Synthesis and Characterization of ZnO and Clay Supported ZnO Nanoparticles and Their Catalytic and Antibacterial Applications

A Dissertation submitted
in the partial fulfillment of the requirements
For the degree of

Master of Science
In
BIOCHEMISTRY

By

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CERTIFICATE

I hereby declare that the thesis entitled **"Synthesis and characterization of ZnO and clay supported ZnO nanoparticles and their catalytic and antibacterial applications"** being submitted by Ms. Savneet Kaur in partial fulfillment of requirement for the award of the degree of **Masters of Science** in **School of Chemistry and Biochemistry, Thapar University, Patiala,** is a bonafied work carried out under the supervision of **Dr. Diptiman Choudhury** and no part of this project has been submitted for award of any degree by me.

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CANDIDATE'S DECLARATION

I hereby declare that the work being presented in the dissertation entitled "**Synthesis and Characterization of ZnO and Clay supported nanoparticles and their catalytic and antibacterial applications**" in the partial fulfilment of the requirements for the award of the degree of Masters in Biochemistry and being submitted to School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of January to July 2017, under the supervision of **Dr. Diptiman Choudhury**. I have not submitted the contents embodied in this dissertation for the award of any other degree.

Patiala
Date: 17-july-2017

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This is to certify that the above statement made by the candidate is correct and true to the best of my knowledge.

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ABSTRACT

The recent studies shown that the contaminants from the industries, polluting the water which make the water incompetent to animals as well as to human beings. Nanoparticles come up with wide range of properties like high photochemical reactivity and it work under gentle response condition and useful in water purification. In this work, ZnO nanoparticles were synthesized from zinc nitrate and were characterized by UV-visible spectrophotometer, XRD, BET surface analyzer and DRS. Doping of ZnO nanoparticles into clay enhanced the applications of ZnO by increasing its surface area. Montomorillonite clays with layered structure, high surface area; porosity was used as a inner support and acted as active surface enhancer for ZnO nanoparticles. Methylene blue dye and nitrophenols are the most widely recognized natural contaminants, which was reduced in water by ZnO/Clay composite. Upon with the comparison between ZnO/Clay composite and only ZnO the rate of reaction was very fast in ZnO/Clay composite. ZnO/Clay composite act as reducing agent as it reduced the 4-NP to aminophenol. In addition to the earth and for the general wellbeing to, microbes are unsafe. The antibacterial activity performed using ZnO/Clay composites, showed efficient results by inhibiting the growth of E.Coli culture. ZnO nanoparticles and its metal oxides was used and pulled the nanoparticles in broad intrigue.

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List of Abbreviations and symbols

Abbreviation	Name
ºC	Degree Celsius
%	Percent
g	Grams
mg	Milligram
min	Minutes
sec	seconds
Conc.	Concentration
nm	Nanometer
XRD	X-Ray Power Diffraction
DRS	Display Refractory Spectroscopic
BET	Brunauer–Emmett–Teller
MMT	Montomorillonite
ZnO	Zinc Oxide
NPs	Nanoparticles
TiO_2	Titanium Oxide

Chapter 1

Introduction

1.1 Overview:

Excellent planet that is earth on which we live, alongside with the wide assortment of plants, creatures and different living beings (May 1988). Earth's development happens around 4 to 5 billion years prior and people advanced around 2 billion years back (Cohen 1995). Development is essentially a procedure in which self-change happens of every single particle exhibit around them. As per this view everything has developed through an essential condition of issue by means of physical and substance forms. From the season of development till now the principle wellspring of life is water (Faull 2006). Earth outside is practically secured by water, 98% water is ocean water which contain high grouping of salt so cannot be taken up by individuals. Fresh water is just 2% by which 0.0036% water is available in lakes and streams which is utilized by the Human resources (Okafor 2011).

1.2 Water pollution:

The hostile change caused in the basic territory is a direct result of the introduction of contaminants in water. Water has such properties which make it more polluted because it act as universal solvent and it can be used again and again in industries. When the quality of water changes it become polluted. Then it cannot be used for drinking, in industry, in agriculture and domestic. The one of a kind properties of water which make it all inclusive dissolvable and inexhaustible assets likewise make it a substance which by temperance of these properties has a substantially more prominent propensity to get contaminated. Water can be respected dirtied when it gets changed in its quality or synthesis either normally or because of human activities to wind up plainly less reasonable for drinking, household, horticultural, mechanical, recreational, untamed life and different uses for which it would have been generally appropriate in its common or unmodified state (Goel 2006).

A water toxin can be characterized as a physical, chemical or natural factor causing tasteful or inconvenient consequences for sea-going life and on the individuals who devour the water. The dominant part of the water toxins is, be that as it may, as chemicals which stay broke down or suspended in water and give a natural reaction which is frequently frightful.

Some of the time, physical and organic factors additionally go about as contaminations. Among the physical elements, warmth and radiations are vital variables which effectively affect living beings. Certain microorganisms exhibit in water, particularly pathogenic species, make maladies man and creatures and can be eluded as pollutants.

1.3 Properties of zinc oxide:

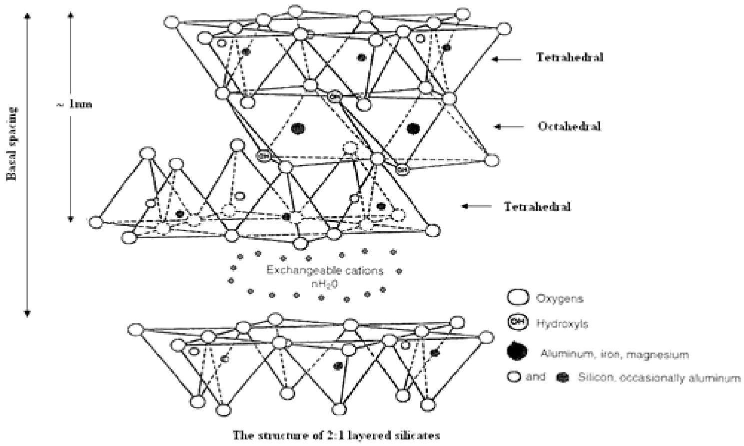
ZnO is a perfect photo catalyst, because of this reason it is utilized as a part of photo catalytic handle. ZnO is eco-accommodating and copious in nature with n-sort conductivity and UV light with the wavelength equivalent or under 385nm (Tokumoto et al. 2003). ZnO with wide band gap (3.3eV) and huge excitation restricting vitality (60 MeV) go about as a semiconductor. ZnO has high photochemical reactivity and it work under gentle response conditions. ZnO is of white colour and it is insoluble in water (Kumar et al. 2010).

1.4 Beneficial properties of clay:

In such manner mud's have additionally discovered appropriate application as backings and diverse dirt sorts, for example, montmorillonite, hectolitre, and kaolinite have increased much consideration in resulting years in regards to application in air and water cleansing (Belessi et al. 2007). Layered structure, higher surface range, porosity and substantial scale accessibility in nature are the components in charge of the use of the mud minerals as backings for photo catalytic (Akar et al. 2010). Bentonite is one of the practical and one of the generally accessible dirt's in nature which can be a premise of new approach for remediation of toxins from squander water.

1.5 Structure of Clay:

It is a type of montmorillonite described by Aluminium octahedral sheet are sandwich in two tetrahedral sheets. The negative charge on its surface results from the substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} on the octahedral layer(Fig 1.5). It has incredible sorptive properties as clear from their high surface territories and their ability to assimilate water in the interlayer sites. Its plenitude and ease makes it a suitable hopeful as an adsorbent for natural applications, for example, squander water treatment (Papoulis et al. 2013).



Source: From google image.

Figure 1.5: Layered structure of Bentonite

.1.6 Types of clay:

On premise of texture contrast dirt's were fundamentally of different sorts which were 2:1 earth or Montmorillonite (MMT) mud's and 1:1 mud, for example, kaolin. MMT dirt's include two tetrahedral layers of silica and octahedral layer of alumina intermediate in the middle of and in this manner shapes a classification of 2:1 mud's (Silva et al. 2012). Cross section defect and is morphological substitution helps in adsorption of basic with soluble earth metal particles in intermediate layer due to net negative charge production. Bentonite laponite and kunipia-F gone under the class of MMT dirt's (Grimm et al. 1998).

1.7 Advanced oxidation process:

Different reacting species are used in advanced oxidation process, having common chemical feature i.e. OH radical which is characterized feature of all these reactions. OH are the species which react extraordinary, OH radicals can attack the organic molecules various functional groups with 106–109 m^{-1} s^{-1} order of rate constant. OH radicals are also having characteristic property of less attack selectivity which shows useful attribution for its oxidant activity useful for the treatment of the waste water and to treat the problems related to pollution. The advanced oxidation process versatility is also increased by the different pathways for the production of OH radicals, thus it acts as a better way to treat (Andreozzi et al. 1999).

1.8 Properties of TiO_2 and ZnO:

Among metal oxide, the semiconductors, TiO_2, on the whole, is famous photo-catalyst, for the evacuation of natural atoms. In any case, it has high band crevice vitality (3.2 eV) and with no obvious affectability of light (Herrmann 1999). Zinc oxide (ZnO), additionally picked as minimal effort photo-catalyst because of its good photo-activity and similar band whole vitality (3.2 eV) to the TiO_2 (Aal et al. 2009). ZnO, an appropriate option photo-catalyst for the photo-bleaching of few colours in mass and suspension shape, and here and there showed higher action than TiO_2 (Bahnemann 2004). Be that as it may, ZnO is temperamental in corrosive conditions and exhibits fast deactivation of in mass use because of total. As of now, a couple of experts have tried to prepare ZnO mixture or the composite structures by affixing or impregnating ZnO in a stable inorganic help, for instance, started carbon, MCM-41, zeolites and SBA silica (Byrappa et al. 2006). Association of ZnO with an inorganic can expand life and reuse of the photo catalyst.

1.9 Photoactivity with catalyst:

Smectite earth is a critical dirt mineral having a one of a kind structure identified with its different properties. A different type of work has detailed benefits and motor investigation the adsorption of dyes on different shaped modified muds. Montmorillonite has potential to act as adsorbent toward the different dyes was studied. Montmorillonite exhibits high capacity towards adsorption of colour atoms by means of a cationic trade and sub-atomic strainer instrument (Liu et al. 2007).

After effects of these examinations proposed that these permeable structure and high surface territory specifically of montmorillonite were advantageous to the photo-activity by means of improving adsorption, which is the deciding stride in the heterogeneous photo-catalytic response. Accordingly, heterogeneous photo-catalysis and a mixture of adsorption make photo-oxidation more powerful for the expulsion of colour mixture from the waste water (Meng et al. 2008).

1.10 Nitrophenol Reduction:

Nitro aromatic mixes are utilized as a part of numerous mechanical procedures, including the arrangement of pesticides, explosives, materials and paper. In this way, these mixes are frequently identified as water toxins because of their discharge in mechanical effluents (Sarasa et al. 1998). Remediation of wastewaters containing these poisons is exceptionally troublesome, since they are normally impervious to organic corruption (Marais et al. 2008). Among these nitro aromatic mixes, nitrophenols are basic poisons. Nitrophenols (NPs) are the most widely recognized natural contaminations in mechanical and farming effluents. Many procedures have been created for phenol mixes evacuation, for example, adsorption (O'Connor et al. 1989), microbial debasement (Marais et al. 2008), photocatalytic corruption (Modirshahla et al. 2008), electrocogulation and electrochemical treatment (Canizares et al. 2004).

P-Nitrophenol has been broadly utilized as a part of the creation of pesticides, herbicides, colours, and other modern chemicals. Then again, 4-nitrophenol is a critical halfway for the maker of pain relieving and antipyretic drugs. Because of these across the board applications, wastewaters and water assets, including groundwater and surface waters, have turned out to be tainted with this compound (Shi et al. 2004).

1.11 Antibacterial Activity:

Abuse of anti-toxins in people and creatures, causes the rapid advancement of pathogenic microscopic organisms that were safe to different medications. In addition to the earth and for the general wellbeing to, these microbes are unsafe (Ma et al. 2010). For antibacterial exercise, the well known metal oxides like metal, Nanoparticles and metal oxides was used and pulled the nanoparticles in broad intrigue. Nanoparticles are of intrigue on account of their high reactivity because of the vast open region to-mass proportion (Motshekga et al. 2013).

It has been noticed that, distinctive properties of nano-materials in nanometre sizes contrasted with the property of similar materials in mass conditions. The properties of Nanoparticles are in consideration because of size and life structures in nanoscale. Several nanoparticles which are very much examined are Ag, ZnO, and TiO2. Zinc oxide has some antibacterial impact, great warm qualities, and dye degradation, with ease and little lethality. Uncommon earth particles have been utilized as antimicrobial specialists in prescription for quite a while because of wide range of antibacterial activity and wide range antibacterial activity (Tan et al. 2008). ZnO Nanoparticles have antibacterial properties which are used in nourishment bundling materials to control sustenance borne pathogens and also deactivate other numerous microorganisms (de Azeredo 2013).

1.12 Doping of Nanoparticles in Clay:

For the metal composites, earth minerals were amazing fillers. Earth minerals are generally alluring for makers and researchers all through the world in view of their ease, high particular surface zone, high substance and mechanical soundness, assortment of surface, good adsorption and auxiliary properties. The adsorption process raises the productivity of scattered nanoparticles by subsequently pulling the contaminants away from any confining influence pores. Bentonite, an individual from the steatite gathering, is for the most part made out of montmorillonite earth. An assortment of combination routes have been accounted for the synthesis of metallic nanoparticles, for instance thermal decomposition, laser removal, microwave illumination, sonochemical, reverse micelles chemical degradation, ultrasonic light, radiolysis, solvothermal and electrochemical. Nonetheless, controlling the molecule estimate circulation and solidness of the particles is greatly troublesome and does not give enough utilization of their properties. Another impediment in utilizing the nanoparticles alone is because of their potential perils related with their size which can influence people and the earth. Considering that such nonmaterial’s can be unsafe and deadly, half procedures in joining nanoparticles with other ecologically inviting, latent and stable materials are in progress to exploit their full properties in different applications. Besides, presenting nanoparticles with different substrates/fillers would bring about composites of novel and improved properties that can be refined by the individual components (Guzmán et al. 2009).

Research gap:

For the water purification process the ZnO/Clay composites were used to degrade the dyes which were polluting the water on large scale. Dyes are releasing in water from industries which has to be degraded for the use of water. In this project ZnO nanoparticles were synthesized from zinc nitrate. As such ZnO nanoparticles can't be used directly for water purification as it can harm the human wellbeing. Due to this reason ZnO nanoparticles are doped in clay which increases the surface area and act as active enhancer for ZnO nanoparticles. ZnO/Clay composites were used to degrade the methylene blue dye and it also act as reducing agent by reducing the 4-NP. By taking the different concentration of ZnO/Clay composite the antibacterial activity on E.Coli culture was performed in all the activities ZnO/Clay composite shows the better result as compared to ZnO.

Objectivess:

- To synthesize ZnO nanoparticles from zinc nitrate.
- Doping of ZnO nanoparticles in bentonite clay.
- To check the antibacterial, photocatalytic activity of ZnO NPs
- Comparison between the activites of ZnO and ZnO/Clay composites.

CHAPTER 2
REVIEW LITERATURE

When we attempt to imagine prebiotic synthesis of life, a couple of point emerge, what are the substances, and what the system of their development may be. We should seriously think about as demonstrated the prebiotic development of little natural atoms similar to sugars, amino acids, by the activity of the then existing vitality source like astronomical radiation, U.V. radiation, and so on (Pizzarello et al. 2004). Clay minerals were chosen as a substrate due to their substantial surface region, geographical plenitude, and compound compatibility (Rabinowitz et al. 1968).

Montmorillonite dirt is of three layers, octahedral, arranged in-between tetrahedral ones. The third layer which is octahedral comprises generally of Al_2O_3-Al $(OH)_3$, while the fourth layer is tetrahedral which comprises of SiO_2. At low focus these mud extend in water to confer all intents and form single layer sheets (Rabinowitz et al. 1968). However, these sheets deliver their stacking because there are some particles which make the sheets to approach each other. Thus, these stacking impact have NH^{3+} gatherings and divalent cations, and in addition numerous macromolecules, which are concerned for the most part with polypeptides (Naseem et al. 2001).

Nanotechnology is the creation, control and utilization of materials at the nanometre measure scale (1 to 100 nm). The most essential segment of nanoparticles is in the creation of a nanostructure, and is far littler than the universe of regular questions that are depicted by Newton’s laws of movement. Metallic nanoparticles have distinctive physical and compound properties that exhibit capturing in various modern applications (e.g. higher particular surface zones, particular optical properties, mechanical strengths). Material having measurements in the nanometre range (<100 nm), nanotechnology likewise manages them(Park et al. 2005). Nanoparticles are viewed as answer for some innovation and ecological difficulties. Green synthesis of nanoparticles decreased the risk for world.

Implantation of these economical procedures should adopt the fundamental principle of green chemistry. Different compound nature of nanoparticles, including: metals, metal oxides, non-oxide pottery generation, carbon and bio molecules (Sau et al. 2010). Nanoparticles have a couple of particular morphology structures, for instance, circles, barrels, platelets, tubes, etc. NPs physical, invention and characteristic properties differ in a general sense from the properties of both individual particles/atom and of mass material.

There are chiefly two classes of nanoparticles: natural and inorganic nanoparticles. Natural nanoparticles are strong particles and are made out of natural mixes which are predominantly lipids or polymeric and may go in distance across from 10 nm to 1m. These may incorporate carbon nanoparticles (Sharma et al. 2009). Inorganic nanoparticles display novel physical properties. Inorganic nanoparticles may incorporate attractive nanoparticles, attractive metal nanoparticles like gold (used in thermo treatment of organic targets and furthermore as medication carriers) and silver and nanoparticles like titanium dioxide and zinc oxide which are semiconductors. Because of the measure of inorganic nanoparticles and their accessibility in compound imaging drugs operators and medications there is a developing enthusiasm for inorganic nanoparticles (Altavilla, et al., 2016).

Mixture of a ZnO/clay and its activity was reported through photo-oxidation of the methylene blue. Like distinctive work of metal oxides immobilization into the structure of earth, the preparation of ZnO/clay grasped a strategy that is sol–gel. The sol–gel course of action was acknowledged to decrease the sharpness, which could harm the earth structure as reported in the arranging of TiO_2/clay. The strategy of sol-gel for ZnO scattering was additionally detailed (Mihai et al. 2010). Before scattering of ZnO, a pre-intercalation method of bentonite, were reported in TiO_2/clay structure. Preintercalation method was performed for bentonite clay with the help of cetyl trimethyl ammonium chloride which further change the properties of montomorillonite, hydrophobic surface and develop the layer in-between the surface for the metal oxide scattering. The prepared material was depicted by X-ray diffraction (XRD), BET surface locale analyzer, scanning electron microscopy with Energy Dispersive Spectroscopy (SEM–EDS), transmission electron microscopy (TEM) and UV–Visible spectrophotometer (Manova et al. 2010). Photo oxidation response of methylene blue (MB) was completed in a water bath by maintaining temperature in it.

The reactor contained a bright light which held in a shut box. The source of radiations was a 20 W UV-B light, put at a separation of 40 cm from the measuring utensil which is made up of glass. Water is circulated from the bath having constant temperature to a reactor coat having consistent temperature of 25±0.5 °C inside reactor. Before the exposure of photons and the stirring process, H_2O_2 solution was included in reactor with the molar proportion of 1:5. Utilizing a spectrophotometer (663 nm) the concentration was determined of dye- methylene blue.

Nitrophenol is poisonous and in this way destructive to general wellbeing and sea-going life (Shi et al., 2005). Nowadays industries are using water in large quantity, thus the amount of toxic chemicals are huge in number. The expulsion of 4-nitrophenol (4NP) from the watery arrangement by ozone consolidated with nano-ZnO was researched in a lab scale reactor in which pH of arrangement, ZnO measurement and beginning 4-nitrophenol focus were considered as factors. The degradation of 4-nitrophenol was resolved and confirmed by UV-Vis spectra and HPLC techniques. Curiously, the debasement of 4-nitrophenol was high under the acidic condition where the corruption was maximum. It was because of accumulation of nano-ZnO particles. This outcome was not the same as the instance of ozonation alone, in which higher pH had a beneficial outcome on the debasement of 4-nitrophenol because of the arrangement of hydroxyl radical. Of course, debasement effectiveness expanded by expanding the nano ZnO measurements and starting 4-nitrophenol focus. It was discovered that the nanosized ZnO upgraded the corruption of ozone and the reactant ozonation improved the debasement of 4-nitrophenol on the surface of the nano-sized ZnO. Likewise, the level of corruption was additionally decided in a roundabout way through Total Organic Carbon (TOC) of the specimens. Nitroaromatic mixes are utilized as a part of numerous mechanical procedures, including the readiness of pesticides, explosives, materials, and paper. In this way, these mixes are frequently distinguished as water contaminations because of their discharge in modern effluents (Sarasa et al. 1998). Remediation of wastewaters containing these toxins is extremely troublesome since they are typically impervious to organic degradation (Connor et al. 1989). Among these nitroaromatic compounds, nitrophenols are basic toxins.

Nitrophenols (NPs) are the most well-known natural contaminations in modern and farming effluents. Many procedures have been created for phenolic compounds evacuation, for example, adsorption (Marais et al. 2008), antimicrobial activity (Movahedyan et al. 2008), photocatalytic corruption (Soltanian et al. 2011), electrocoagulation (Modirshahla et al., 2008) and electrochemical treatment (Cañizares et al., 2004),etc. P-Nitrophenol has been generally utilized as a part of the generation of pesticides, herbicides, colors, and other modern chemicals. As of late, nanophase materials have increased more consideration on account of unique physical and substance highlights. The nanosized ZnO with the components of substantial volume to territory proportion is a notable synergist material which is utilized as a heterogeneous impetus, with high reactant movement, non-danger, insolubility and minimal effort (Huang et al. 2005).

Antibacterial materials, for example, metals and metal oxides (Li et al. 2012) restrain microscopic organism’s development by oxidative stress with the creation of reactive oxygen species. Zinc oxide (ZnO) acts as semi-conductor which is utilized as, antibacterial material because of minimal effort, wealth, and earth neighbourly component. A few investigations have proposed the counter bacterial component of zinc oxide nanoparticles (ZnO NPs) to be harming the cell layer and discharging reactive oxygen species (Raghupathi et al. 2011). Characteristic mud minerals, for example, kaolinite, halloysite, montmorillonite also, palygorskite are generally utilized as a part of the catalysis (Cai et al. 2013), and wastewater treatment application by stacking the conventional nonmaterial's, which implies that they can be utilized as cost-effective framework to enhance the scattering of ZnO given to their normal nanostructures, remarkable particle trade limits, unrivalled hydrophilic, and magnificent mechanical properties. Such components may not just bring ZnO NPs to be nearer to the layer of microscopic organisms to hamper the ordinary capacity of microbes be that as it may, likewise increment the neighbourhood zinc focus to hinder the development of microbes (Dawson et al. 2013).

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Materials:

3.1.1 Bentonite Clay: Bentonite is permeable aluminium phyllosilicate dirt comprising for the most part of montmorillonite. The clay named by Wilbur C. Knight in 1898 after the Cretaceous Benton Shale close Rock River, Wyoming. Dirt's are a standout amongst the most explored adsorbents for the expulsion of colours because of their extensive particular surface region, huge pore structure, high swelling limit, high cations trade limit and idle substance nature.

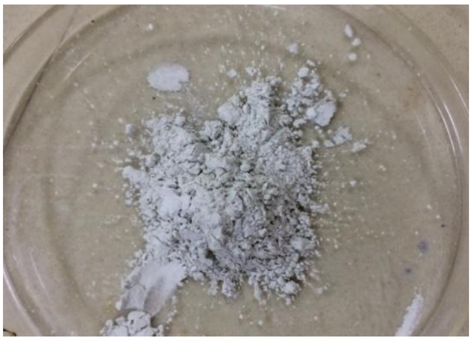


Figure 3.1: Montomorrillonite Clay

3.1.2 Methylene blue: Methylene blue, otherwise called methylthioninium chloride, is a pharmaceutical and colour. Particularly it is utilized to treat methemoglobinemia levels that are more noteworthy than 30% or in which there are side effects in spite of oxygen treatment. Methylene blue was first arranged in 1876 by Heinrich Caro. Basic symptoms incorporate migraine, spewing, disarray, shortness of breath, and hypertension. Opposite symptoms incorporate serotonin disorder, red platelet breakdown, and unfavourably susceptible responses.

Figure 3.2: Methylene Blue

3.1.3 ZnO: Zinc oxide is known as inorganic compound with the formulation of ZnO. ZnO, white powder that is insoluble in water and it is broadly utilized as an added substance in various materials and items including rubbers, plastics, earthenware production, glass, bond, greases, paints, treatments, cements, sealants, shades, sustenance's, batteries, ferrites, fire retardants, and medical aid tapes. In spite of the fact that it happens actually as the mineral zincite, most zinc oxide is delivered artificially. Zinc oxide takes shape in two fundamental structures, hexagonal wurtzite and cubic zincblende. Zinc oxide has high refractive file, high warm conductivity, official, antibacterial and UV-insurance properties.

Figure 3.3: ZnO powder

3.2 Apparatus:

Beakers (50ml and 250ml), conical flask (250ml and 500ml), round bottom flask (250ml), test tubes, micro pipette, measuring cylinder, spatula, filter paper, glass rod, magnetic beads, petri plates, tarson tubes.

3.3 Reagents and Chemicals:

Zinc nitrate, ZnO nanopowder, Methylene blue, Nitrophenol, Sodium borohydride (NaBH4), Luria broth (LB), Agar, E.Coli (MTCC77), HCl, Titanium etoxide, Sodium hydroxide (NaOH).

3.4 Instruments:

3.4.1 Magnetic Stirrer: An magnetic stirrer of REMI 2MLH is a laboratory gadget which utilizes magnetic field to blend fluid specimens, since just a little attractive bar needs to put inside the fluid example to begin the way toward blending. It is utilized as a part of the analysis for the planning of dirt slurry and furthermore for the blending of Zinc oxides with the arrangement. Attractive stirrer regularly incorporates a hot plate or some different means for warming the fluid.

Figure 3.4: Clay Slurry

3.4.2 Measuring Balance: Accurate amounts of utilized chemicals can be accomplished with the assistance of measuring balance (SARTORINS)
Most extreme 250gm; Density-0.01mg

3.4.3 Hot air oven: The hot air broiler otherwise called advanced temperature marker cum controller of PHYSILAB was utilized to dry the precipitates after the filtration procedure. By and large they are worked at the temperature of 50°C-300°C utilizing an indoor regulator to control the temperature.

3.4.4 Laboratory centrifuge: Centrifugation is a procedure that includes utilization of outward compel for the sedimentation of heterogeneous blends. This procedure is utilized to isolate two immiscible fluids. The research facility rotator (PHYSILAB) works under the rule where the centripetal speeding up will make denser substances move outward in the radical heading, the substances which are less thick are dislodged and move to the inside.

3.4.5 Muffle furnace: Muffle heater (PREFIT INDIA) is box sort stove for high temperature applications. These are utilized as a part of different research labs by scientific experts keeping in mind the end goal to decide the extent of test which is non-flammable and non-unpredictable. It is utilized to calicle the examples. Calcinations' is a warm treatment prepare for the expulsion of unstable division. Mute heater comprises of remotely warmed chamber, so material being abhorred has no contact with the fire. This stifle heater can accomplish a most extreme temperature of 600°C.

3.4.6 Photochemical reactor: The photochemical reactor of PERFIT is utilized for the corruption of colour. The photochemical reactor utilized as a part of the test needs no water cooling. The typical working temperature is around 35°C with the fan and without the fan it is roughly 60-70°C. No hazardous high voltage is required and serious wellspring of these reactors is of bright light roughly 1.65*10 photons/sec/cm3 at 2537 A°. The reactor comes finish in a prepared to utilize bundle with no get together required. The UV - light has long existence of around 3000 hours and is flexible, shoddy with the power utilization of 400 watts.

Figure: 3.5 Photochemical Reactor

3.4.7 Autoclave: Autoclave is a pressurized chamber which is used to do mechanical and industrial procedures requiring hoisted temperature and pressure not quite the same as encompassing pneumatic stress. Autoclaves are utilized as a part of medicinal applications for performing the sanitization and in the synthetic business to cure coatings and vulcanize elastic and for aqueous amalgamation. Almost, autoclaves are utilized to clean equipments by subjecting them to high-pressure immersed steam at 121 °C (249 °F) for around 15–20 minutes relying upon the extent of the heap and the substance.

3.5 Methodology:

3.5.1 Preparation of Acid Treated Clay: Corrosive treated clay was set up by blending 10gm of bentonite earth with 500ml water and 1ml of HCl. The response was continued stirrer for 24 hours. At that point centrifuged at 8000 rpm for 5 minutes (3 times washing). Dried in a hot air oven at 80°C for 10 hours on a petriplate.

3.5.2 Preparation of ZnO: 40 g SDBS and 1g NaOH were added to 250 ml water and stirred vigorously. Zn (NO3) solution was prepared by adding 3.5 g of Zn (NO_3) to 250 ml water. The Zn (NO_3) was then added slowly to solution containing SDBS and NaOH. White precipitate was formed upon addition of Zn (NO_3) indicating the formation of ZnO. The white precipitate was washed thoroughly with water and dried at 60°C in oven and calcined at 200°C in a muffle furnace.

3.5.3 Preparation of ZnO/Clay: 2 gm of Bentonite clay was blended with 200ml of water and this arrangement was kept for mixing for 7-8 hours. At that point stock arrangement of zinc nitrate (3.5gm) was prepared in refined water (200ml), which was included drop wise in the clay slurry. The response was continued stirrer for 12 hours. After this sodium hydroxide pellet (0.4gm) was broken down in water (100ml) which was included drop wise in the response. The response mixing time was of 30 minutes. At that point centrifuged at 8000rpm for 5 minutes. Dried in a hot air stove at 80°C for 10 hours on a petriplate.

3.5.4 Preparation of media: For the antibacterial movement media was set up by blending 2gm of Luria broth and 2gm of agar in 100ml water. At that point this media was autoclaved at 15lb pressure for 15 minutes.

3.5.5 Preparation of stock arrangement: Stock arrangement was set up by blending nitro phenol (10^{-2} M) in 10ml of water and another arrangement of sodium borohydride ($NaBH_4$ – .1M) in 5ml of water was set up for the nitro phenol lessening.

3.5.6 Preparation of Silver Nanoparticles: Add up to 4ml of arrangement was set up by blending of 3.5ml tri-sodium citrate with .5ml of silver salt arrangement, at that point this arrangement was kept under microwave reactor for 10 seconds (3 times) at 100°C.

3.5.7 Preparation of Gold Nanoparticles: Add up to 4ml of arrangement was set up by blending of 3.5ml tri-sodium citrate with .5ml of Gold salt arrangement, at that point this arrangement was kept under microwave reactor for 10 seconds (3 times) at 100°C.

3.5.8 Preparation of clay doped with nanoparticles: Diverse sort of earth was set up by doping of Nanoparticles (zinc, gold, silver) into corrosive treated mud. 200mg of mud was doped with 2ml of gold, silver, zinc nanoparticles.

3.5.9 Preparation of Dye solution: The colour arrangement was set up by including a little measure of colour into appropriate amount of distilled water. The concentration of dye was 10^{-2}M.

3.6 Characterisation:

For the characterization of ZnO particles following methods were done by means of which we can confirm the production of ZnO Nanoparticles, we can have the idea of its size and distribution profile, surface morphology and capacity of degradation as well. The following instruments were used to characterize the ZnO Nanoparticles that we synthesized chemically:

- UV-visible spectroscopy
- X-Ray diffraction
- BET Surface area analyzer
- Display refractory spectroscopy

3.6.1 UV-visible spectrophotometer: Ultraviolet and visible adsorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample. Absorption measurements can be at a single wavelength or over an extended spectral range. The spectrum for the photo degradation of dye was taken with the help of UV-Visible spectrophotometer. It refers to absorption spectroscopy in the ultraviolet-visible spectral region and uses near UV and near IR regions. Molecules absorb energy in the form of visible light and ultraviolet light due to non-bonding electrons which excite the electrons to further higher molecular orbitals. The reduction of dyes was confirmed by UV-vis spectrophotometer. The addition of ZnO nanoparticles to the solution of dyes resulted in colour change of the solution due to the degradation of dyes. To observe the degradation of dyes, and reduction of nitro phenol, samples were analyzed for UV-vis spectroscopic studies at room temperature operated at a resolution of 1 nm between 250nm and 700nm range.

3.6.2 XRD: XRD is an analytical technique which is mostly used as phase identification for the crystalline material and then it provide data on unit cell dimensions. The material which has to be analyzed was first finely chopped then homogenized and then average bulk composition was determined. XRD is divided into three parts; X- beam tube, sample to be analyzed, and an x-ray detector. Cathode ray tube generate the X-rays which produce monochromatic radiation which was then concentrated and through towards the sample. The electrons are produced by the filament which is heated up, and then this electron accelerates towards target by applying some voltage and then bombardment occur between the electrons and target sample. The characteristic spectra are obtained when the electrons have some energy to dislocate the electrons from inner shell of the sample.

Precipitation method was done to obtain ZnO nanoparticles from the Zinc nitrate, then this powdered material was characterized by XRD. X-ray diffraction analysis (XRD) of ZnO nanocomposites was performed through PANalytical X-ray diffractometer using CuKα radiation (λ=1.54Å), operating at 45 kV with a scan rate of 2° per minute and the scan range of 2-60° .

3.6.3 BET: BET is an analytical technique which measures the specific surface area of materials by adsorbing the gas molecules on the solid surface which serves as a important analysis for that particular material. Theory of BET, which applies on a system having multi layer adsorption and it usually use, probed gas which does not react with the surface of the material. During BET method, the most commonly used gas is nitrogen for the probing of material surface. Nitrogen sorption analysis (BET) of ZnO nanocomposite was carried out using BEL mini-II surface area and pore size analyzer after pre-treating 100 mg of the sample at 150° C for 3hrs under the nitrogen atmosphere.

Figure: 3.6 BET Surface analyzer

CHAPTER 5
APPLICATIONS

5.1 Antibacterial activity:

E.coli culture was collected from the way of life accumulations of the Department of Biotechnology at Thapar University. Microorganisms were kept up on agar plates. From the agar plate's inoculation of *E.coli* was performed in 5ml of fresh media of Luria broth which was first autoclaved at 15lb for 15 min. Then this stock was kept under incubation for 12 hours for the growth of *E.coli*. Then 5ml volume was drawn out from the stock prepared above and added into the media. Different concentration of ZnO and ZnO composites was used against the *E.coli* culture. For the antibacterial activity the agar diffusion method was performed in which the agar and Luria broth (2:2) was mixed in 100 ml of distilled water. *E.coli* culture and ZnO composites was added in the media then this media was poured in petri plates. Petri plates were kept in incubator cum shaker at 200rpm/min for 24 hrs.

5.2 Degradation of methylene blue:

Precise quantities of solid dye (methylene Blue-5mg in 50ml) were dissolved in double distilled water to prepare the stock solution of reactive dye. Solution of various concentration of dye was obtained by diluting this stock solution making it as a working solution. Then the ZnO was added in the dye solution and kept for incubation in dark with stirring and after this the solution was incubated in UV-light for different intervals at stirring conditions after this the colour of the solution changes from blue to colourless (showing in fig5.1). Same procedure was followed for ZnO/Clay. The methylene blue showed its peak at 660nm.

Figure: 5.1 Degradation of Methylene blue

5.3 Nitro phenol reduction:

Kinetics studies for reduction of 4-NP is done using ZnO and ZnO/Clay catalyst at different intervals. Nitro phenol solution was prepared (10^{-2}M in 10ml) by adding 50µl of stock in 10ml of water. Then the solution of sodium borohydride (0.1M $NaBH_4$ in 5ml) was prepared and 600µl of this was added in nitro phenol solution. After 5 mins of addition, catalyst was added and kept for stirring for 1 min. Then it was centrifuged for 2 minutes, UV spectra was obtained at 250nm to 700nm (Canizares et al. 2004).

Figure: 5.2Nitrophenol reduction

CHAPTER 6

RESULTS AND DISCUSSION

6.1 BET surface analyser:

Specific surface area, pore volume and mean pore diameter of as-synthesized nanocomposites were determined from nitrogen adsorption/desorption analysis. Clay, ZnO and clay/ZnO has type I isotherm (Fig 6.1). The specific surface area of ZnO, clay and clay/ZnO are 100 m^2g^{-1}, 23m^2g^{-1} and 77 m^2g^{-1}. The surface area of clay/ZnO is less as compared to ZnO which can be described due to intercalation of ZnO between clay sheets.

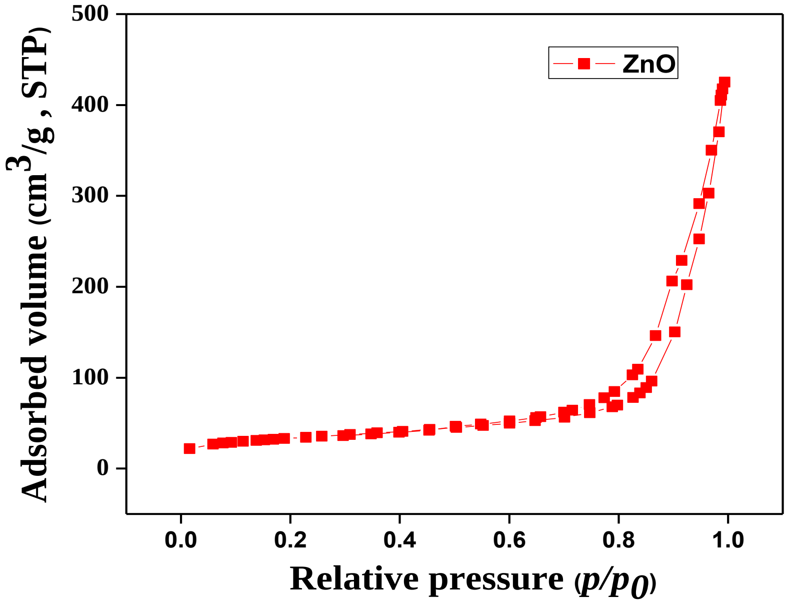


Figure: 6.1a) BET of ZnO

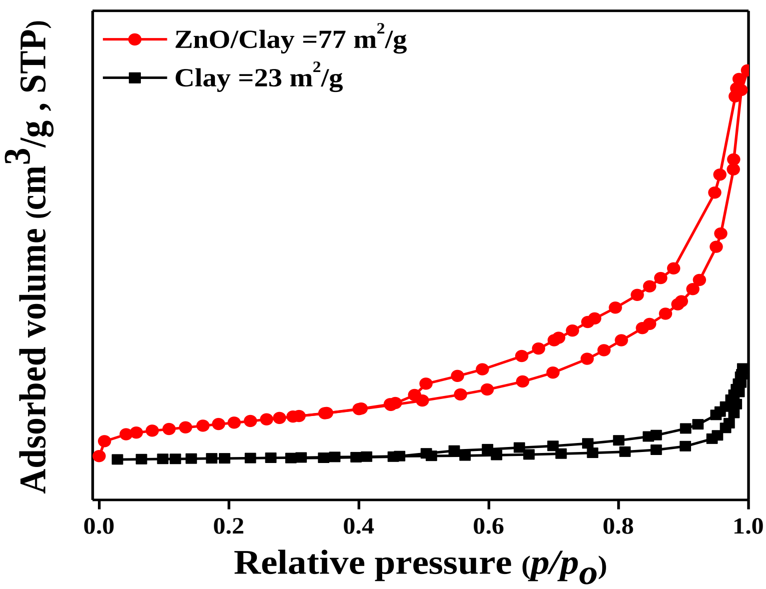


Figure: 6.1: b) BET of ZnO/Clay

6.2 DRS and Band gap of ZnO:

UV-Visible diffuse reflectance spectra of as-synthesized nanocomposites have been shown in (Fig.6.2.a). The absorption edge of ZnO is not much affected upon loading of clay. Band gap was calculated from tauc plot (Fig.6.2.b) obtained from UV-visible DRS spectra using the equation $(\alpha h\nu)^n = A(h\nu - Eg)$, where α is the absorption coefficient, A is constant, Eg is band gap and n depends upon the type of electronic transition. For direct transition n=2 and for indirect transition n=1/2 which is determined from the linearity of the tauc plot between $(\alpha h\nu)^n$ and hν. Straight lines are obtained by extrapolating the plot between $(\alpha h\nu)^{1/2}$ and hν reveal the electronic transition to be indirect in our as-synthesized nanocomposites. The values of band gap energies are hereby given in (Fig.6.2.b)

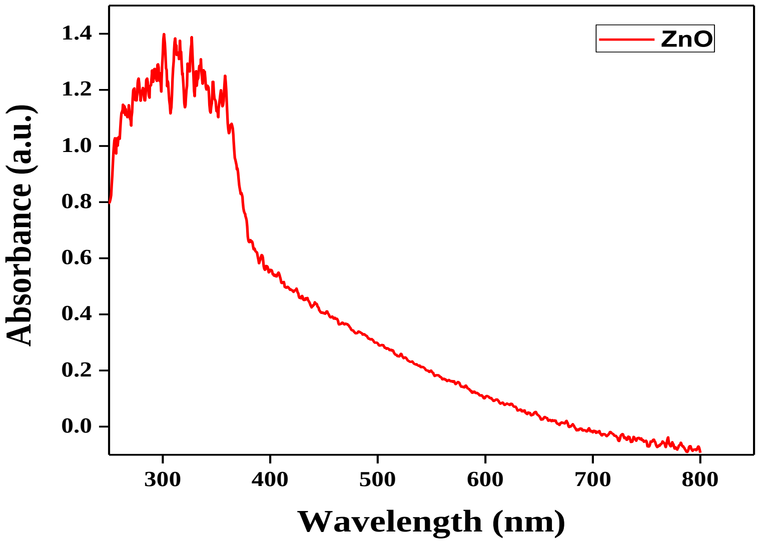


Figure: 6.2 a) DRS of ZnO

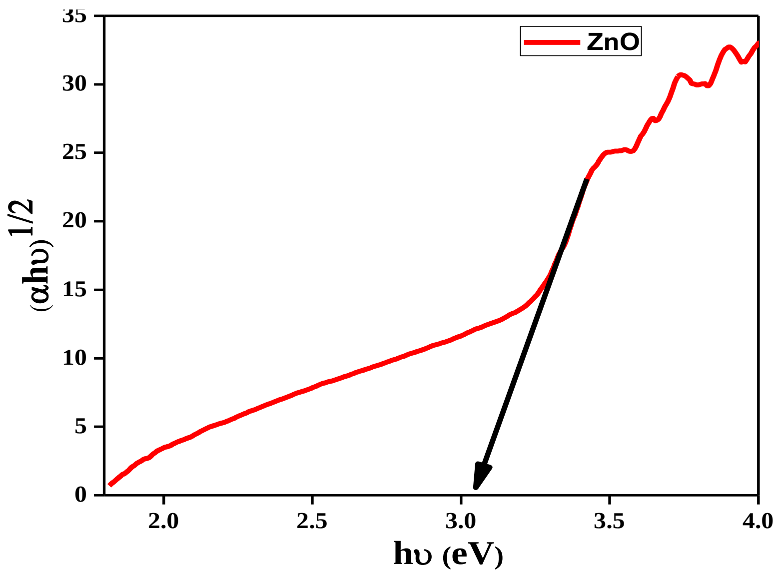


Figure: 6.2 b) Band gap of ZnO

6.3 XRD:

X-ray diffraction patterns of the nanocomposites are shown in Fig. 6.3. Diffraction peaks of ZnO appear at 2ɵ=31.85, 34.53, 36.33, 47.70, 56.75, 63.02 and 68.17 correspond to (100), (002), (101), (102), (110), (103) and (201) diffraction planes respectively. The diffraction pattern of ZnO reveals the presence of zincite phase having hexagonal crystal system.

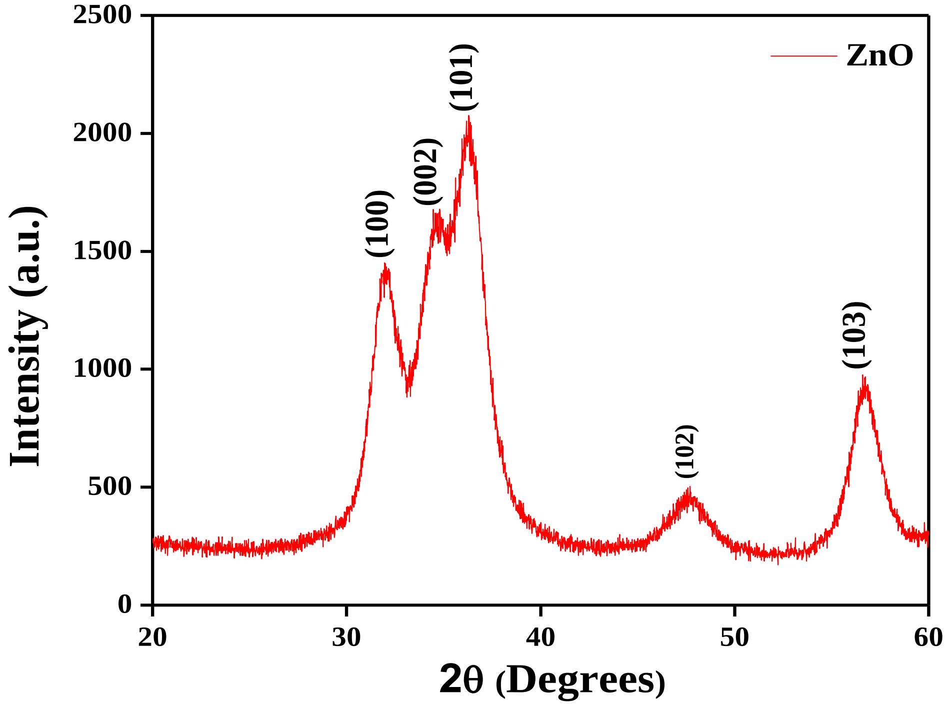


Figure 6.3 XRD of ZnO

6.4 Antibacterial activity:

E.coli culture was used for the antibacterial activity. ZnO is used as a drug against *E.coli* culture to kill the colonies of *E.coli*. Different concentration of ZnO was added in the media containing *E.coli* culture and then the media was poured in the petri plate which was incubated. After interval of time the growth of colonies were checked. With the varying concentration of ZnO the colonies of *E.coli* culture was killed(Fig 6.4).

If the concentration of ZnO is less then was more colonies, if the concentration is more than the colonies was less due to this we concluded that ZnO contain antibacterial properties. Second experiment was performed with ZnO clay composites which show better results against the culture of *E.coli*. ZnO clay composite inhibits the growth of colonies and also kill the colonies of bacterial culture very fast as compared to ZnO nanoparticles.

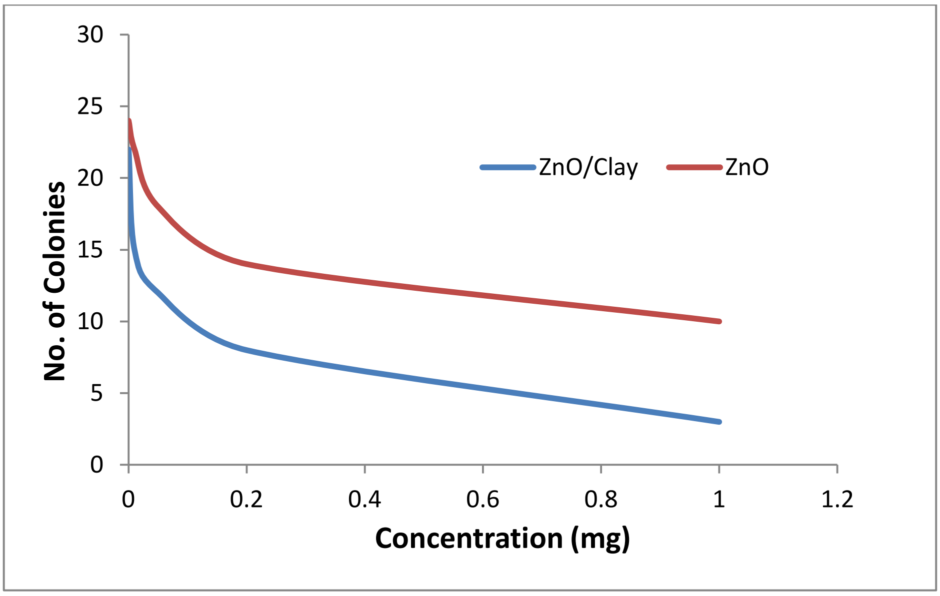


Figure: 6.4 Growth inhibitory curve

6.5 Degradation of Methylene blue:

UV-visible spectrophotometer is a spectroscopy technique which has been used for the characterization of metal and metal oxides nanoparticles. Degradation of dye was examined by UV-vis spectrophotometer; due to Surface Plasmon resonance there is change in colour of reaction mixture which indicates that there is a presence of reducing agent. Methylene blue dye was degraded with ZnO nanopowder; it changes the colour of dye from blue to a colourless solution which was examined through this spectroscopy technique. The change in absorbance indicates the degradation of dye with ZnO. First the reaction was kept in dark for 1 hr on stirring conditions. The concentration of dye was 0.01mM in 10 ml and the concentration of ZnO catalyst was 10mg which was kept for incubation of 1 hr after this reaction was centrifuged for 2 mins then UV spectrum was obtained. After this the reaction was again incubated in UV-light for different intervals of time. After some time the change in colour was observed due to the degradation properties of ZnO, at the end the solution will become colourless which means all the dye was degraded. After the reaction was completed UV-spectrum was obtained which clearly shows the difference in peaks of degraded dye.

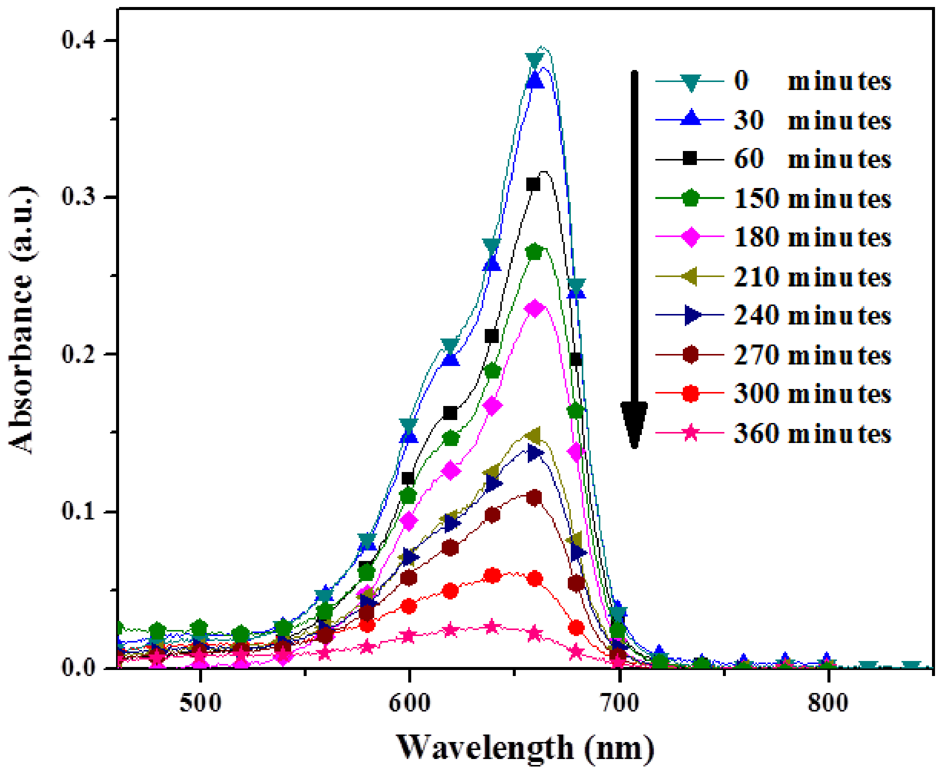


Figure: 6.5 a) UV-visible spectrum of Methylene blue degradation by ZnO

The same procedure was performed for ZnO/Clay which shows the fast reaction because clay was used as catalyst for the adsorption of ZnO on the clay surface. The clay catalyst enhances the properties of ZnO which degrade the dye in quick manner. Clay increases the surface area due to which the degradation of dye was enhanced. Layered structure, higher surface range, porosity and substantial scale accessibility in nature are the components in charge of the use of the clay for photo catalytic activity. Bentonite is one of the practical and one of the generally accessible clay in nature which can be a premise of new approach for remediation of toxins from squander water.

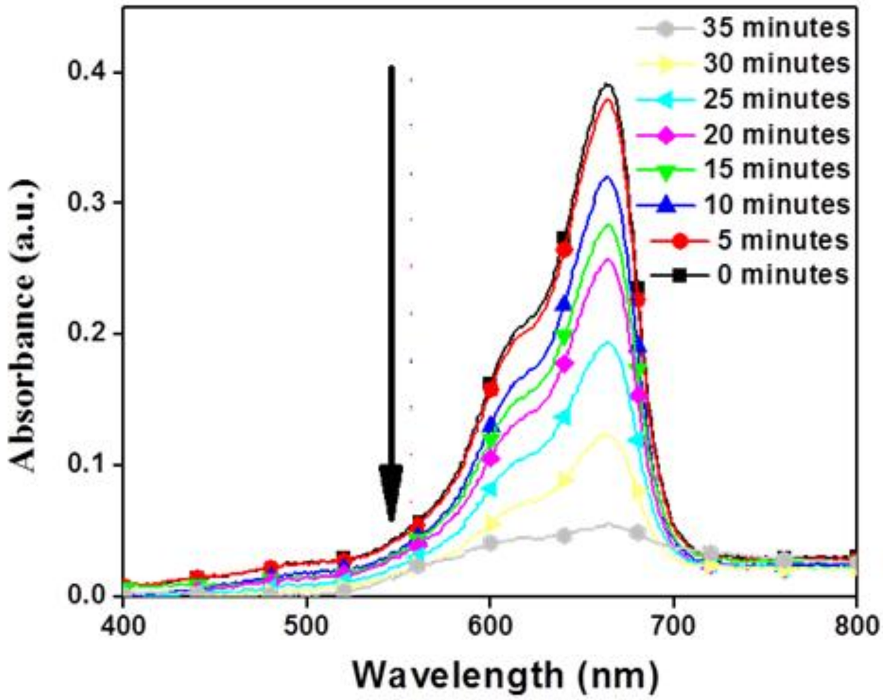


Figure: 6.5 b) UV-visible spectrum of methylene blue dye degraded by ZnO/Clay

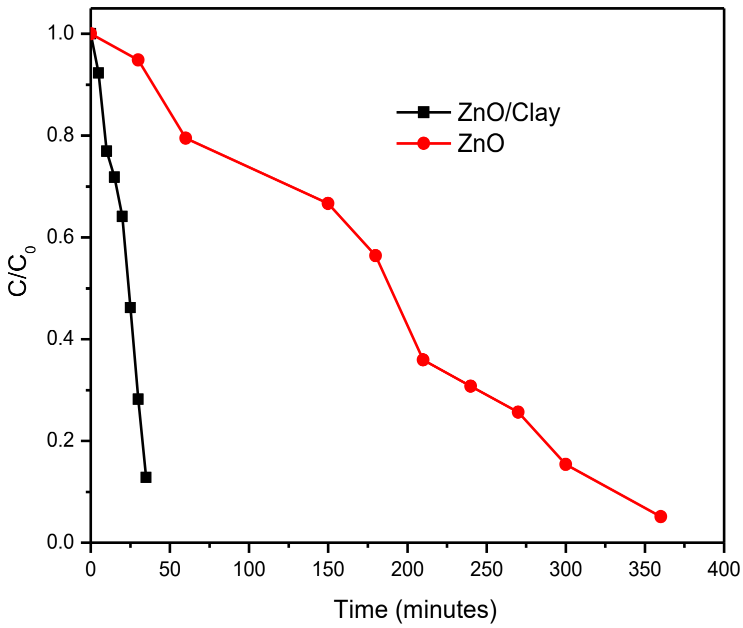


Figure:6.5 c) Kinetics study of ZnO and ZnO/Clay composite

6.6 Nitrophenol reduction

Kinetics studies for reduction of 4-NP is done using ZnO nanoparticles at different time intervals. UV spectra were obtained at 250nm to 700nm then after every 5mins spectra were obtained of the same solution. Nitrophenol is known as waste material come out from the industries which pollute the water. It decreases the water purity which affects the marine system more than the human beings. Using ZnO to degrade it is of great interest. Zno changes the colour of the solution from yellow to transparent which clearly shows that there is a reduction of 4- NP. It shows that ZnO contains reducing properties. As in this way ZnO can be easily used as a reducing agent, which can work as a water purifier substance. But in this spectrum there is no peak of phenolate ion which indicates that only half of 4-NP was reduced.

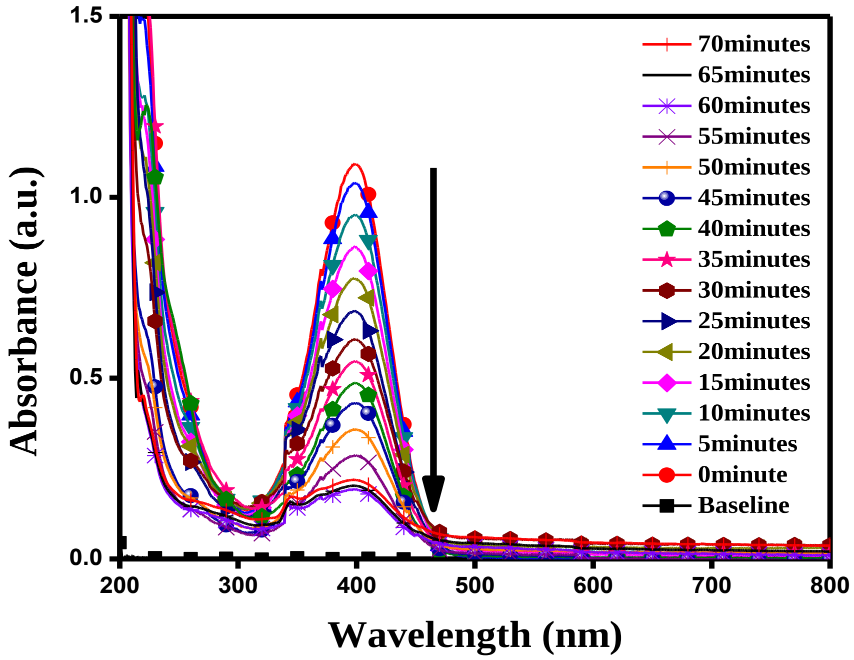


Figure: 6.6 a) UV-visible spectrum of 4-NP reduction by ZnO

In this 4-NP was reduced with ZnO/Clay. Clay act as a good adsorbent for ZnO and act as a catalyst which fasten the degradation process of nitrophenol. It converts the 4-NP into phenolate ion by shifting the peak below 400nm. It exhibits better properties as compared to ZnO. A characteristic change is observed with the addition of $NaBH_4$ which shows the peak around 300nm. It indicates the formation of 4 amino phenol which can be clearly observed by changing in the colour of the solution from yellow to transparent and peak shifted to 300nm.

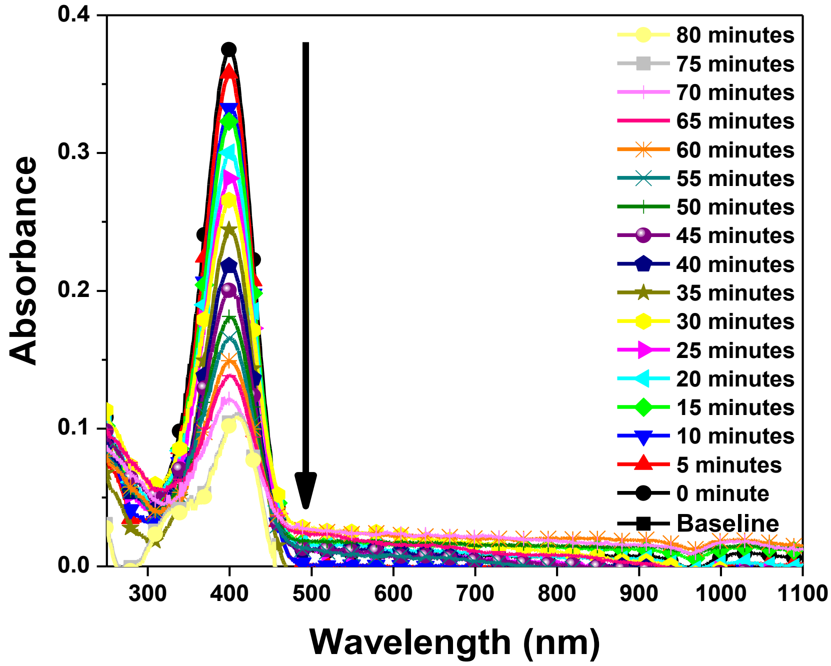


Figure: 6.6 b) Nitrophenol reduction by ZnO/Clay

Conclusion:

Nowadays, the contaminants from the industries, polluting the water which make the water incompetent to animals as well as to human beings. Nanoparticles have different kinds of properties like high photochemical reactivity, chemical degradation, so it can be used in the process of water purification. In this work, ZnO nanoparticles were synthesized from zinc nitrate and were characterized by UV-visible spectrophotometer, XRD, BET surface analyzer and DRS. Doping of ZnO nanoparticles into clay enhanced the applications of ZnO by increasing its surface area. Montomorillonite clays with high surface area were used as a inner support and active surface enhancer for ZnO nanoparticles. Methylene blue dye and nitrophenols are the most widely recognized natural contaminants, which is used by the industries in large scale which was reduced in water by ZnO/Clay composite. Upon with the comparison between ZnO/Clay composite and only ZnO the rate of reaction was very fast in ZnO/Clay composite. ZnO/Clay composite act as reducing agent as it reduced the 4-NP to aminophenol. For the general wellbeing, microbes are unsafe for which he antibacterial activity performed using ZnO/Clay composites, which showed the efficient results by inhibiting the growth of E.Coli culture. Different concentration was used to inhibit the growth of E.Coli. ZnO nanoparticles and its metal oxides was used and pulled the nanoparticles in broad range. Against dyes and bacterial infection ZnO nanoparticles with its metal oxides can be used on a large scale because it shows effective results.

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