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FULL LENGTH ARTICLE

ZnO Nanoparticles as Adsorbent for Removal of Methylene Blue dye

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ABSTRACT

Methylene Blue (MB) is a heterocyclic aromatic chemical compound with molecular formula $C_{16}H_{18}N_3SCl$. It is used extensily in textile, paper, food, cosmetics and other industries for coloration purposes. Because of the synthetic and complex structure of the dye its difficult to treat the hazardous effluent wastewater from these industries. So, various physical, chemical and biological methods such as filteration, precipitation, coagulation, oxidation, adsorption have been used to remove dyes. In our studies, Zinc Oxide (ZnO) nanoparticles have been used as low cost, efficient adsorbent for the removal of MB dye from synthetic wastewater in batch studies. ZnO particles were synthesized using simple precipitation method with zinc sulfate heptahydrate and sodium hydroxide as starting materials. Thus, prepared material was calcined for 2 hrs at different temperatures. X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) were performed to evaluate the characterisation [1]. The experimental parameters such as pH (3, 6.5, 8, 9, 10 pH), adsorbent dosage (0.1, 0.25, 0.5, 0.75 1 gm), initial dye concentration (50,100, 150, 200, 300 ppm), contact time were evaluated during the batch studies to measure the percentage removal and uptake capacity of MB dye by ZnO nanoparticles. The isotherm studies were also performed to evaluate the best fit.
Keywords: ZnO nanoparticles, Methylene Blue dye, batch adsorption studies.

INTRODUCTION

Nanotechnology research has gained momentum in the recent years by providing innovative solutions in the field of biomedical, materials science, optics and electronics. Nanoparticles are essentially a varied form of basic elements derived by altering their atomic and molecular properties of elements.

Nanotechnology is defined as the study of manipulating matter on the atomic and molecular scale. In General, nanotechnology deals with structures whose sizes vary between 1 to 100 nm in one dimension at least, and involves developing materials having at least one dimension within that size range. It covers various areas ranging from conventional device physics to completely new approaches based on molecular self-assembly, from developing materials having dimensions of the nanoscale to finding out whether we can control matter on the atomic scale. It is able to create many new materials with a vast range of applications, such as in medicine, biomaterials, electronics, and production of energy. However, nanotechnology raises many concerns about toxicity and impact of nano materials on environment, and their effects on global economics.

Nanoparticles are particles that have one dimension that is 100 nanometers or less in size. The properties of many conventional materials change when formed from nanoparticles. This is typically because nanoparticles have a greater surface area per weight than larger particles; this causes them to be more reactive to certain other molecules. Nanoparticles are used, or being evaluated for use, in many fields.

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nanoscale size-dependent properties are often observed. Thus, the properties of materials generally change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material starts to become significant. For bulk materials larger than one micrometer (or micron), the percentage of atoms at the surface is insignificant in comparison to the number of atoms in the bulk of the material. The interesting and sometimes unexpected properties of nanoparticles are therefore largely due to the large surface area of the material, which dominates the contributions made by the small bulk of the material. Nanoparticles often possess unexpected optical properties as they are small enough to confine their electrons and produce quantum effects. Other size-dependent property changes in the

nanoparticle include quantum confinement in semiconductor particles, surface plasmonresonance in some metal particles and super paramagnetism in magnetic materials.
Alternative synthetic technique for nanoparticles involves controlled precipitation of nanoparticles from precursors dissolved in a solution. A micro emulsion can also be formed between two immiscible liquids, using surfactants, with the reactants isolated inside a micelle, through hydrophobic versus hydrophilic forces. The resultant nanoparticles form a colloidal suspension. Various thermodynamic factors as well as Van der Waal's forces induce particle growth and agglomeration, resulting in bigger particles that settle down over time.
Zinc oxide (ZnO) nanopowders are available as powders and dispersions. These nanoparticles exhibit antibacterial, anti-corrosive, antifungal and UV filtering properties. Zinc is a Block D, Period 4 element while Oxygen is a Block P, Period 2 element. Some of the synonyms of zinc oxide nano-particles are oxy datum, zincoxicum, permanent white, ketozinc and oxozinc.

EXPERIMENTAL

Material preparation and characterization

Preparation of Adsorbent

To prepare the aqueous solution of zinc sulphate, sodium hydroxide solution was added slowly dropwise in a molar ratio of 1:2 under vigorous stirring at rate 600 rpm, and the stirring was continued for 12 hrs. The precipitate obtained was filtered and washed thoroughly with demonized water. The precipitate was dried in a muffle furnace at 100°C and ground to fine powder using agate mortar. The powder obtained from the above method was calcined at 500°C and 700°C temperatures for 2 hrs in muffle furnace.

Fig 1: Experimental setup for preparing adsorbent

Fig 2: Precipitate formed

Chemical preparation

A stock synthetic standard solution of methylene blue was used to prepare the adsorbate solutions of required strength. Deionised water, Zinc Sulphate heptahydrate ($ZnSO_4.7H_2O$) and sodium hydroxide, etc analytical grade chemicals were used.

Apparatus

Pipette, magnetic stirrer, conical flask, volumetric flask, Whatman filter paper, funnels etc.

Adsorbent Characterization

The crystallinity was determined by XRD powder diffraction. Analysis was performed by using Lab X XRD-6100 SHIMADZU X-ray diffractometer equipped with a Cuk_α(λ =1.54 A°) source, maintaining applied voltage of 40 kV and current at 30 mA. About 0.3 g of dried ZnO particles were deposited as a randomly oriented powder into a plexiglass sample container, and the XRD patterns were recorded between 20°and 80° angles, with speed of 5.0 deg /min. The crystalline domain diameter (D) was obtained from XRD peaks using the following

Scherrer'sequation : $D=\frac{K*\lambda}{\beta*cos\theta}$

Where;λ is the wavelength of the incident X-ray beam;Θ the Bragg's diffraction angle;

β the width of the X-ray pattern line at half peak – height in radian and the dimensionless shape factor (K) has a typical value of 0.89, but varies with the actual shape of the crystalline. The data obtain from X-Ray diffractometer was plot by using origin 8 software.

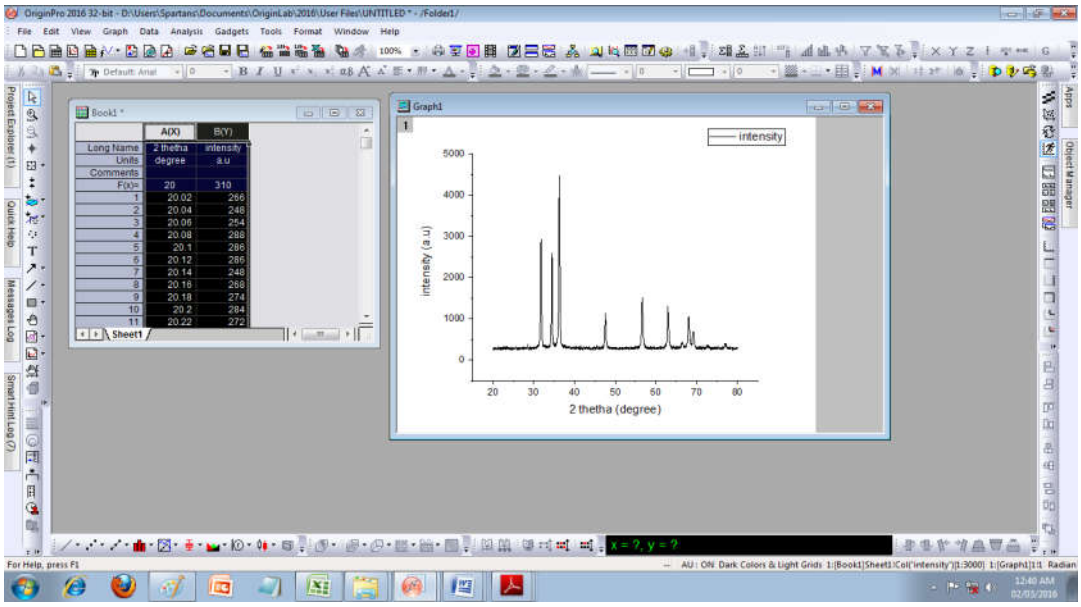

Fig 3: The snapshot of the XRD pattern generated in Origin 8 software

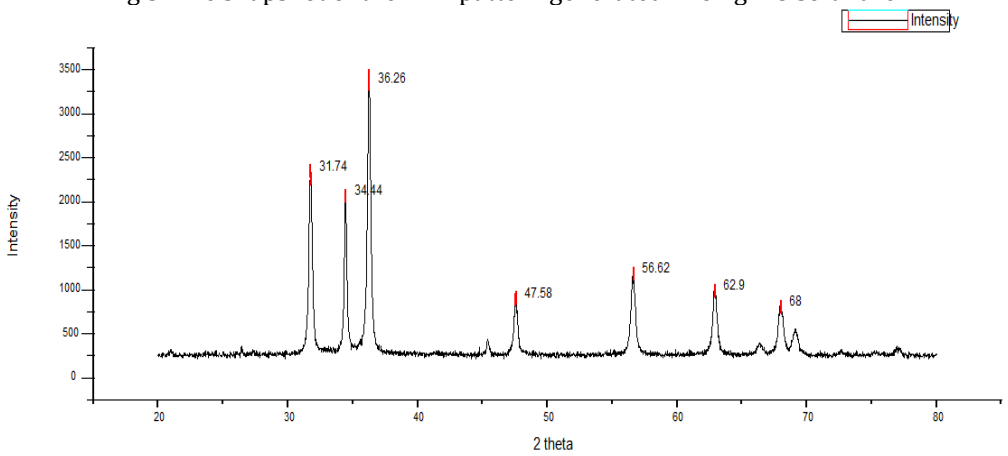

Fig 4: XRD pattern for sample calcined at 500^{O}C

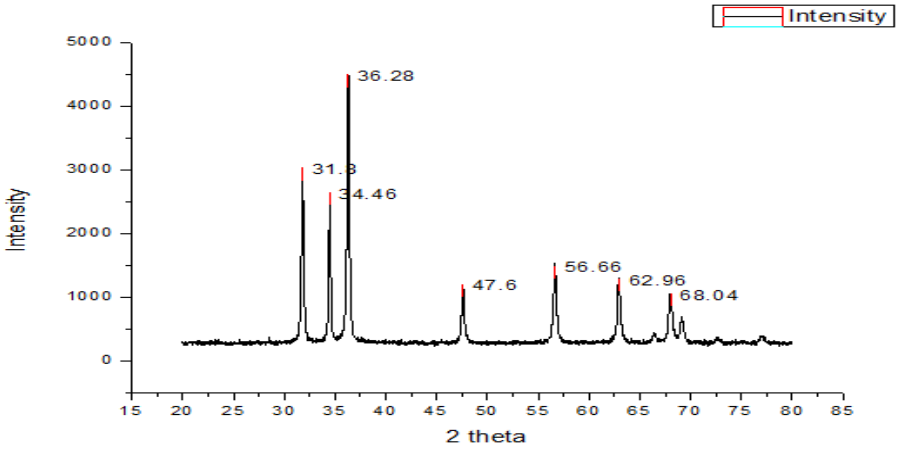

Fig 5: XRD pattern for sample calcined at 700^{O}C

SEM (Scanning Electron Microscope) images

The scanning electron microscope uses a beam of high-energy electrons to produce a variety of signals at the surface of specimens used. The signals show information about the sample including chemical

composition, and crystalline structure, external morphology (texture) and orientation of materials which make up the sample. SEM analysis is normally considered to be non-destructive because the x-rays generated do not lead to loss of volume of the sample, so it becomes possible to repeatedly analyze the same materials. A scanning electron microscope is a kind of electron microscope which images a sample by scanning it using a high-energy electron beam. The electrons then interact with the atoms making up the sample, thus producing signals which reveal information about the sample's composition, surface topography and other propertiessuch as electrical conductivity. In the present studies, the SEM ananlysis as carried out at Pune University lab. The analysis shows flake like morphology.

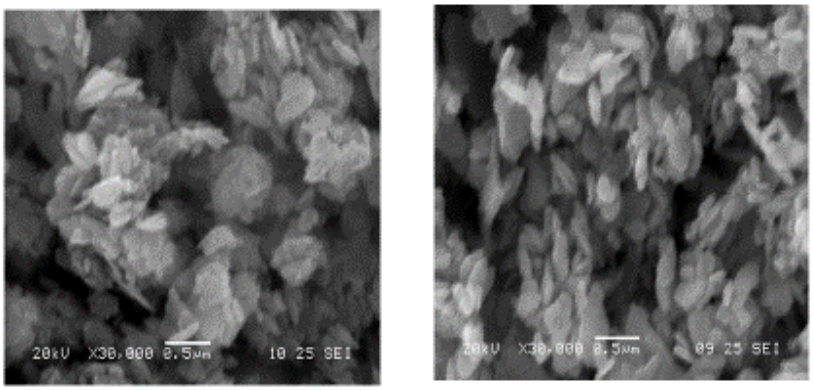

Fig 6: Sample calcined at 500°C and 700°C respectively.

Adsorption Study

The batch experiment studies were carried out in lab scale equipment as shown in fig… The 500ml capacity closed batch reactor with the provision to collect the samples at different interval was used. This reactor as placed on magnetic stirrer setup along with stirrer in the reactor. To this, the dye solution of known concentration, known amount of ZnO particles were added at fixed pH. The run as carried at predetermined rpm which found to give good results. 10 ml of sample solutionwas collected after 30 min of starting the agitation in a sample bottles after filtration. The same procedure was repeated for different adsorbate doses, adsorbent doses, interval of time and pH. Collected samples were marked properly and used it for analysis to determine the removal efficiency.

Fig 7: Batch experimental setup.

RESULTS AND DISCUSSION

Effect of Contact Time on Adsorption

The ZnO nanoparticles dosage and Methylene blue concentrationwere agitated at room temperature. After filtration, the dye concentration was determined by using UV analysis. It was observed that the dye removal efficiency of nano ZnO particles increased effectively hen contact time was increased from 10 min to 180 min. After which equilibrium conditions were attained.

Effect of Adsorbate Concentration

The Methylene blue solution of different concentration (50,100,150,200, 300) were prepared and by using 0.1gm of ZnO nanporticles the solution was agitated at room temperature for different time (5, 10,15,20,25,30,60,90,120, and 150,180 min). After filtration, the dye concentration was determined by

using UV analysis. The dye concentration was determined by analysis. The effects are as shown in table and fig 8.

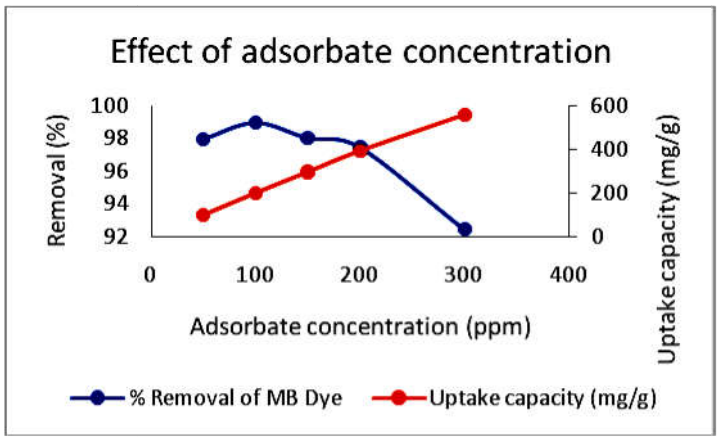

Fig 8: Effect of adsorbate concentration

4.3 Effect of Adsorbent Dosage

The effect of adsorbent dosage towards the removal of methylene blue dye percentage and q, amount of dye adsorbed per unit of adsorbent weight (mg/g) is shown in fig 9. The ZnO nanoparticles dosage was varied from 0.1 to 1gm. The studies were conducted at 1000 rpm, 100ppm, 6.5pH. The results obtained showed the good removal efficiency for all the loading of over 90% with highest for 0.1 gm.

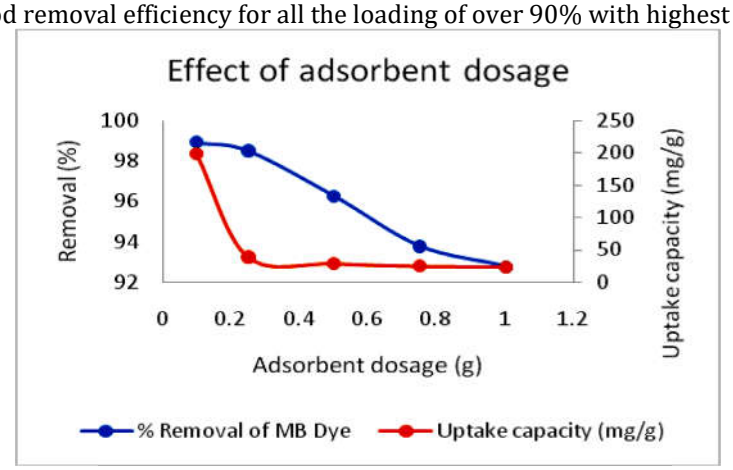

Fig 9: Effect of adsorbent dosage

Effect of pH

The effect of pH was examined by varying the pH of the test solution in the range of 3-10. The pH of 200 ml of MB solution (20 mg /200ml) was adjusted to the desired value using HCland/or NaOH solution (0.1 M). The dye concentration was determined by analysis. The effects are as shown in fig10.

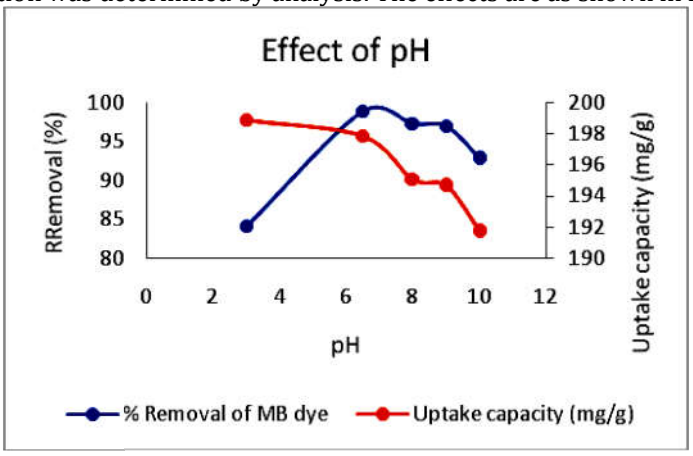

Fig 10: Effect of pH for adsorption dye

Adsorption Isotherm Models:

Freundlich and Langmuir Isotherms were studied. Langmuir Isotherm Model fitted well with the present studies.

CONCLUSION

ZnO nanoparticles prepared using the precipitation method. The precipitate obtained as calcined at to different temperature 500 and 700^{0}C to get powdered form on ZnO. This was analysed using XRD and SEM analysis. XRD analysis showed that the particles were of average 30 nm size. That proved that the particles obtained were pure nanoparticles. SEM images gave clear indication that the flake like morphology. The nanoparticles calcined at 700^{0}Cwere chosen for batch adsorption studies. The effect of contact time, adsorbent dosage, adsorbate concentration and pH were varied. It found that at 180 min contact time equilibrium was achieved, 0.1 gm of ZnO loading and 100 ppm dye concentration and 6.5 pH conditions showed highest removal efficiency. Langmuir Isotherm Model fitted well to the data obtained.

REFERENCES

1. Adsorption of Methylene Blue from Aqueous Solutions using Fe3O4/Bentonite NanocompositeHashem FS, Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt.
2. Cheng, XL, Zhao, H, Huo, LH, Gao, S, Zhao, JG: ZnOnanoparticulate thin film: preparation, characterization and gas-sensing properties. Sens. Actuators B. 102, 248–252 (2004)
3. Hamid Reza Ghorbani, FerdosParsaMehr, Hossein Pazoki and BehradMosavarRahmani.Synthesis Of Zno Nanoparticles By Precipitation Method,Department of Chemical Engineering, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran.April 04, 2015
4. HK Farag1, Z M Hanafi1, M Dawy2 and EM Abd El Aziz1, Characterization Of ZnO Nanopowders Synthesized By The Direct Precipitation MethodSenra Academic Publishers, Burnaby, British Columbia Vol. 4, No. 3, pp. 1303-1309, October 2010 Online ISSN: 1920-3853;
5. Huang, YH, Zang, Y, Liu, L, Fan, SS, Wei, Y, He, J: Controlled synthesis and field emission properties of ZnO nanostructures with different morphologies. J. Nanosci. Nanotechnol. 6, 787–790 (2006)
6. J.TamilIllakkiya, S. Hemalatha1, Rachel Oommen, P.Usha Rajalakshmi1, Characterization of ZnO Nanoparticles synthesized by wet chemical method, International Journal of ChemTechResearchCODEN (USA): IJCRGG, Vol.6, No.3, pp 2159-2161, May-June 2014
7. M. Vafaee, M. SasaniGhamsari, Preparation and characterization of ZnO nanoparticlesby a novel sol–gel routeDepartment of Material Science and Engineering, Sharif University of Technology, 11365-9898, Tehran, Iran. Solid State Laser Division, Laser Research Centre, 11365-8486, Tehran, Iran
8. OmkarBehera, Dr.Subhankar Paul. Synthesis and Characterizationof ZnO nanoparticles of various sizes andApplications in Biological systems. Department of Biotechnology and Medical Engineering. National Institute of Technology Rourkela
9. Riyadh M. Alwan, Quraish A. Kadhim, Kassim M. Sahan, Rawaa A. Ali, Roaa J. Mahdi, Noor A. Kassim, Alwan N. Jassim,, Synthesis of Zinc Oxide Nanoparticles via So– Gel Route and Their Characterization, Nanoscience and Nanotechnology, 2015.
10. SiminArabi and Mahmoud Reza Sohrabi.Removal of methylene blue, a basic dye, from aqueous solutions using nano-zerovalentiron.Department of Chemistry,North Tehran Branch, Islamic Azad University,Tehran,
11. Surabhi Siva Kumar, PutchaVenkateswarlu, VankaRanga Rao and GollapalliNageswara Rao, Synthesis, characterization and optical properties of zinc oxide nanoparticles,International Nano Letters 2013.
12. T. Jesper Jacobson, Synthesis and characterization of ZnO nanoparticles. An experimental investigation of some of their size dependent quantum effects. Uppsala UniversitetMaterialkemi Höstterminen 2009.
13. T.V.Kolekar, H.M.Yadav, S.S.Bandgar, A.C.Raskar, S.G.Rawal, G.M.Mishra, Synthesis By Sol-gel Method And Characterization Of ZnO Nanoparticles, Indian Streams Research Journal , Volume.2, Issue.1,Feb. 2011
14. Wang, ZL: Zinc oxide nanostructures: growth properties and applications. J. Phys. Condens. Matter. 16, R829–R858 (2004).

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