MAGNESIUM OXIDE NANOSTRUCTURES: SYNTHESIS, CHARACTERIZATIONAND ENVIRONMENTAL APPLICATION

A Dissertation

Submitted in partial fulfilment of the requirements for the degree of

Master of Science

in chemistry

By

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DECLARATION

I hereby declare that the matter embodied in report is the result of investigations carried out by me in National Institute of Technology, Rourkela, Rourkela-769008, Odisha, India, under the supervision of Dr.Garudadhwaj Hota.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

Place: Rourkela *Meenaketan Sethi*

Date: 06, May, 2014

CERTIFICATE

This is to certify that the thesis entitled "**Magnesium Oxide Nanostructures: Synthesis, Characterization and Environmental Application**" being submitted by Meenaketan Sethi to the National Institute of Technology, Rourkela, India, for the award of the degree of **Master of Science in chemistry** is a record of bonafide research work carried out by him under my supervision and guidance. I am satisfied that the thesis has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Supervisor

Place: Rourkela
Date: 06, May, 2014

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Meenaketan Sethi

Place: Rourkela

Date: 06, May, 2014

ABSTRACT

In this work we have reported the synthesis of nanostructured MgO of different morphologies by wet chemical methods such as hydrothermal, reflux and co-precipitation method. The synthesized MgO nanomaterials were characterized by using FTIR, XRD, FE-SEM and EDAXanalytical techniques in order to evaluate the formation, crystalline phase morphologies, microstructures and chemical compositions. The XRD results reveal the well crystalline nature of the prepared compounds. From the FE-SEM images, it is observed the formation of MgO nanoflakes by hydrothermal method, nanorods by precipitation method and hierarchical structure by reflux method. The prepared MgO nanomaterials were used as adsorbents for removal of organic dyes such as Malachite green (MG) and Congo red (CR) from aqueous solutions.It is observed from the adsorption experiments that the hierarchical MgO nanostructures are excellent adsorbents for decontamination of both MG and CR dyes as compared to other MgO nanostructures. Hence, the MgO hierarchical nanostructure may be considered as an efficient adsorbent for removal of MG and CR dye from waste water.

Key words: Nanostructured MgO, Adsorption, Wet Chemical method, Malachite green, Congo red

1. Introduction

1.1 Introduction to nanomaterials

The materials world can be divided into five sub-divisions like ceramic, metal, polymer, semiconductor and composites. Among them Nanomaterial are one of the subdivision which is the study of fundamental relationships between physical properties and dimensions of the materials on the nano meter scale. Nanomaterials are the materials possess in the order of a billionth of a meter on the nanometer scale or in other words, we can say that the materials whose size ranges from 1-100nm are referred as nanomaterials [1]. Since past few decades different nanoarchitectures such asNanorods, nanowires, nanotubes, nanoribbons, nanoflakes, nano particles, nanoflower, nanocubes, nanobelts, nanoclusters,nanofibersand nano porous materials [2-13] have been reported by various groups.

1.2 Method of preparation of nanomaterials

1.2.1 Physical methods

High energy ball milling

Flame spray pyrolysis

Laser ablation

1.2.2 Chemical methods

Co-precipitation method

Sol–gel method

Hydrothermal method

1.3 Magnesium oxide nanomaterials

N. K. Nga et.al. [14] have shown the formation of MgO nanoparticles by hydrothermal method using CTAB (cetyltrimethyl ammonium bromide) which serves as a morphologicalcontrol to obtain a high specific surface area and enhance the adsorptive performance of MgO nanoparticles. In this synthesis they have used $MgCl_2.6H_2O$ and NaOH as starting materials. F. E. Tantawy et al. [15] have reported the synthesis of 1D nanowires of diameter 6nm and length about 10 µm by hydrothermal synthesis at very low temperature. X. Qiao et al. [16] prepared Magnesium oxide (MgO) nanoplates having thickness around 10–20 nm and a length about 100 nm are synthesized by co- precipitation method using $MgCl_2 \cdot 6H_2O$as salt precursor, ammonia hydroxide as precipitator and anonionic surfactant such as polyethylene glycol (PEG 400). M. Rezaei et. al [17] have synthesized high surface area nanocrystalline magnesium oxide by reflux method using Pluronic P123 block copolymer surfactant, $Mg(NO_3)_2.6H_2O$ and ammonia solution as starting materials.

1.3 Objective of the study

(1) Synthesis of magnesiumoxide nanomaterials ofdifferent morphologies by chemical methods such as precipitation, reflux and hydrothermal method.

(2) Synthesis and characterization of metal doped MgO nanomaterials.

(3) Characterization of synthesized nanomaterial by different scattering and microscopic techniques like XRD, FESEM, FTIR & UV-VIS DRS etc. to obtain the information on the structural, morphological and spectroscopic properties.

(4) Environmental application of the prepared MgO nanomaterials towards adsorptive removal of organic contaminants/dye from aqueous media.

2. Experimental

2.1 Materials used

Magnesium chloride ($MgCl_2.6H_2O$) from Merek India private limited, ammonium carbonate ($(NH_4)_2.6H_2O$) from Merek India private limited, Malachite Green (oxalate) from Merck India private limited, and Congo red from Merck Germany private limited. All the reagents used in the synthesis were of analytical grade and used as received without further purification.

2.2 Synthesis of Magnesium oxide nanoflakes by hydrothermal method

Magnesium oxide nanoflakes (MgO) were synthesized by hydrothermal method using the starting precursors as magnesium chloride as salt precursor. $MgCl_2.6H_2O$ was dissolved in distilled water and stirred for 5 min & ammonium carbonate $(NH_4)_2CO_3$ was also dissolved in distilled water. This $(NH_4)_2CO_3$ solution was then added to the above solution and again stirred for 15 min to form a homogeneous solution. Then the solution was transferred into a Teflon-linked sealed autoclave followed by hydrothermal treatment for 6 hr at 150^0C. Then the sample was collected, centrifugedand washed for several times with ethanol and distilled water and then dried at 60 °C for 2 hours. Then the dried sample was calcined at 400°C for 3 hours with heating rate 10°C/min to form MgO nanoflakes.

2.3 Synthesis of Magnesium oxide nanorods by co-precipitation method

In this synthetic method $MgCl_2.6H_2O$ was dissolved in distilled water (solution A) and $(NH_4)_2CO_3$ was dissolved in water (solution B). Then the solution B was added to solution A with vigorous stirring for 6 hr, then the white precipitates were filtered and washed several times with distilled water followed by alcohol. The product was dried at 100 ^{0}C and calcined at400 ^{0}C for 3hr to obtain MgO nanorods.

2.4 Synthesis of Magnesium oxide hierarchical nanostructures by reflux method

In this typical process $MgCl_2$ was dissolved in distilled water (solution A) and $(NH_4)_2CO_3$ was dissolved in distilled water(solution B). Then $(NH_4)_2CO_3$ solution was added to $MgCl_2$ solution and stirred to form a homogeneous solution. After this the whole mixture was transferred into a round bottomed flask and refluxed. The obtained products were collected, filtered and dried at 80 ^{0}C for 2 hr, then the dried products were calcined at 400 ^{0}C for 3hr to obtain MgO hierarchical nanostructures.

2.5 Adsorption of Malachite green (MG) and Congo red (CR)

The Dye adsorptionefficiencies of the prepared MgOnanomaterials were tested towards adsorption of Malachite Green (MG) and Congo Red (CR) in an orbital shaker. Initially a stock solution of 1 g of Malachite green (oxalate) and Congo red was dissolved in 1000 ml of double distilled water. In a typical experiment, significant amount of adsorbate were added to 20 ml of 100 mg/L Malachite green and Congo red solution in a 100 ml of beaker for adsorption. After adsorption the solution was filtered. Then the solution was put into a quartz cell, and adsorption spectrum was measured using

Shimadzu UV-2450 spectrometer. The percentage removal can be calculated by the following equation.

$$\textbf{Percentage of removal} = \frac{C_0 - C_e}{C_0} X 100 \qquad \textbf{(1)}$$

3. Results and discussions

3.1 Surface morphology and microstructure

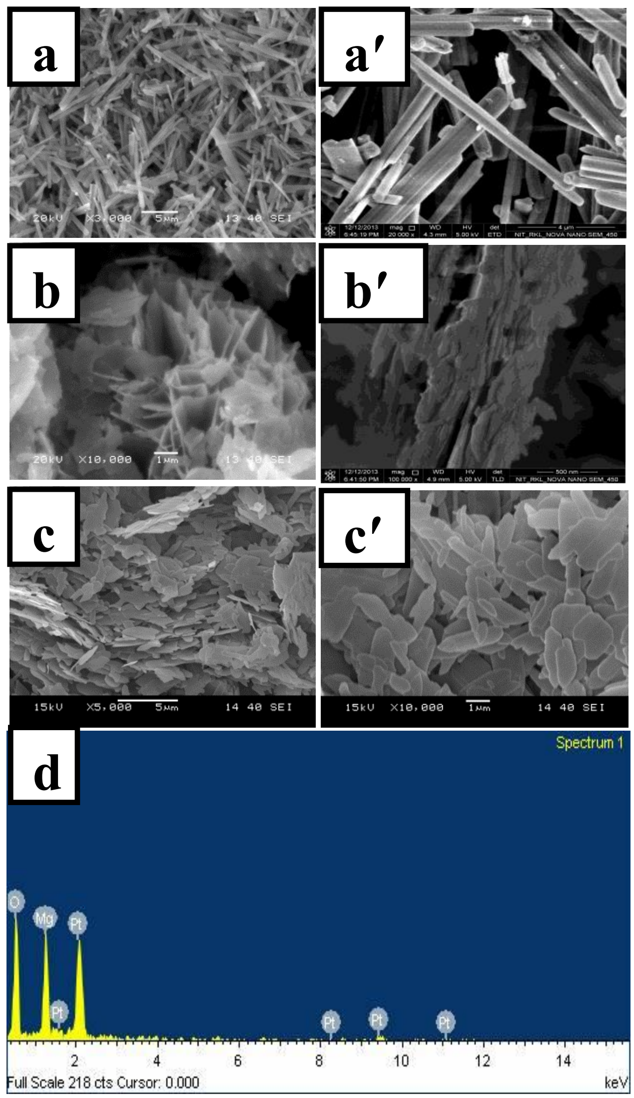

Figure 1: Shows the SEM images of MgO nanomaterials prepared by precipitation method, reflux method and hydrothermal method.

Figure 1 (a) represents the SEM image of MgOnanomaterials prepared by precipitation method. It is observed from the figure that, the obtained MgO are of rod shaped having diameter in the range of 300 to 500 nm. However figure 1 (b) and (c) represents the SEM images of MgO prepared by reflux and hydrothermal method. It is observed from the figure that a hierarchical morphology was obtained for reflux method and flakes like structure can be obtained incase of hydrothermal method. EDAX (figure 1 d) represents the presence of MgO which confirm the formation of MgO.

3.2 X-ray Diffraction Analysis

The X-ray diffraction study of as synthesized and calcined samples of magnesium oxide (MgO) nanomaterials prepared under different wet chemical methods were done and the patterns of reflux method are given below.

Hierarchical nanostructure

The X-ray diffraction studies of reflux synthesized hierarchical nano structures before and after calcination were shown in figure 2. The before calcined as-synthesised sample contains mixture of monoclinic and orthorhombic hydromagnesite crystal structures according to JCPDS file number 25-0513 and 70-1177, respectively. Figure 2 (b) pattern contains 400 °C calcined sample. The pattern contains characteristics peaks of MgO and can be indexed to cubic crystalline structure according to JCPDS file number 78-0430.

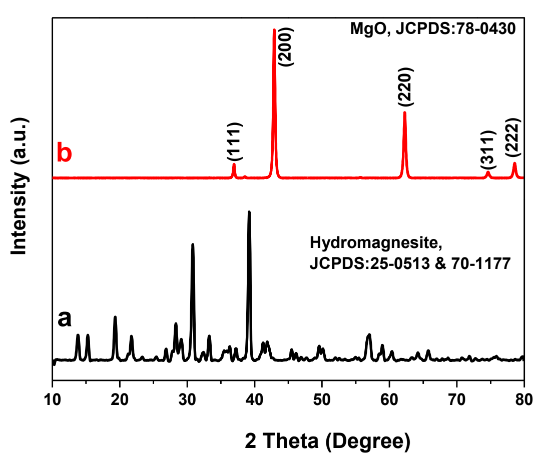

Figure 2 :XRD profile of reflux synthesized sample (a) before calcination, (b) calcination at 400^0C

3.3 FT-IR analysis

The FTIR patterns of prepared MgOnanoflakes by hydrothermal method, hierarchical structure by reflux method and nanorods by precipitation method were shown in figure 3. It was clearly observed a broad band at at 3600 – 3200cm^{-1} which is the characteristics for crystalline hydrates of MgO. A broad band at 1460 – 1400 cm^{-1} corresponds to Mg-O stretching vibrations. A band at 850 – 900 cm^{-1} corresponds to v1 and v2 stretching vibrations of metal oxygen bond [18], which corresponds to the formation of MgO. Similarly a broad band at 400 – 450 cm^{-1} corresponds to Mg-O or deformation vibrations of Mg-O-Mg for MgO.

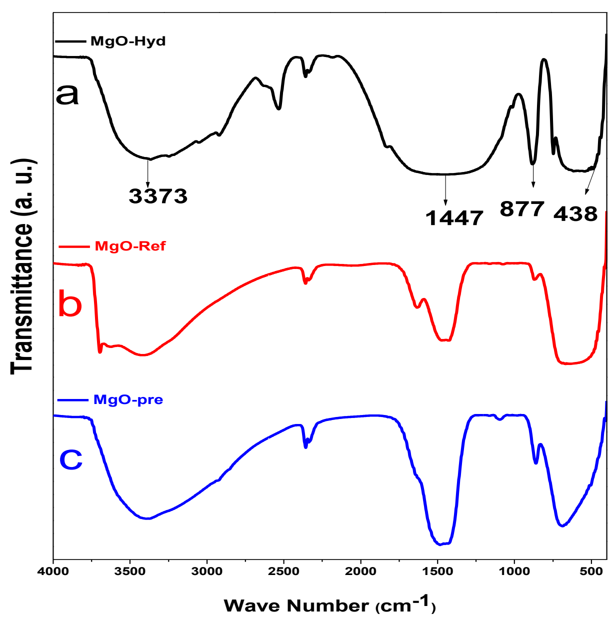

Figure 3 : FTIR spectra of(a) nanoflakes(b) hierarchical structure (c) nanorods.

3.4 Adsorption experiments for Malachite green and Congo red

3.4.1 Effect of different Adsorbents

The different architectures MgO prepared by hydrothermal method, reflux method and co-precipitation method were used as adsorbents to remove organic dyes such as Malachite green and Congo red from aqueous solutions. The MgO hierarchical nanostructure shows better removal capacity for both the dye than the two other adsorbents. Hence we have choosen MgO hierarchical nanostructure for further adsorption study by varying the amount of dose, pH, reaction time and concentration.

3.4.2 Effect of pH on Adsorption

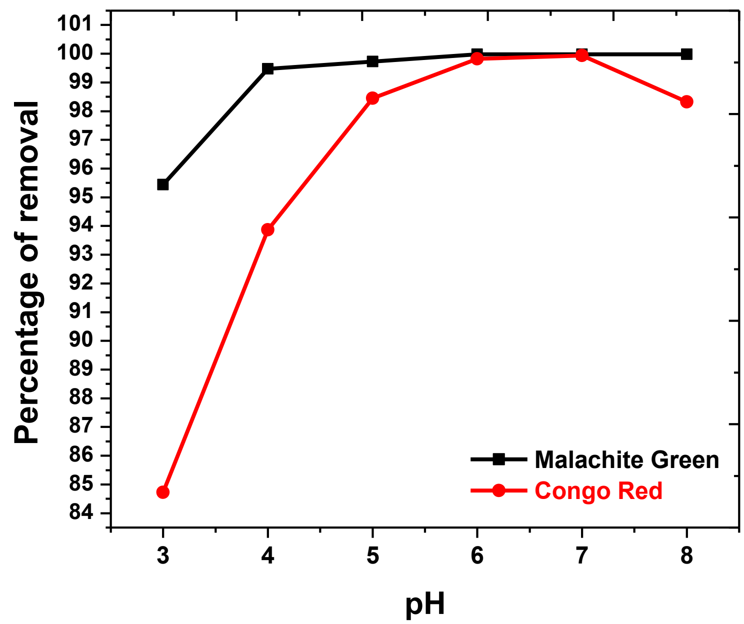

Figure 4: Effect of pH on the removal of Malachite green and Congo red.

3.4.3 Effect of Dose on Adsorption

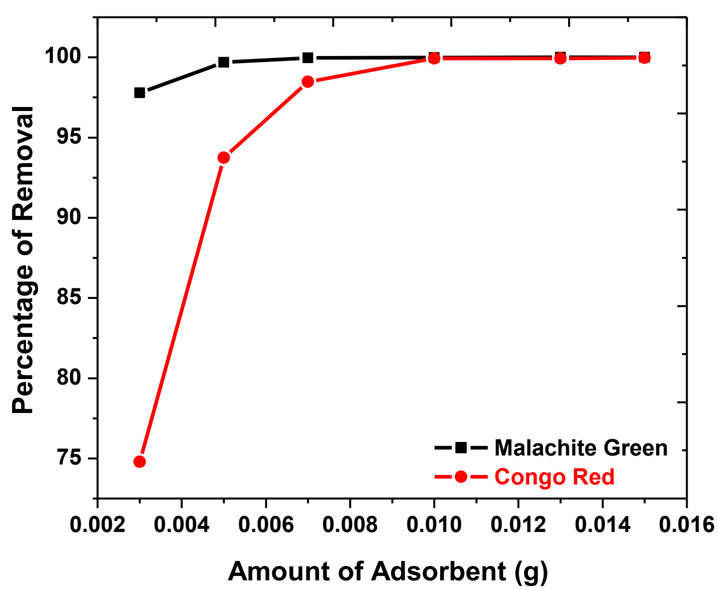

Figure 5: Effect of amount of dose on the adsorption of Malachite green and Congo red.

4. Conclusions and future work

4.1 Conclusions

MgOnanomaterials such as nanoflakes, hierarchical nanostructures and nanorods were successfully synthesized by hydrothermal, reflux method andco-precipitation followed by calcination at 400^0C. The as-prepared and calcined samples were characterized by SEM, XRD and FTIR to know the surface morphology, microstructure, crystallinity and physical properties. From SEM micrographs we observed the formation of different morphologies of MgO such as nanoflakes, hierarchical nanostructures and nanorods prepared by these methods. The XRD results reveals the well crystalline nature of the prepared MgO nanostructures. The FT-IR result also confirms the formation of Mg-O bands. The MgOnanomaterials were used towards the adsorptive removal of Malachite green and Congo red from aqueous solution. It was observed that the MgO having hierarchical nanostructures showed better percentage of removal than nanoflakes and nanorods. This results shows that MgO nanomaterials can be used as excellent adsorbents for decontamination of Malachite green and Congo red from waste water.

4.2. Future work

- Synthesis, of metal doped MgO nanostructure and their photocatalytic properties study.
- Preparation of composite nanostructure of different metal/metal oxide doped MgO and their antibacterial study.
- TEM characterization and BET surface area study of the prepared nanomaterials.
- Photocatalytic and antibacterial study of doped and un-doped MgO.

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