Synthesis and characterisation of alumina-iron oxide mixed nanocomposite for removal of Congo red dye

A Dissertation

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NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

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CERTIFICATE

This is to satisfy that the thesis entitled "**Synthesis and characterisation of alumina-iron oxide mixed nanocomposite for removal of Congo red dye**" being submitted by Deepak Sahu (Roll No. – 410CY2031) & Madhushree (Roll No. 410CY2001) for the partial fulfillment of the requirements for the award of M.Sc. degree in Chemistry at National Institute of Technology, Rourkela, is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University or Institute for the award of a degree or diploma.

Date: Signature of the guide

Place: Dr. Garudadhwaj Hota

DECLARATION

We, Deepak Sahu & Madhushree hereby declare that this project report entitled "**Synthesis and characterisation of alumina-iron oxide mixed nanocomposite for removal of Congo red dye**" is the original work carried out by us under supervision of Dr. G. Hota, Department of chemistry, National Institute of Technology Rourkela (NITR), Rourkela and the present work or any other part thereof has not been presented to any other University or Institution for the award of any other degree regarding to my belief.

May 1, 2012

Deepak Sahu

Madhushree

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(Deepak Sahu & Madhushree)

ABSTRACT

Synthesis of mixed AlOOH and FeOOH nanocomposite was performed by using ferrous sulphate, aluminium nitrate, sodium hydroxide and ammonia solution as starting materials via hydrothermal method. X-ray diffraction (XRD), scanning electron microscope (SEM) and Elemental detection X-ray analysis (EDAX) were used to characterize the features of the mixed nanocomposite obtained by the hydrothermal synthesis. From X-ray analysis it was observed that the mixed AlOOH and FeOOH nanocomposite obtained were crystalline in nature and the crystallinity increased when the mixed oxy-hydroxide was calcined at 1000^{o} C for 2 hour. The SEM images indicated the formation of irregular shape particles, having diameter in the range of 300-500 nm. The presence of Fe, Al and O elements in the mixed composite were confirmed by the EDAX analysis. The adsorption of Congo red over the mixed nanocomposite was investigated for different parameters and the adsorption capacities were evaluated using the Langmuir and Freundlich isotherm models. The mixed oxide nanocomposite prepared by sintering the mixed oxy-hydroxide (AlOOH-FeOOH) at 500^{0} C showed a very high adsorption capacity of Congo red and thus these nanocomposites can be used as good adsorbents and can be used for the removal of the dye Congo red from the waste water system. The sorption of congo red dye onto the mixed nanocomposite surface follows pseudo-second order kinetics and better fitted to Freundlich isotherm model.

Keywords: Nanotechnology, Nanoparticles, Nanocomposite, Hydrothermal route, Alumina, Iron oxide, Synthetic dyes.

1. INTRODUCTION

Nanotechnology promises the possibility of creation of nanostructures of metastable phase with non-conventional properties including super conductivity and magnetism. Materials in micrometer scale mostly exhibit physical properties the same as that of bulk form but materials in the nanometer scale exhibit properties distinctively different from that of bulk due to quantum size effects and the occurrence of large amounts of surfaces and interfaces because of their reduced size in nanometer scale [1]. And thus the materials having three dimensional network consisting of at least two phases with one dispersed in another i.e., matrix are known as nanocomposites. Many of the nanocomposites are synthesized via various synthetic routes such as sol-gel synthesized CdO-ZnO nanocomposite are used in gas sensing [2]. Chitosan silver oxide nanocomposite synthesized via solution casting method shows the property of antimicrobial activity [3]. Apart from the various nanocomposites prepared having characteristics application nanocomposites of alumina and iron oxide are of great importance. Al_2O_3 is amphoteric in nature and due to its hardness it is used as an abrasive and due to its high melting point is used as a refractory material. It has a high thermal conductivity for ceramic material instead of being an electrical insulator. Corundum is the most common form of crystalline alumina and the alpha and gamma phase of AlOOH are commonly known as Diaspore and Boehmite respectively [4]. Alumina is also used as filler in plastics, as catalysts [5], again they are widely used for the removal of water from gas stream and alumina acts as a very good adsorbent as well. Iron oxides are considered as one of the most important transition metal oxides. These oxides have huge applications as adsorbents [6], catalysts [7], sorbents, pigments, flocculants, coatings, gas sensors[8], ion exchangers and as lubricants. Iron oxide nanocomposite has various potential applications in the areas of magnetic recording, magnetic data storage devices, toners, magnetic resonance imaging, waste water treatment, bioseparation, medicines etc. Hydrothermal Synthesis is a method used for the preparation of fine powders of ceramic oxides which involves the exploitation of the properties of water under high pressure and temperature. Thus hydrothermal technique has been considered to be a very effective route for the preparation of nanoscale ceramic oxides like iron oxide and alumina [9]. Dyes impart colour to substances and thus dyes are used in different industries such as paper, plastics, leathers, pharmaceuticals, foods, cosmetics, medicines, textiles etc to colour the products. But in the present scenario, the disposal of dye has become a threatening to the environment because of its hazardous and poisonous effects. The degradation by-products of these dyes have very dangerous impact on environment as it contains toxic aromatic amines compounds whose removal rate are very slow and difficulties are faced in the biodegradation due to their complex aromatic structure which provide them physio-chemical, thermal and optical stability[10]. Thus adsorption technique for the removal of dyes has become quite popular these days because of their simplicity, high efficiency and as a wide range of adsorbents are available.

1.2 Objective of the research work:-

- Synthesis of mixed iron oxide and aluminium oxide nanocomposite using hydrothermal synthetic method.
- Characterization of the synthesized iron and alumina oxide using the experimental techniques- SEM, SEM-EDAX and XRD.
- Adsorptive removal of Congo red dye from aqueous system by using mixed nanocomposite.
- Optimization of the parameters, concentration, time and pH for adsorption study of dye molecules.

2. EXPERIMENTAL SECTION

2.1 SYNTHESIS OFAl_2O_3 –Fe_2O_3 NANOCOMPOSITES

In this experimental work, Al_2O_3-Fe_2O_3 nanocomposites were prepared by hydrothermal method. The Al $(NO_3)_3 \cdot 9H_2O$ and $FeSO_4.7H_2O$ salts were taken in a molar ratio of 1:1 and were mixed in a 50 ml distilled water. Then the mixed solution is stirred vigorously. Then a mixed precipitant was prepared by adding 25ml of 2M NH_3 solution into 25 ml of NaOH solution so as to maintain a ratio of 1:1. The mixed precipitant was added drop wise to above mixture solution with vigorous stirring. Simultaneously the pH of the solution was measured using pH meter. At pH 5.6 green precipitate was formed. After the formation of precipitate the whole mixture solution was transferred to a100ml Teflon lined pressure pot. The pressure pot was sealed and kept in an electric oven at 180°C for 6 h. After that the autoclave was cooled at room temperature and the resultant product was centrifuged, washed with deionised water several times and dried at 50°C for 5-6 hr followed by grinding. Further it was calcined at both 500°C and 1000°C, which was found to be reddish brown in colour, and was assumed to be Al_2O_3-Fe_2O_3 nanocomposite.

2.2 Adsorption Experiments for Congo red dye by batch process:

Adsorption study of mixed nanocomposite both sintered and unsintered samples for organic pollutants were carried out by taking 100mg of powder samples into 10ml of Congo red ($C_{32}H_{22}N_6O_6S_2Na_2$) solution (100 mgL^{-1}) under stirring condition. . This procedure continued at different time intervals at different pH and at different concentration of Congo red. After appropriate time of stirring, the solution was filtered by whatmen-40 filter paper, and finally analyzed by UV-Visible spectrophotometer (UV- 2450).

3. RESULT AND DISCUSSIONS

3.1. XRD Analysis:

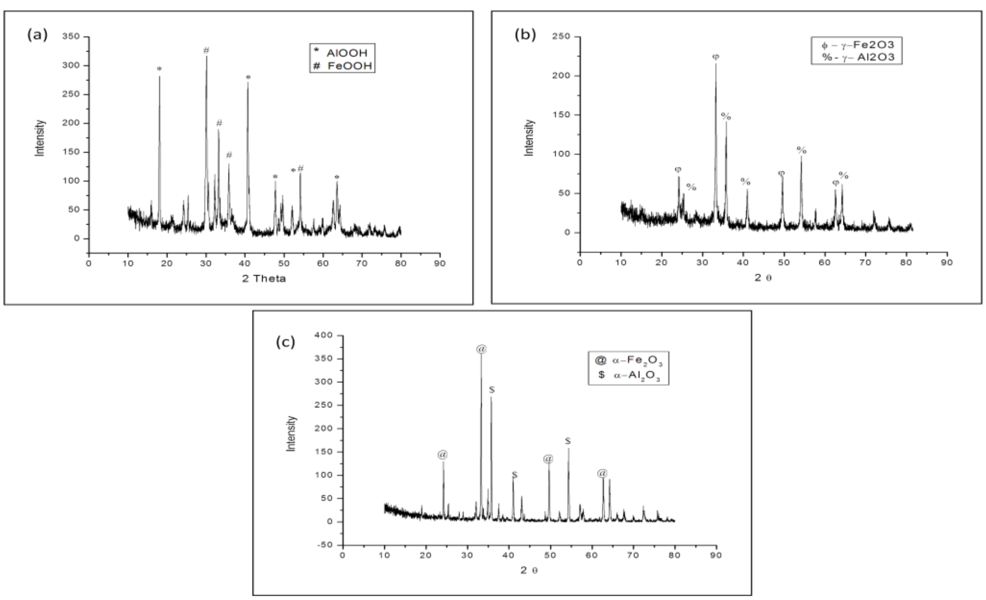

Fig1 XRD data of (a) unsintered mixed oxy-hydroxide nanocomposite, (b) mixed oxide sintered at 500^{o}C, (c) mixed oxide sintered at 1000^{o}C.

Fig.1(a) The 2θ value of boehmite sample was found to match with JCPDS – 84-0175 confirming the formation of AlOOH. Similarly the 2θ value of goethite sample was found to match with JCPDS – 77-0247 confirming the formation of FeOOH. Fig 1(b) Here the 2θ value of alumina sample was found to match with JCPDS – 29-0062 confirming the formation of γ-Al_2O_3 and the 2θ value of Iron oxide sample was found to match with JCPDS – 89-8104 confirming the formation of γ-Fe_2O_3. Fig 1(c) The 2θ value of alumina sample was found to match with JCPDS – 76-0144 confirming the formation of α-Al_2O_3 and the 2θ value of Iron oxide sample was found to match with JCPDS – 84-0311 confirming the formation of α-Fe_2O_3.

3.2 SEM and EDAX ANALYSIS:

The surface morphology of alumina and iron mixed oxide composites have been studied by scanning electron microscopy method. Fig.2 represents the SEM and EDAX images of mixed AlOOH-FeOOH and γ-Al_2O_3-γ-Fe_2O_3 nanocomposites prepared by hydrothermal synthesis.

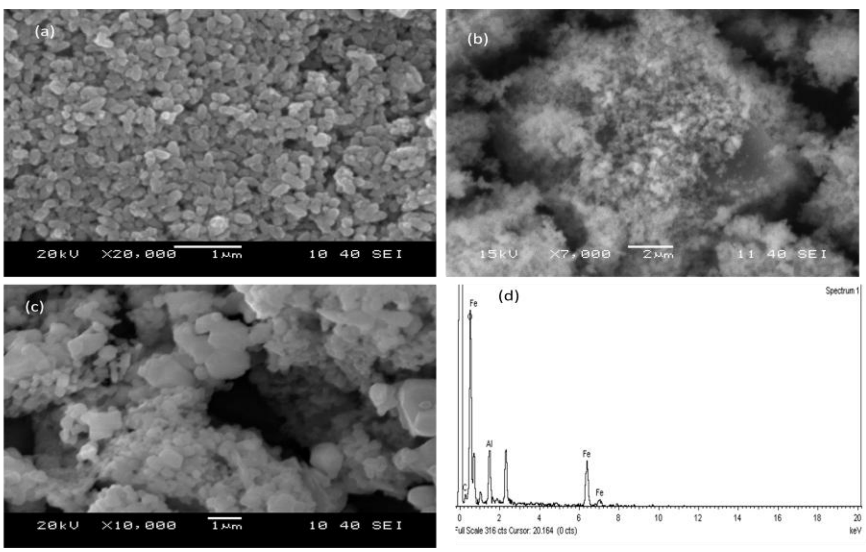

Fig 2 SEM image of (a) mixed AlOOH and FeOOH nanocomposite, (b) mixed γ-Al_2O_3 and γ-Fe_2O_3 nanocomposite sintered at 500^{o}C, (c) mixed α-Al_2O_3 and α-Fe_2O_3 sintered at 1000^{o}C, (d) EDAX image of mixed alumina and iron oxide nanocomposites .

The presence of Fe, Al and O elements in the mixed composite were confirmed by the EDAX spectrum (Fig 2d).

3.3. Adsorption Study:

3.3.1. Effect of Contact time:

The effect of contact time on the adsorption of Congo red was studied to determine the time taken by samples to remove 100 mgL^{-1} congo red solution. The variation of Congo red adsorbed with time is shown in the figure 3. It was observed from the figure that the Congo red absorptions by fixed amount of γ-Al_2O_3-γ-Fe_2O_3 (sintered at 500^oC) and oxy-hydroxy nanocomposites increase with increase in time achieves the equilibrium after 15 min contact time. This is because, a large number of vacant surface sites were available for adsorption during initial stage.

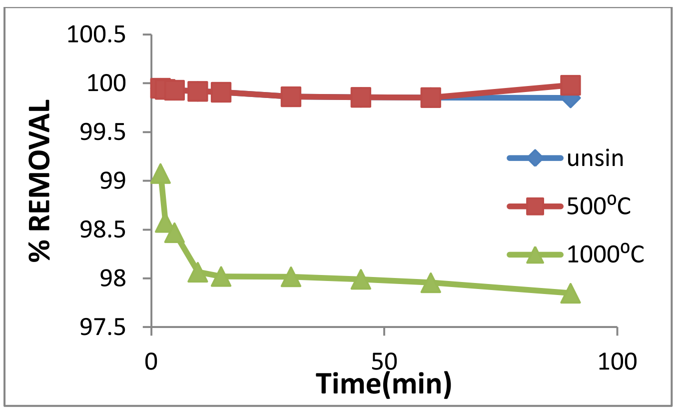

Fig 3: Effect of contact time on removal of the Congo red dye

3.3.2. Effect of concentration

The variation of Congo red adsorbed with concentration of the solution is shown in fig 4. The percent removal of Congo red solution onto mixed AlOOH and FeOOH nanocomposites (unsintered sample) by adsorption was decreased with increase in concentration of Congo red shown in figure given below. Whereas the percent removal of Congo red onto γ-Al_2O_3 and γ-Fe_2O_3 nanocomposites with concentration increases by increase in concentration of Congo red.

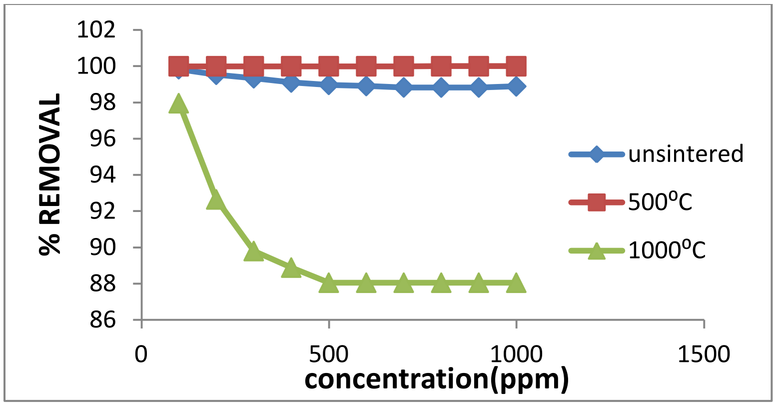

Fig 4: Effect of concentration on percentage removal of the Congo red dye

3.3.3. Effect of pH

The variation of Congo red adsorbed with pH of the solution is shown in figure 5. We have varied the pH in the range 3-8 to study the effect on the removal of Congo red. The pH of the solution was adjusted by using 0.01 mol L^{-1} HCl or NaOH solutions. From the graph it was shown that the percent removal of Congo red has no effect on the pH of the solution and therefore we have carried out all the adsorption experiment at neutral pH 7. It was observed that percent removal of Congo red by both sintered and un-sintered samples with different pH have almost same values. But the sample sintered at 1000°C showed less removal percent as compared to the oxy-hydroxy sample and the sample sintered at 500°C.

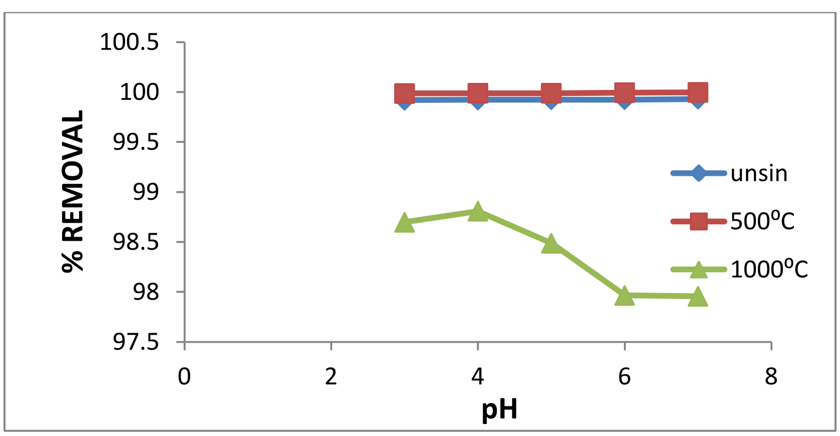

Fig 5: Effect of pH on percentage removal of the Congo red dye

3.4 Adsorption Isotherms:

Adsorption isotherm is important to describe how solutes interact with the sorbent. The capacity of an adsorbent towards a specific adsorbate can be described by different equilibrium sorption isotherm models.

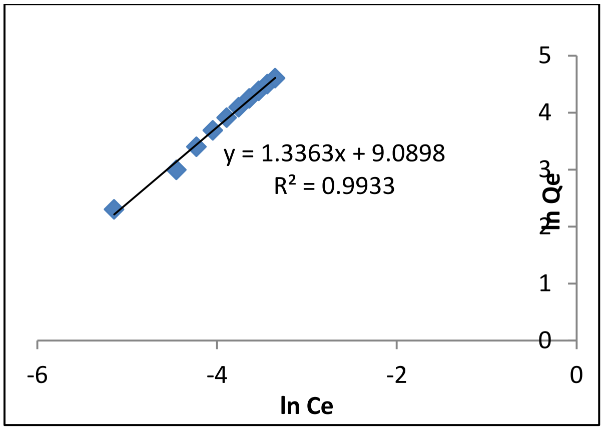

Fig 7: Freundlich isotherm data of Congo red adsorption onto sintered sample at 500°C .

It was observed that the unsintered mixed nanocomposites and sintered mixed nanocomposites fitted best in Freundlich Isotherm than Langmuir Isotherm model.

3.5 Adsorption kinetics:

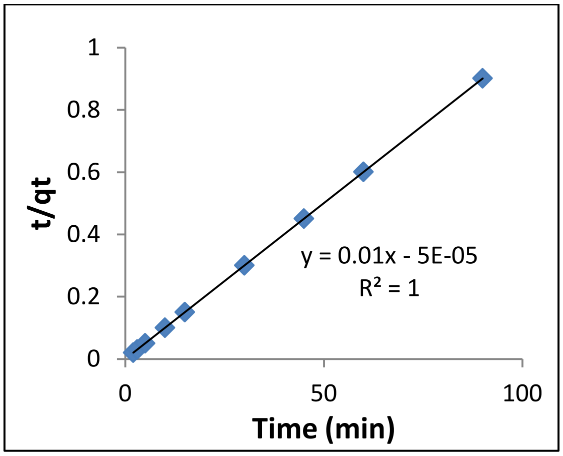

Fig 8: Pseudo-second order sorption kinetics of Congo red dye adsorptions onto mixed AlOOH-FeOOH.

It was observed that the un-sintered as well as the sintered (500^0 C) mixed nanocomposites obeyed pseudo-second order kinetics.

4. CONCLUSION:

- Mixed alumina and iron oxide nanocomposites were prepared by the method of hydrothermal synthesis and were characterized by SEM , EDAX and XRD.
- Adsorption study was carried out for the removal of Congo red dye using the above prepared mixed nanocomposite and the parameters such as effect of concentration, time and pH were studied for sorption of congo red from aqueous solution.
- The mixed nanocomposites obeyed Freundlich isotherm model as compared to Langmuir isotherm and obeyed Pseudo second order kinetics.
- The obtained nanocomposites both un-sintered and materials sintered at 500^0 C can act as a very good adsorbent for the removal of Congo Red.

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