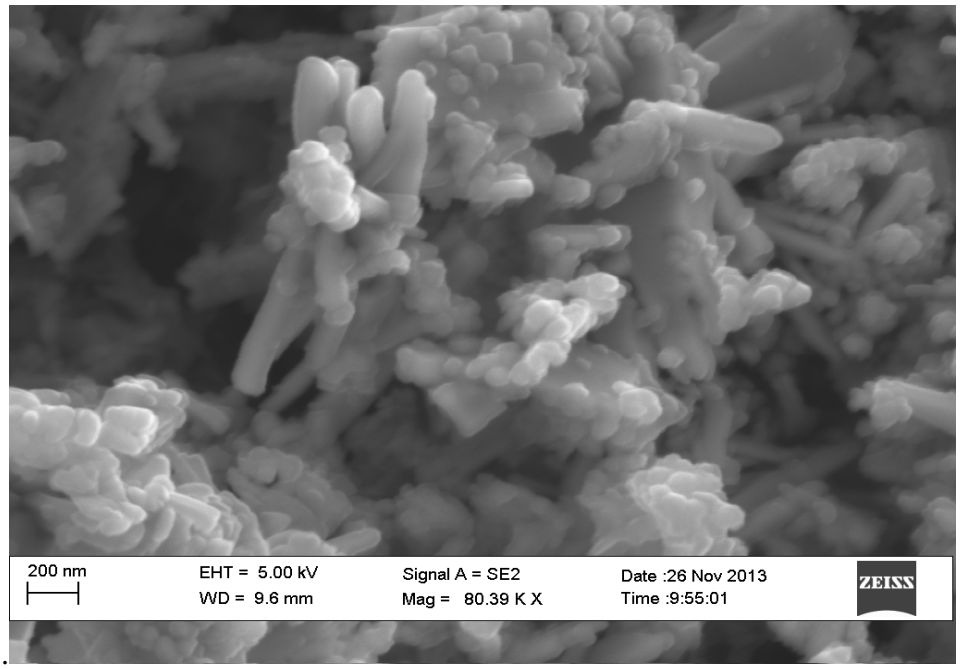


Figure 4.5: L_1 SEM diagram (Magnification = 80.39K X)

(**Source: Author, 2015**)

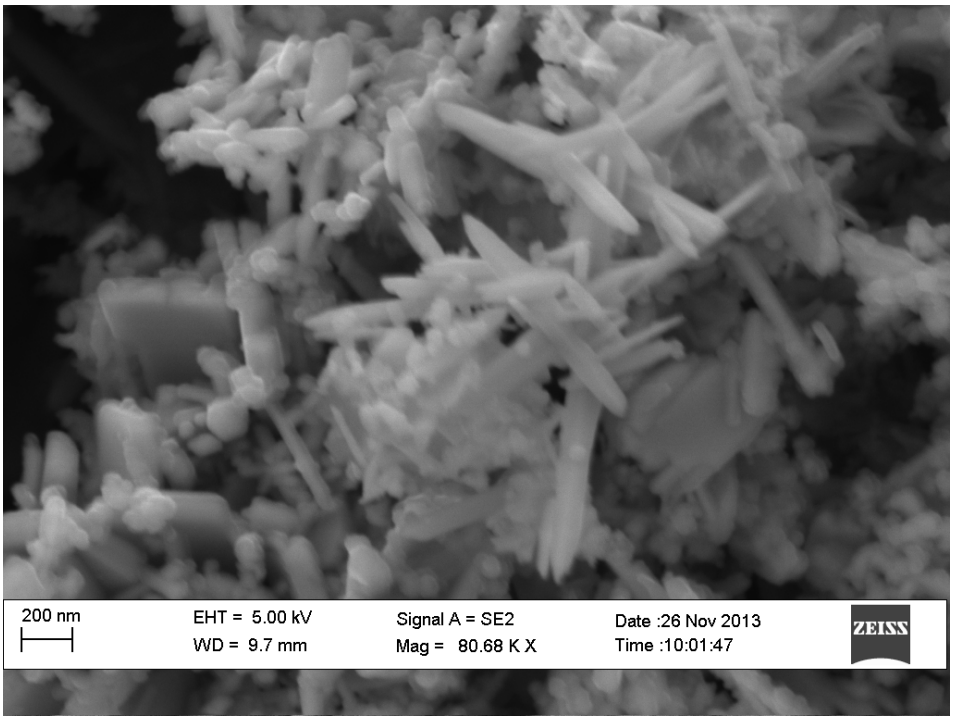


Figure 4.6: L_2 SEM diagram (Magnification = 80.68K X)

(**Source: Author, 2015**)

These images showed that the ZnO nanoparticles obtained formed rod shaped clusters distributed within the range of 200nm. The diagrams also show that the surface was not uniform but porous in nature. It shows that the nanocatalyst has considerable number of pores where there is a good possibility for the dye and heavy metals to be trapped and adsorbed onto these pores and it is a good sign for effective adsorption of dye and heavy metals (Joshi and Shrivastava, 2012).The photographs also showed different surfaces for

$L_1$and L_2.The L_1showed round ended while L_2 showed sharp ended nanoclustures.This showed that the stabilizing agent had an influence on the morphology of the samples.

Similar studies were made by Soltaninezhad and Amrnifar, (2011). They studied surface morphology of ZnO nanoparticles produced by Spray Pyrolysis. The pictures observed showed particles that were spherical in shape.However Joshi and Shrivastava, (2012) determined the surface texture which was found to be rough and porous in nature.

Also Shanthi and Muthuselvi, (2012) under a similar study, characterized nano ZnO synthesized by precipitation and the SEM pictures showed sphere and cube like nanoparticles which were distributed within the range of 100nm.

Due to these close similarities, the ZnO nanoparticles were confirmed. The difference in distribution range is attributed to the level of consistency during synthesis and also method of synthesis (Joshi and Shrivastava,2012).

4.4EDXAnalysis

Figures 4.7 and 4.8 showed the EDXresultsfor samples$L_1$and L_2,respectively.

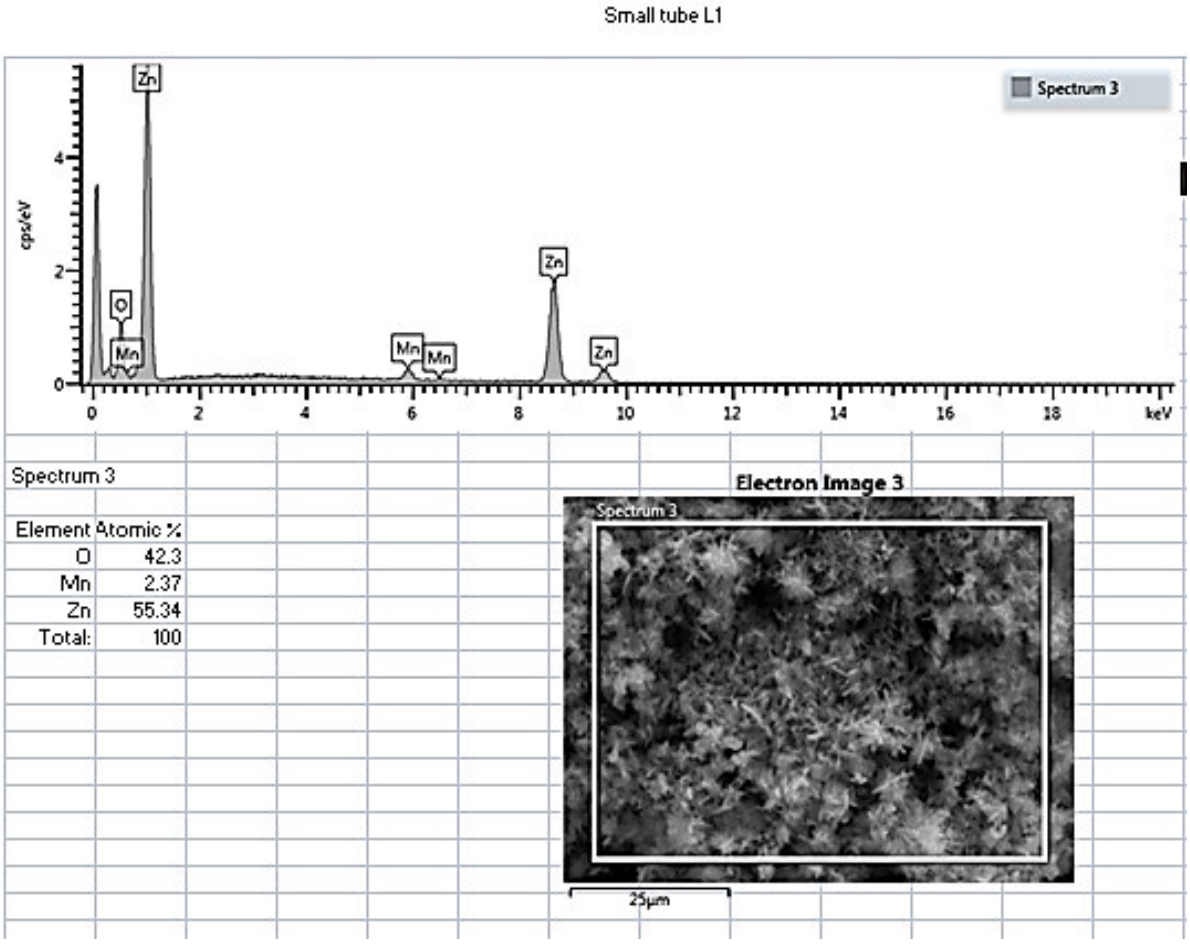


Figure 4.7: EDX Pattern ZnO L_1

(**Source: Author, 2015**)

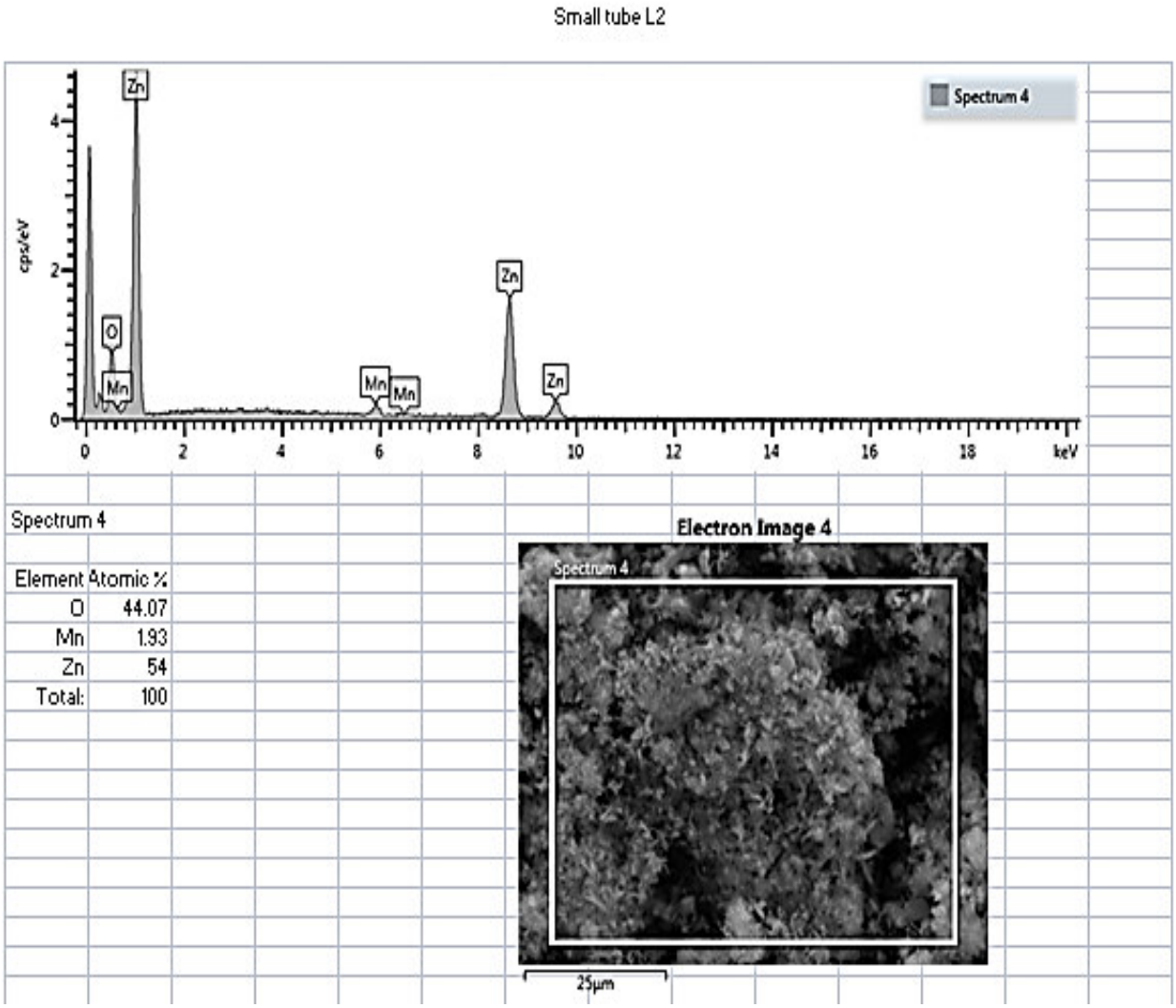


Figure 4.8: EDX Pattern ZnO L_2 (Source: Author, 2015)

The EDX spectra indicated that the samples were made up of Zn, O and traces of Mn impurities. The most intense peak is assigned to the bulk ZnO and the less intense on to the surface ZnO. The peak at 0.5 Kev can only be attributed to O and not Mn due to

overall position of the peaks.The elemental composition of the nanomaterial was found to be 55.34% Zn, 42.3% O and 2.37% Mn for $L_1$and 54% Zn, 44.0% O and 1.93% Mn for L_2.

Similar work has been done by (Joshi and Shrivastava 2012) who characterized nano ZnO synthesized by precipitation technique. Their EDX spectra showed a peak at 0.5 Kev for oxygen 1 Kev for ZnLα, 8.6 for ZnKα and 9.6 Kev for ZnKβ. The elemental composition was found to be 71% Zn, 18.5% CO and 10% C with carbon as the impurity.

4.5 Heavy Metals Analysis

4.5.1 Effect of initial heavy metalsconcentration on Adsorption capacity of ZnO nanoparticles

To evaluate the capacities of ZnO to remove heavy metals, batch experiments were performed with fixed adsorbent dosage of 250 mg at various initial concentrations (100-400 mgL^{-1}) of heavy metal solution.The effect of the initial Cd^{2+} , Ni^{2+} and Cu^{2+} concentration on the adsorption and adsorptivity (percentage of heavy metals adsorbed) is shown in figure 4.9.

Figures 4.9 – 4.11 were plotted using data in appendices 3, 4 and 5 respectively.

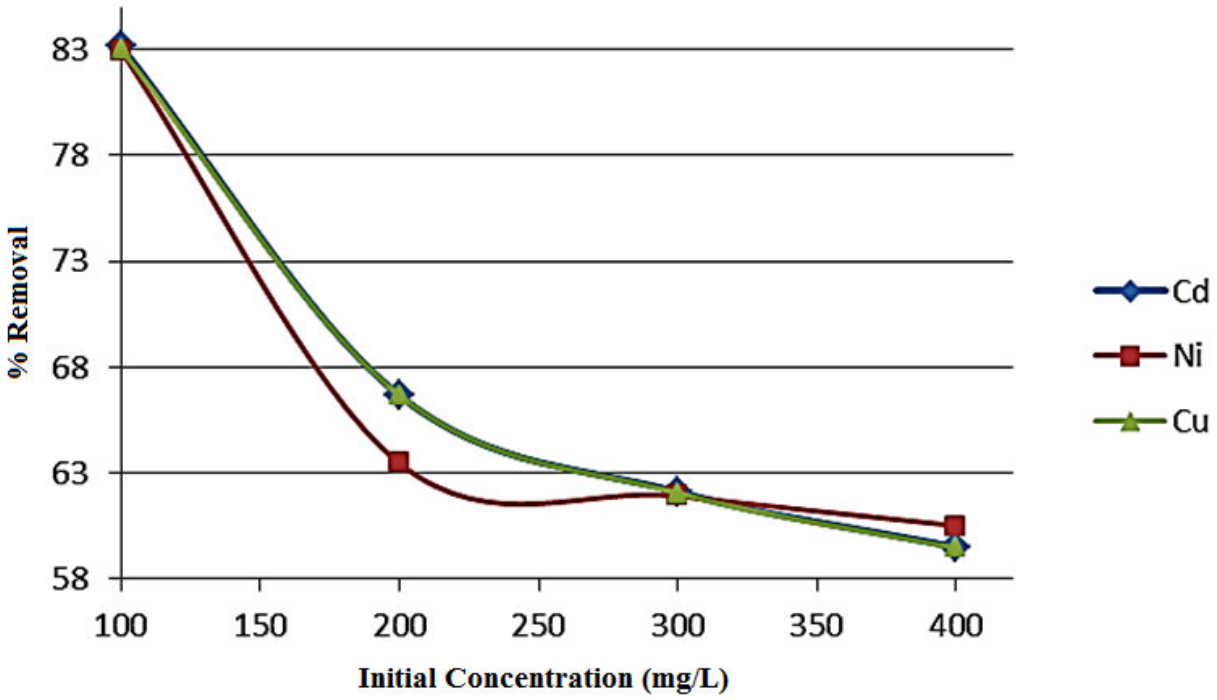


Figure 4.9: Effect of initial heavy metals concentration on adsorption capacity of ZnO nanoparticles

The adsorptivity decreased with increasing heavy metal concentrations. Further, sorbents active sites were saturated and further increase in the concentration would have no effect on the metal uptake. The maximal levels of uptake adsorption reached for ZnO were Cd(83.1%), Ni (82.9%) and Cu (83.0%) at initial concentration of 100 mgL^{-1}.

4.5.2 Effect of adsorbent dose on percentage removal of heavy metals

The adsorbent dosages were varied from 100mg to 500mg, while all the other variables such as contact time, pH and temperature were kept constant at 90 minutes, 7.0 and 25^0C respectively and the results are shown in Figure 4.10.

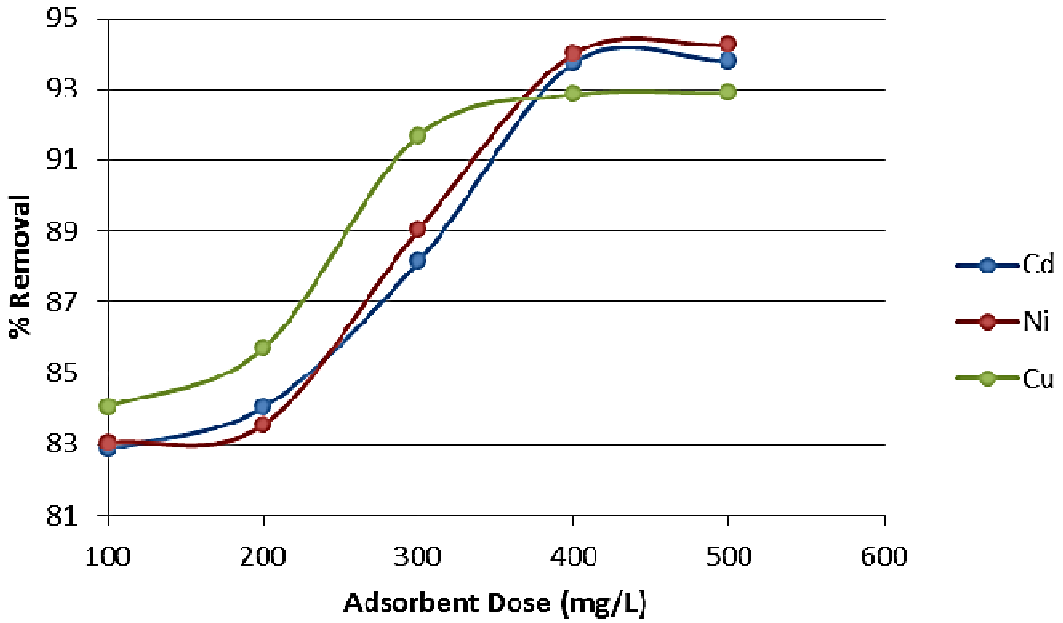


Figure 4.10: Effect of adsorbent dose on percentage removal of heavy metals

Adsorbent dose is an important parameter in the determination of adsorption capacity. As the adsorbent dosage increased from 100mg to 500mg, the adsorption sites available for heavy metal ions also increased and consequently better adsorption took place.For a fixed initial concentration of heavy metals,the amount of metal retained by gram of ZnO nanoparticles increased with the amount of ZnO nanoparticles(increase in the number of active sites).When more was added,retention was almost total.The same cations were

distributed on greater amount of surface and therefore resulted in reduction of adsorption amount on adsorbent (Kansal *et al.,* 2006).

The results agree with those found by Engates and Shipley (2011) who carried out a study to determine adsorption of Pb^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} by ZnO nanoparticles, by studying adsorption of single and multi-metal ions by ZnOnanoparticles. They found a 100% removal efficiency of Pb^{2+}, Cd^{2+} and Ni^{2+} ions at 0.1 g L^{-1}within 120 min.of 50 mg, pH 8 and 24 hours contact time.

4.5.3 Effect of pH on Heavy Metal adsorption

The effect of pH on the surface species is responsible for the adsorption of ions from the solution. Effect of pH on the adsorption capacity of ZnO nano particles was evaluated by agitating 200 mgL^{-1} metal ion solution with 250 mg of ZnO for 90 minutes at pH ranging from 2, 4, 6 nad 8.The quantities of heavy metals adsorbed on ZnO adsorbent was represented in figure4.11

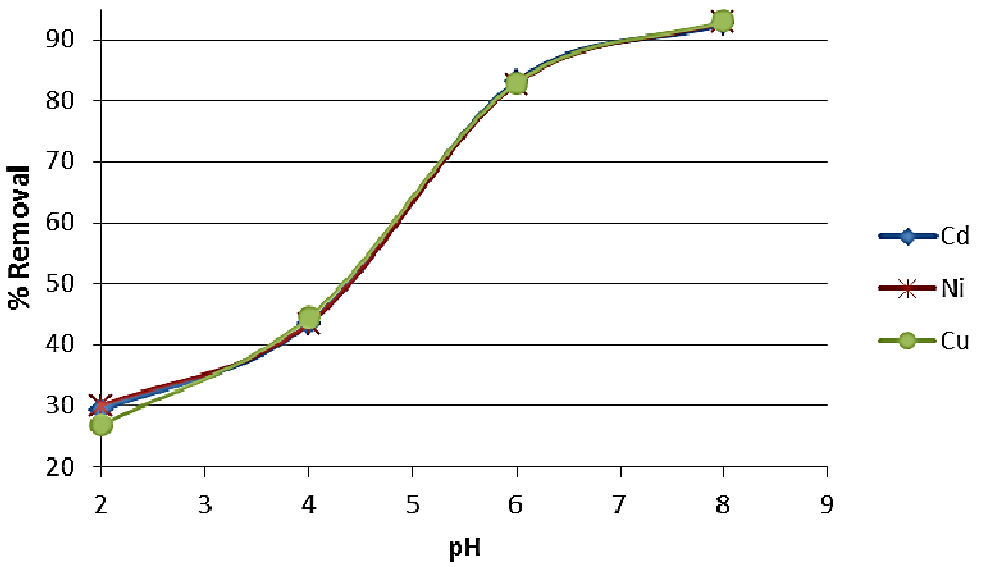


Figure 4.11: Effect of pH on ZnO nano particles heavy metals adsorption

The results on adsorption percentages of Cd^{2+}, Ni^{2+}, and Cu^{2+}at pH 2 showed that the maximum amount adsorbed was; Cd^{2+} (28.5 %), Ni^{2+} (29.1%) and Cu^{2+}(26.5%).Increasing the pH to 8, the adsorbed amounts were; Cd^{2+} (92.1%), Ni^{2+} (92.8%) and Cu^{2+}(92.0) as shown in Figure 4.11. The results agree with Yuan*et al.* (2013) who found that adsorption of metal ions (Pb^{2+}, $Cu^{2+}$and Cd^{2+}) gradually increased with an increase of the pH of the medium, and maximum removal efficiency was observed at pH 8.

The results suggestthat athigh pH the surface charge of ZnO nanoparticles is more negative due to presence of OH^-groups that leads to formation of hydroxyl complexes. Formation of such hydroxyl compounds at higher pH is responsible for the uptake of the metal ions from solution. In contrast, the low degree of sorption at low pH can be

attributed to the competition of cations (metal ions) and protons (H^+) for the same sites, as well as the repulsion between ions of the same surface charge (Kumar *et al.,* 2013).

4.6Photo-catalytic degradation studies

The optical density of each dye was measured using UV-VIS spectro-photometer at maximum wavelength of 480 nm. A plot of optical density versus initial concentration is shown in Figure 4.12.This plot was used as standard graph for estimation of dye concentration by interpolation technique.

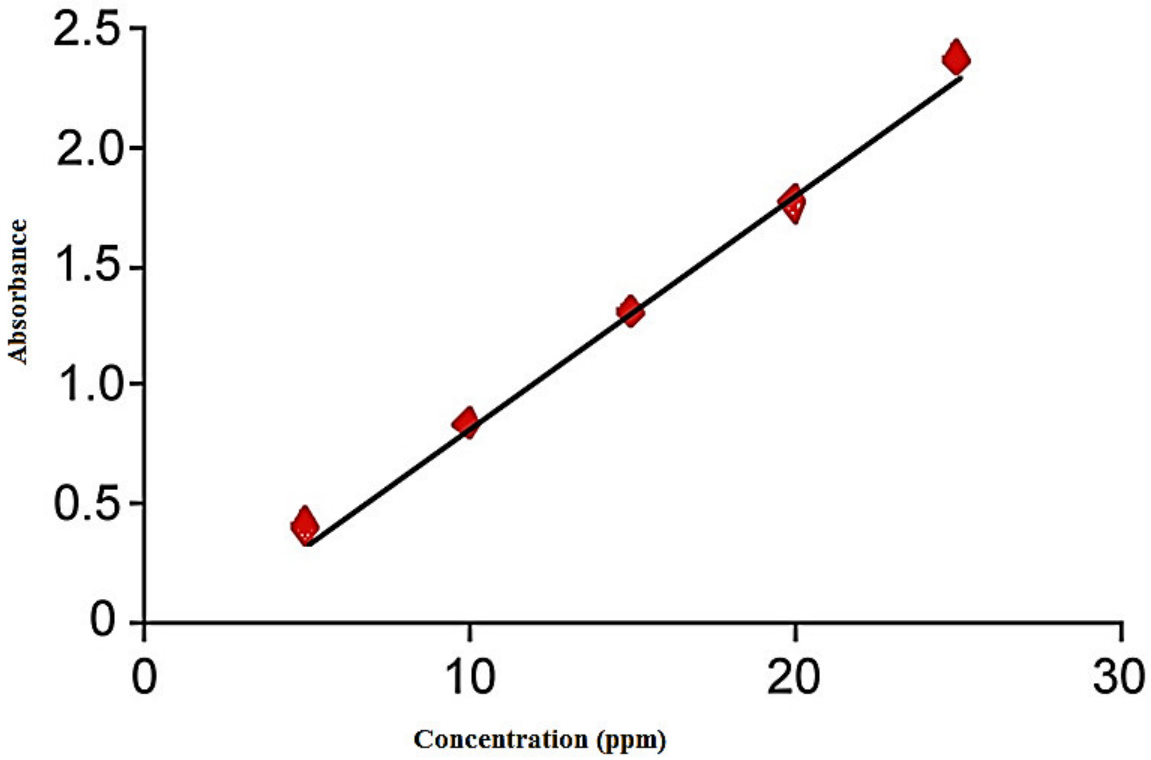


Figure 4.12: Standard curve for methyl orange dye

4.6.1 Effect of variation of initial concentration of dye on photo degradation of methylorange dye

Table 4.1 shows the effect of variation of initial concentration of Methyl orange dye on photodegradation.

Table 4.1: Effect of variation of initial concentration of dye on photo degradation of methyl orange dye

Radiation	Sample	Concentration of dye		
		15 mgL^{-1}	30 mgL^{-1}	45 mgL^{-1}
Sunlight	L_1	0.85	2.68	10.77
	% removal	98.4%	96.1%	94.7%
	L_2	2.49	6.83	20.89
	% removal	97.4%	97.2%	93.6%
Fluorescent	L_1	14.23	26.40	41.31
	% removal	92.0 %	89.0%	88.2%
	L_2	14.04	29.81	38.03
	% Removal	91.8%	88.9%	88.0%

Photo catalytic degradation of the dye was found to decrease with increase in initial concentration of methyl orange. This could be due to more dye molecules than ZnO nanoparticles; in this case the photo-catalyst became the limiting factor. It was noted that degradation rate decreased with increase in dye concentration. The decrease in dye degradation could be attributed to reduction of $OH^{\cdot}$ radicals on the catalyst

surfacewhencovered by dye ions (Poulis and Tsachpinis, 1999). Appendices 1 and 2 shows photodegradation based on contact time.

The results are similar to those reported by Li *et al.* (2005) when methyl orange was irradiated with sunlight source, the degradation of the dye decreased as the dye concentration increased. This due to the fact that the generation of $OH^{\cdot}$radical on the catalyst surface is reduced since theactive sites are covered by dye ions. Also Kansal *et al*.(2006) concluded that photo-catalytic degradation of methyl orange decreased as the dye concentration increased.

This decrease isas a result of increasing the number of photons absorbed by catalyst lower concentration (Davis, 2006). Acording to Shanthi and Muthuselvi (2012), the decrease in photo degradation is as a result of dye molecules imparting darker colour to the solution which acts as a filter to the incident light reaching the photo catalyst surface. Sampa and Biney (2004)further explained that the increase in the concentration of a dye solution result in the photons getting intercepted before they can reach the catalyst surface, thus decreasing the absorption of Photons.

4.6.2 Effect of variation of dose of photocatalyst (L_1 and L_2) on photo degradation ofMeOdye

The initial concentration 30 mgL^{-1} of the dye and pHin all beakers were kept constant at pH 7.0 and the dose of photo-catalyst was varied from 200 mgto 400mg with a contact time of four hours and the results are shown in Table 4.2.

Table 4.2: Effect of variation of dose of photo catalyst (L_1 and L_2) on photo degradation of MeO dye

Radiations	Sample	Amount of photo-catalyst		
		200mg	300mg	400mg
Sunlight	L_1	6.57	2.39	1.50
	% removal	92.1	94.2	96.0
	L_2	10.99	6.83	4.06
	% removal	93.4	97.2	96.5
Fluorescent	L_1	26.40	26.88	26.55
	% removal	92.0	96.4	98.5
	L_2	29.81	27.46	25.23
	% removal	92.6	97.5	97.9

Photo catalytic degradation of methyl orange dye increased with an increase in concentration of ZnO particles. This is due to increase in photocatalyst molecules available to degrade the dye. Further increase of ZnO nanoparticles concentration increase turbidity of the solution and decreases light penetration into the solution and therefore, removal efficiency decreases (Kartal*et al*., 2001).

The results of this study are similar to those of Joshi and Shrivastava (2012) who studied removal of methylene blue using ZnO nano particles, by varying the dose of photo catalyst from 2.0 g/l to 5.0 g/l and degradation increased from 86.0% to 92.8% as shown in Table 4.2. The increase in the amount of catalysts increased the number of active sites

of the photo catalyst surface, which in turn increased the number of hydroxyl and superoxide radicals (Sampa and Biney, 2004).

4.6.3 Effect of variation of contact time on photo degradation of MeO dye

The results are presented in Table 4.3 below.

Table 4.3: Effect of variation of contact time on photo degradation of MeO dye

Radiations	***Sample***	***Contact time in hours***				
		1	2	3	4	5
Sunlight	L_1	11.84	6.83	5.99	1.45	0.58
	% removal	60.5	77.2	80.0	95.2	98.0
	L_2	9.12	4.23	2.68	0.97	0.53
	% removal	69.6	85.9	91.1	96.8	98.2
Fluorescent	L_1	10.95	8.77	5.95	2.68	1.32
	% removal	63.5	70.8	80.2	91.1	95.6
	L_2	11.57	8.15	5.33	2.06	0.70
	% Removal	61.4	72.8	82.2	93.1	97.7

The mixture of L1 and L2 affects percentage removal of MeO which is higher than non-stabilized and lower than the stabilized as indicated in appendices 1 and 2.

The results indicated that, the percentage removal of dye increases with increase in contact time. This is in agreement with the results reported by Shanthi and Muthuselvi,(2012), who studied the effects of contact time on removal of malachite green using ZnO nano particles. The increased contact time causes the photogenerated

OH˙radicals and other peroxide radicals all being highly oxidant species decompose the dyes completely to mineral end products (Hofman, 2005).

4.7 Equilibrium isotherm models for photo degradation of MeO dye using sunlight

Two isotherm models were tested in the present study and these are Langmuir and Freundlich. The applicability of the isotherm equation is compared by judging the correlation coefficient R_2 (Fytianos *et al.,* 2000). Langmuir theory was based on the assumption that adsorption was a type of chemical combination or process and the adsorption layer was unimolecular (Samarghadi *et al.,* 2009).

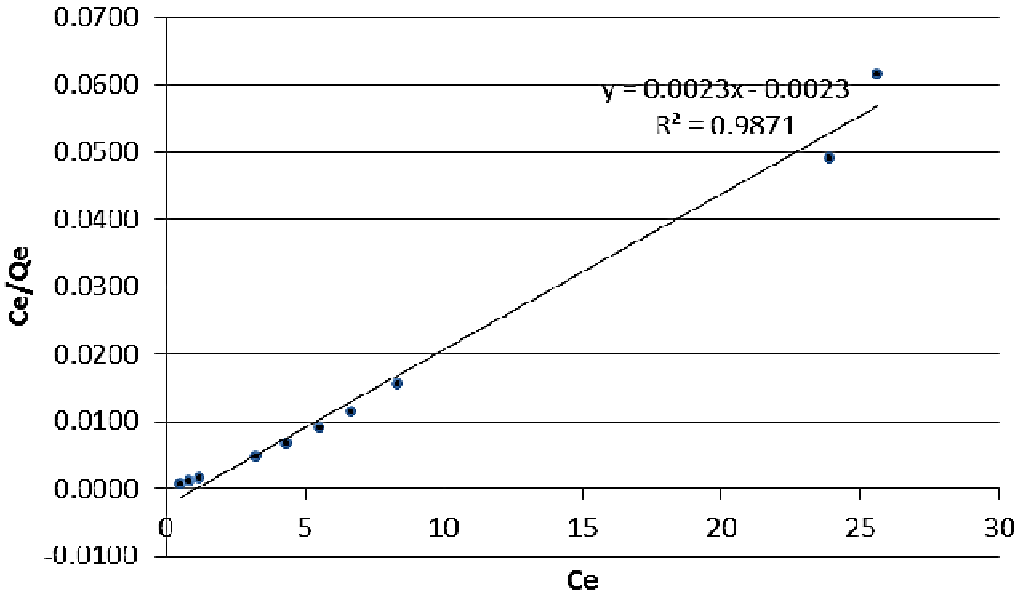


Figure 4.13: Langmuir adsorption isotherm of methyl orange adsorption

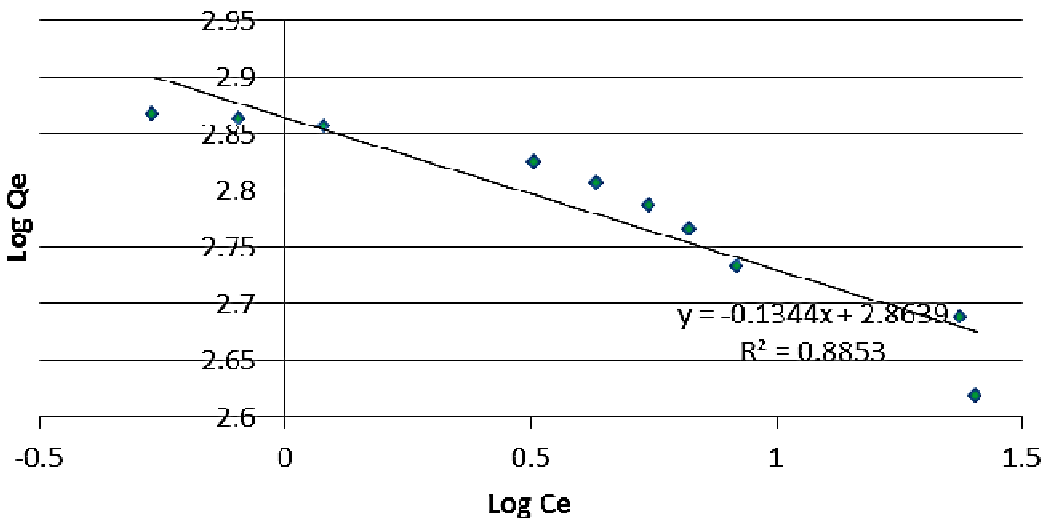


Figure 4.14: Freundlich adsorption isotherm of methyl orange adsorption

Figures 4.13 to 4.16 were plotted from appendices 3, 4, 8 and 9.The coefficient of correlation for ZnOnanoparticles obtained from figure 4.13 for Langmuir expression (R^2= 0.9871) and ZnO coefficient of correlation obtained from figure 4.14 for Freundlich expression (R^2= (0.8853) indicated that Langmiur expression provided better fit for the experimental data of photocatalytic degradation of methyl orange using ZnO nanoparticles than Freundlich expression.

These findings are in agreement with thoseof a study conducted by Joshi & Shrivastava (2012) on degradation of alizarine red-s (a textiles dye) by photocatalysis using ZnO and TiO_2 as photo-catalyst. In their study, the good fit for the experimental data and the correlation coefficients R^2 higher than 0.9996 indicated the applicability and suitability of Langmuir isotherm model more than the Freundlich isotherm.

4.8 Equilibrium isotherm models for photo degradation of MeO dye using florescent

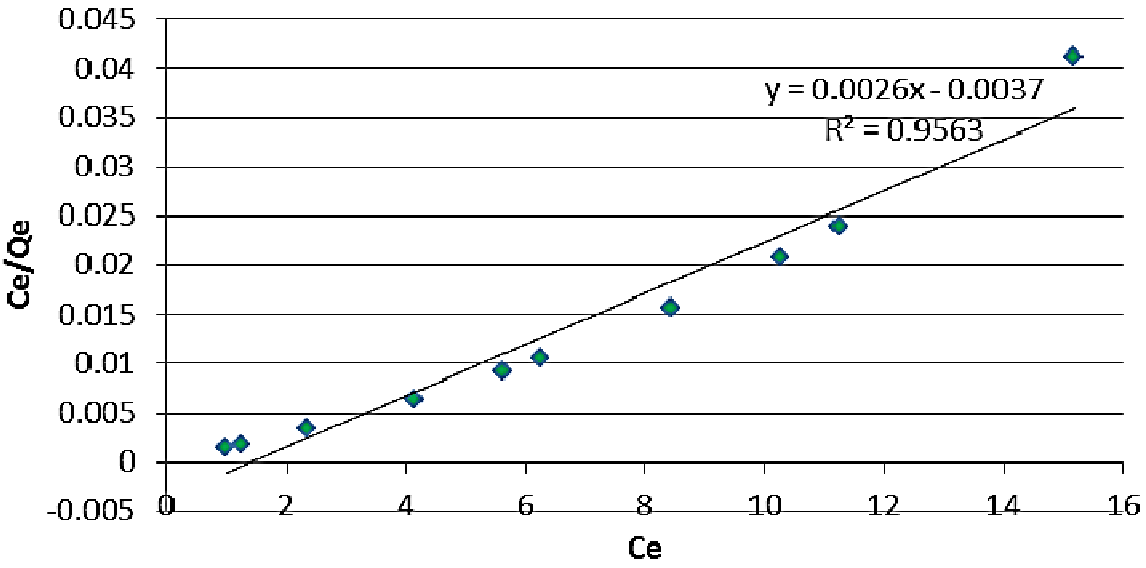


Figure 4.15: Langmuir Isotherm for photo degradation of MeO dye using florescent

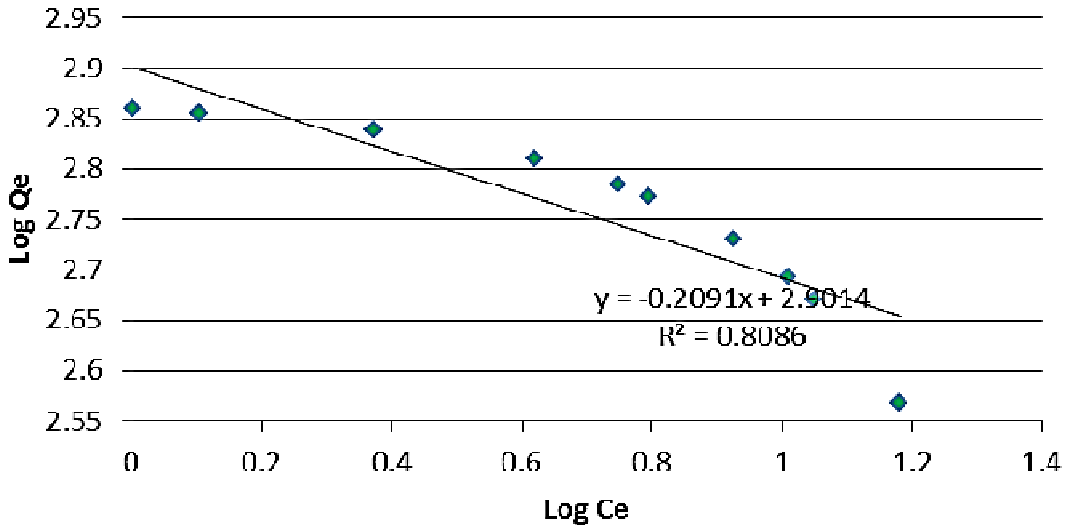


Figure 4.16: Freundlich Isotherm for photo degradation of MeO dye using fluorescent

The coefficient of correlation for ZnO nanoparticles obtained from figure 4.15 for Langmuir expression (r^2= 0.9563) and ZnO coefficient of correlation obtained from figure 4.16 for Freundlich expression (r^2= (0.8086) indicated that Langmiur expression provided better fit for the experimental data of photocatalytic degradation of methyl orange using ZnO nanoparticles under florescent than Freundlich expression.

These findings are in agreement with the findings of study conducted bySamarghandi *et al.* (2009), on two-parameter isotherms of methyl orange sorptionusing pinecone derived activated carbon. In their study, the good fit for the experimental data and the correlation coefficients r^2 higher than 0.9271 indicated the applicability and suitability of Langmuir isotherm model more than the Freundlich isotherm(0.5893).

4.9 Adsorption kineticsfor photo degradation of MeO dye using sunlight

For the evaluating the adsorption kinetics of methyl orange on ZnO nanoparticles, the data was treatedwith Lagergren first order model expressed as

----------16

The first order rate constant k_1 is obtained from the slope of the plot log (q_e-q_t) versus time,

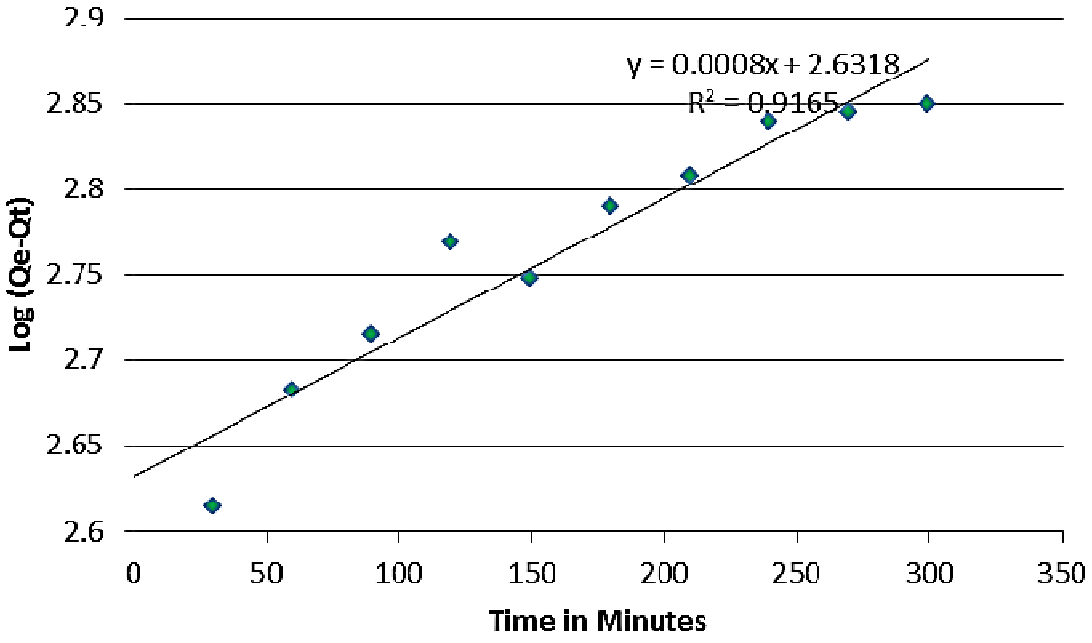


Figure 4.17: Lagergren first order plot of methyl orange degradation under sunlight

Adsorption kinetics were also explained by the pseudo second order model (Yuh-Shan, 2004)

— — —

where K_2 is the second order rate constant (g $mg^{-1}min^{-1}$). The value of K_2 is different initial

dye concentration for all adsorbents which were calculated from the slope of the respective linearplot of t/qt vs t.

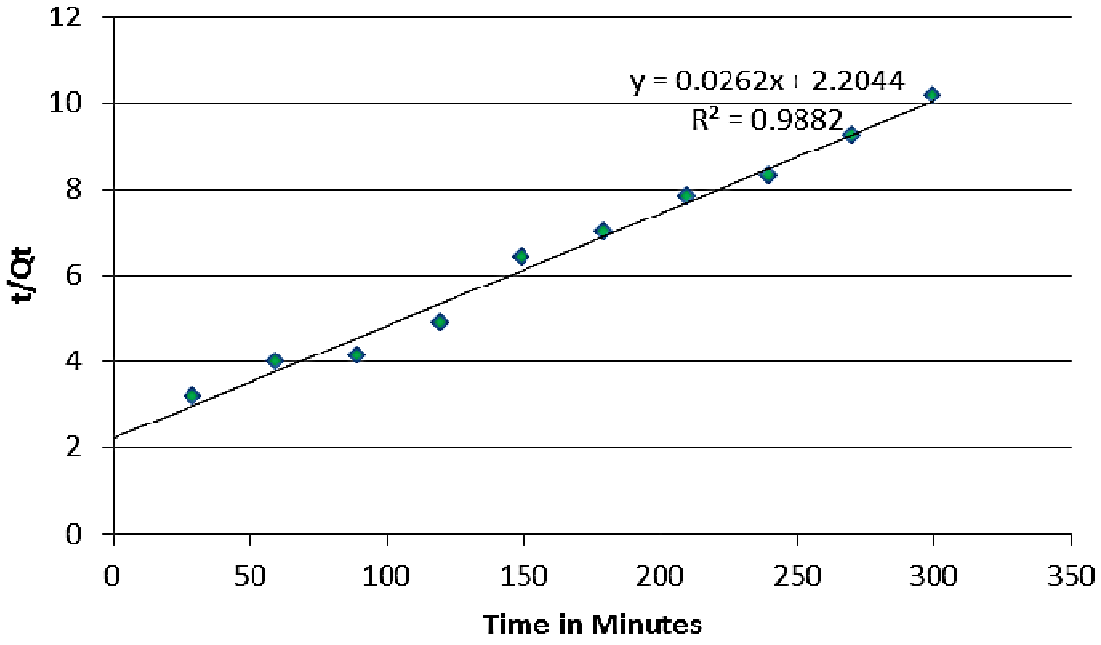


Figure 4.18: Lagergren second order plot of methyl orange degradation under sunlight

The correlation coefficients from figures 4.15 and 4.16for these two tests ranged from 0.9165 for the first order kinetics to 0.9882 for the second order kinetics. This suggests that there existed a strong relationship between theparameters and also that the process

followed the pseudo second order kinetics figure 4.16. This shows that the degradation process of methyl orangeonZnO nanoparticles followedpseudo second order kinetics. These findings are in agreement with those of Joshi & Shrivastava (2012) who conducted a study on the degradation of alizarine textile dye by photocatalysis using ZnO and TiO_2 as photocatalyst. For their study, the correlation coefficients were 0.9946 and 0.9998 for first order and second order, respectively suggesting a strong relationship between the parameters and also explaining that the process followed the pseudo second order kinetics.

The findings also correlate with the findings of Sampa and Biney (2004) who conducted a study on photo-catalytic degradation of modern textile dyes in waste water using ZnO nanocatalyst. For their study, the correlation coefficients were 0.9849 and 0.9988 for first order and second order, respectively, suggesting a strong relationship between the parameters and also explaining that the process followed the pseudo second order kinetics.

4.10 Adsorption kineticsfor photo degradation of MeO dye using florescent

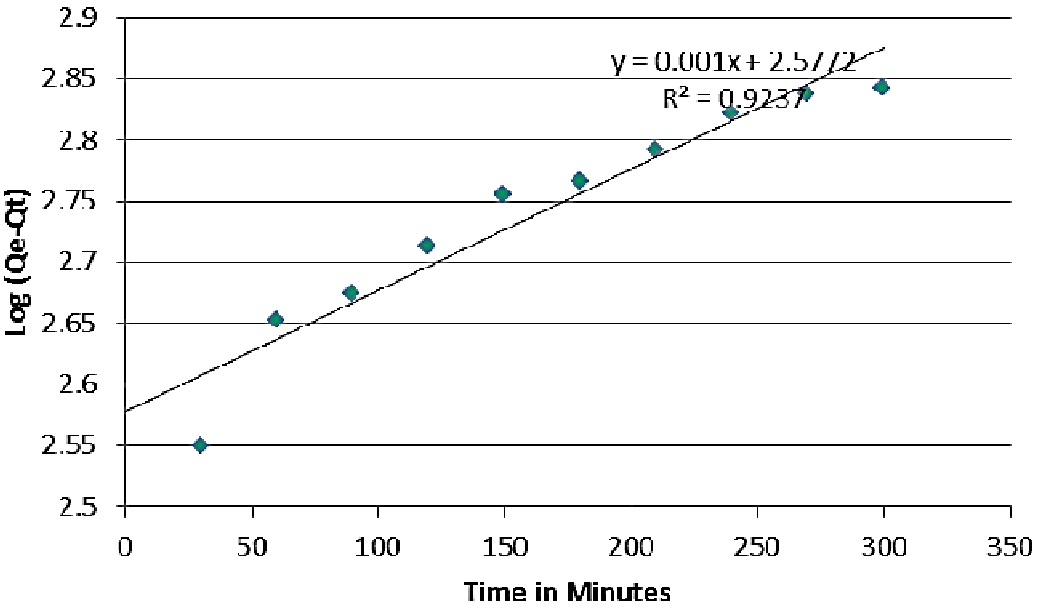


Figure 4. 19: Lagergren first order plot of methyl orange adsorption under fluorescent illumination

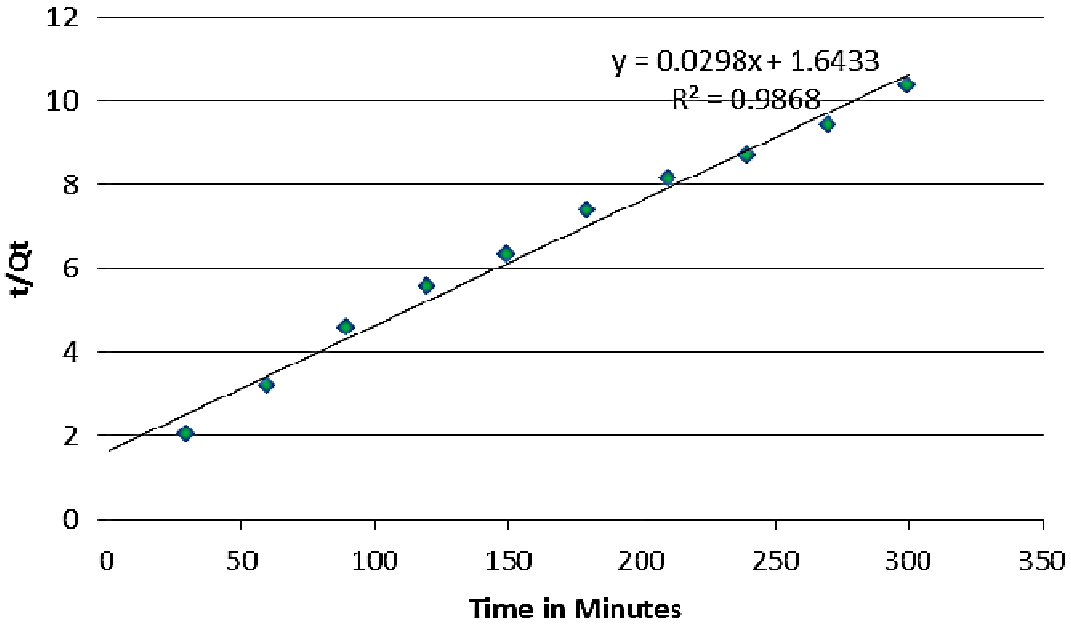


Figure 4. 20: Lagergren second order plot of methyl orange adsorption under fluorescent illumination

The correlation coefficients from figures 4.19 and 4.20 for these two tests ranged from 0.9237 for the first order kinetics to 0.9868 for the second order kinetics. This suggests that there existed a strong relationship between the parameters and the process followed the pseudo second order kinetics figure 4.19. This shows that the adsorption process of methyl orange on ZnO nanoparticles under florescent follows pseudo second order kinetics.

These findings are in line with those of Jalil*et al.* (2010) who conducted a study on the adsorption of methyl orange from aqueous solution onto calcined lapindo volcanic mud under fluorescent conditions. For their study, the correlation coefficients were 0.9643 and

0.9898 for first order and second order respectively, suggesting a strong relationship between the parameters and that the process followed the pseudo second order kinetics.

4.11 Comparison of Adsorption Efficiency of ZnO nanoparticles

The findings clearly showed that increased adsorption power was evidenced when the photocatalyst was enhanced using a stabilizer. The difference in adsorption was minor but appreciable. This could be attributed to the fact that the oxalic acid used is a capping agent which provided protective organic shell to particles to prevent the nanoparticles from aggregating in solution. It also promotes formation of fewer, larger nuclei and thus nanocrystal particle sizes (Gnanasangeetha and Sarala, 2013). Stabilizers enable the nanoparticles to be resistant to deactivation and thus its performance which depends on the nature and concentration of the stabilizing agent used (Gnanasangeetha and Sarala, 2013).

In addition, the useof sunlight as a source of radiation was found to give better results than fluorescent light.Adsorption of heavy metals and photodegradation of methyl orange by the nanoparticles was found to be more efficient when done under sunlight than when performed under fluorescent light. This is attributed to the fact that sunlight intensity is higher than that of fluorescentlight. Increase in intensity increases the number of photons reaching the adsorbent and thus its adsorption and photo degradation ability.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The XRD results of the synthesized sample were confirmed to be for ZnO nanoparticle. The size of ZnO nanoparticles were found to have an average crystal size of 26 nm which is within the range of 1-100nm for nanoparticles. The FTIR spectrum of the synthesized ZnO nanoparticles synthesizedwas in the range of 400-4000 cm^{-1}.The band range of 430cm^{-1} correlated to zinc oxide bond (Zn-O).

The adsorptivity of ZnO nanoparticles was found to decrease with increase in heavy metals concentrations, this indicates that sorbents active sites were saturated and further increase of the concentrationwill have no effect on the uptake. The maximal levels of uptake adsorption reached for ZnOnanoparticles wereCd^{2+} (83.1%), Cr^{2+}(82.9%) and Cu^{2+} (83.0%) at initial concentration of 100 mgL^{-1} and contact time of 90 minutes. Increase in adsorbent dosage increased adsorption percentage for the three metal ions.

At pH 2, the maximum amounts adsorbed were; Cd^{2+} (28.5 %), Cr^{2+} (29.1%) and Cu^{2+}(26.5%). Increasing the pH to 8, the adsorbed amounts were; Cd^{2+} (92.1%), Cr^{2+} (92.8%), and Cu^{2+} (92.0).

Photodegradation can be used for treatment of industrial effluents containing heavy metals and dyes. In place where we have plenty of sunlight solar radiation can be used for degradation.

Also we are using minute quantities of ZnO nanoparticles and there will be no harm in mixing this small quantity of Zn in water streams. As Zn is one of the essential trace elements. These results will be helpful in designing effluent treatment plants in industries.

5.2 Recommendations

In future, researchers should focus on the development ofnovel nanomaterials/nanocomposites with a high surfacearea, sufficient surface functional groups and highsorption ability, for the removal of different heavy metalions and organic dyes. The microbial threats to humanhealth and safety are also a serious public concern. Thus,further improvements must be made in the direction ofthe development of materials with greater stability(resistance to pH changes and concentrations ofchemicals present in contaminated water) and thecapacity for the simultaneous removal of multiplecontaminants, such as toxic metal ions, organic dyes andbacterial pathogens.

Considering the economics ofadsorbents, it is necessary to synthesize low-cost effective and recyclable adsorbents for their extensiveapplication in our daily life. Treatment technologies should be developed for thepurification of water in order to meet the demand ofincreased environmental pollution.

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APPENDICES

Appendix I: Effect of variation of contact time on photegradation of MeO dye under sunlight

Time in Min	*Initial Conc*	*Final Conc*	*Adsorbed Value*
0	30	30	0
30	30	13.36	16.64
60	30	10.48	19.52
90	30	8.36	21.64
120	30	5.53	24.47
150	30	6.69	23.31
180	30	4.34	25.66
210	30	3.23	26.77
240	30	1.21	28.79
270	30	0.81	29.19
300	30	0.54	29.46

Appendix II: Effect of variation of contact time on photegradation of MeO dye under fluorescent

Time in Min	*Initial Conc*	*Final Conc*	*Adsorbed Value*
0	30	30	0
30	30	15.21	14.79
60	30	11.26	18.74
90	30	10.29	19.71
120	30	8.46	21.54
150	30	6.26	23.74
180	30	5.64	24.36
210	30	4.18	25.82
240	30	2.37	27.63
270	30	1.28	28.72
300	30	1.01	28.99

Final Conc	*Adsorbed Value*	*Ce*	*Qe*	*Ce/Qe*	*Log Ce*	*Log Qe*	*Log Ce/qe*
30	0		0	0			
13.36	16.64	25.64	416	0.0616	1.408918	2.61909333	0.537941
10.48	19.52	23.91	488	0.0490	1.37858	2.68841982	0.512784
8.36	21.64	8.36	541	0.0155	0.922206	2.73319727	0.337409
5.53	24.47	5.53	611.75	0.0090	0.742725	2.78657398	0.266537
6.69	23.31	6.69	582.75	0.0115	0.825426	2.76548228	0.298475
4.34	25.66	4.34	641.5	0.0068	0.63749	2.80719666	0.227091
3.23	26.77	3.23	669.25	0.0048	0.509203	2.82558838	0.180211
1.21	28.79	1.21	719.75	0.0017	0.082785	2.85718167	0.028974
0.81	29.19	0.81	729.75	0.0011	-0.09151	2.8631741	-0.03196
0.54	29.46	0.54	736.5	0.0007	-0.26761	2.86717275	-0.09333

AppendixIII: Adsorption Langmiur Isotherms Data (Under Sunlight)

Final Conc	*Adsorbed Value*	*Ce*	*Qe*	*Ce/Qe*	*Log Ce*	*Log Qe*	*Log Ce/qe*
30	0						
15.21	14.79	15.21	369.75	0.041136	1.182129	2.56790818	0.460347
11.26	18.74	11.26	468.5	0.024034	1.051538	2.6707096	0.39373
10.29	19.71	10.29	492.75	0.020883	1.012415	2.69262663	0.375995
8.46	21.54	8.46	538.5	0.01571	0.92737	2.73118571	0.339549
6.26	23.74	6.26	593.5	0.010548	0.796574	2.77342072	0.287217
5.64	24.36	5.64	609	0.009261	0.751279	2.78461729	0.269796
4.18	25.82	4.18	645.5	0.006476	0.621176	2.80989625	0.221067
2.37	27.63	2.37	690.75	0.003431	0.374748	2.83932089	0.131985
1.28	28.72	1.28	718	0.001783	0.10721	2.85612444	0.037537
1.01	28.99	1.01	724.75	0.001394	0.004321	2.86018822	0.001511

Appendix IV: Adsorption Langmuir Isotherms Data (Under Fluorescent Light)

Appendix V: Effect of adsorbent dose on percentage removal of heavy metals

Adsorbent dose (mg)		100		200		300		400		500	
		L_1	L_2	L_1	L_2	L_1	L_2	L_1	L_2	L_1	L_2
% Removal	Cd	82.8	82.9	84.1	84	88.3	88	93.5	93.5	93.2	94.4
	Ni	83	83.1	83.6	83.5	89.1	89	94	94	94.0	94.6
	Cu	84.1	84	86.4	85	91.4	92	92.7	92.7	92.5	93.3

Appendix VI: Effect of initial concentration of heavy metals

Heavy metals initial (mgL^{-1})		100		200		300		400	
		L_1	L_2	L_1	L_2	L_1	L_2	L_1	L_2
Removal %	Cd	83.1	83.2	66.8	66.5	62	62.2	59	60
	Ni	82.9	83	63.4	63.5	61.8	62	60.1	60.9
	Cu	83	83	66.6	66.7	62.2	61.9	59.4	59.5

AppendixVII: Effect of pH

pH		2		4		6		8	
		L_1	L_2	L_1	L_2	L_1	L_2	L_1	L_2
Removal %	Cd	28.5	30	44	43	82.3	84	92.1	93
	Ni	29.1	31	43.8	43.2	82.3	83.2	92.8	93
	Cu	26.5	27.2	45.1	44	82.9	83	92	94.1

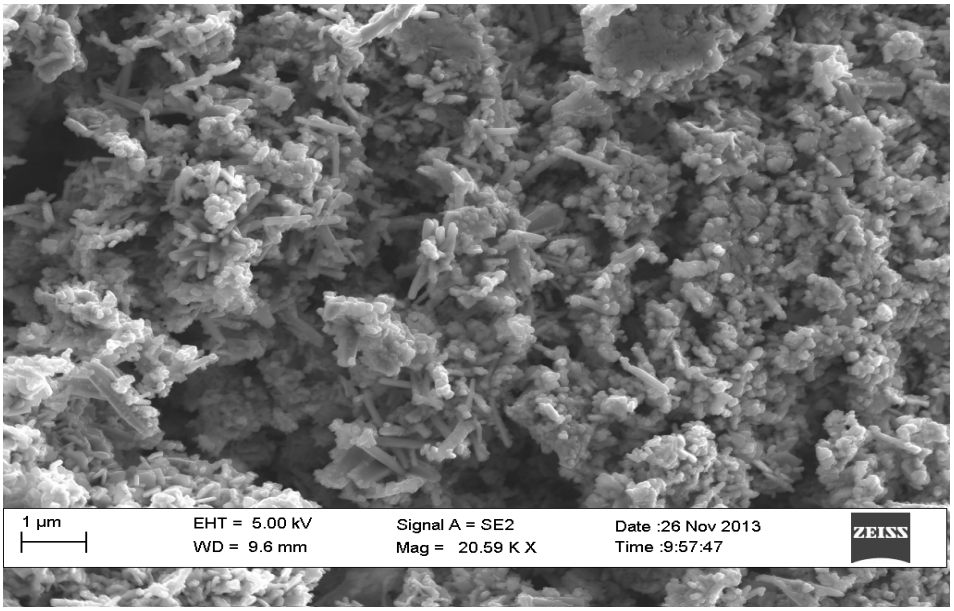
Appendix VIII: Lagergren Adsorption Kinetics Data (Under Sunlight)

Qt	*Qe-Qt*	*log(Qe-Qt)*	*t/Qt*
4.36	411.64	2.614518	3.2101
6.09	481.91	2.682966	3.9917
21.64	519.36	2.715468	4.158965
24.47	587.28	2.768845	4.903964
23.31	559.44	2.747754	6.435006
25.66	615.84	2.789468	7.014809
26.77	642.48	2.80786	7.844602
28.79	690.96	2.839453	8.336228
29.19	700.56	2.845445	9.249743
29.46	707.04	2.849444	10.1833

Appendix IX: Lagergren Adsorption Kinetics Data (Under Fluorescent)

Qt	*Qe-Qt*	*log(Qe-Qt)*	*t/Qt*
14.79	354.96	2.550179	2.028398
18.74	449.76	2.652981	3.201708
19.71	473.04	2.674898	4.56621
21.54	516.96	2.713457	5.571031
23.74	569.76	2.755692	6.31845
24.36	584.64	2.766889	7.389163
25.82	619.68	2.792167	8.13323
27.63	663.12	2.821592	8.686211
28.72	689.28	2.838396	9.401114
28.99	695.76	2.842459	10.3484

Appendix X: Observed SEM diagram ZnO nanorods, L_1 at low magnification (Mag 20.59 K)



Appendix XI: Observed SEM diagram L_2 at Low Magnification (Mag 20.66 K)