

**SYNTHESIS AND CHARACTERIZATION OF
Al₂O₃-CeO₂ NANO-COMPOSITES FOR REMOVAL
OF ORGANIC DYE MOLECULES**

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CERTIFICATE

This is to satisfy that the thesis entitled “*SYNTHESIS AND CHARACTERIZATION OF $Al_2O_3-CeO_2$ NANO-COMPOSITES FOR REMOVAL OF ORGANIC DYE MOLECULES*” being submitted by **Ms. Susmita Kumari Sahu** (Roll No. 409CY2028) for the partial fulfilment of the requirements for the award of M.Sc. degree in Chemistry at the National Institute of Technology, Rourkela, is an authentic work carried out by her 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.

N.I.T Rourkela

05 May'2011

Supervisor

Dr.Garudadhvaj Hota

DECLARATION

I, **Susmita Kumari Sahu** hereby declare that this project report entitled “***SYNTHESIS AND CHARACTERIZATION OF $Al_2O_3-CeO_2$ NANO-COMPOSITES FOR REMOVAL OF ORGANIC DYE MOLECULES***” is the original work carried out by me under the supervision of **Prof. 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 5, 2011

Susmita Kumari Sahu

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SUSMITA KUMARI SAHU

ABSTRACT

The Al₂O₃-CeO₂ mixed nanocomposites were successfully prepared by using combustion synthetic process. The resulting nanocomposite has been characterized by using XRD, SEM and SEM-EDAX analytical techniques. The X-Ray diffraction (XRD) analysis studies clearly suggest the formation of alumina-ceria mixed composite. The SEM analysis indicates the formation of porous and flakes like morphology in mixed composite nanomaterials. The SEM-EDAX (Element detection X-Ray analysis) results indicate the presence of Al, Ce & O elements in the alumina/ceria mixed composites. The results of combustion synthesis elucidate that the fuel to oxidizer ratio is the most effective factor for the formation and surface morphology of mixed nanocomposite. The synthesized Al₂O₃-CeO₂ mixed nanocomposite has been used for the adsorption studies of Congo red and Methyl orange dye by batch experiments. It is found from the adsorption studies that the removal percentage of Congo red is much better than methyl orange. CeO₂ particles are good adsorbent materials for removal of Congo-red and Methyl Orange dyes as compare to the pure alumina nanopowder. However, the adsorption capacity of alumina can be improve by doping with CeO₂.

Keywords: Al₂O₃-CeO₂ composite, Combustion Synthesis, Congo red, Methyl Orange

INTRODUCTION

Nanotechnology is a field of applied science focused on the design, synthesis, characterization and application of materials and devices on the nanoscale. Nanotechnology relying on the manipulation, control and integration of atoms and molecules to form materials, structures, components, devices, and systems at the nanoscale, is the application of nanoscience, especially to industrial and commercial objectives. In particular that nanotechnology consists of materials with small dimensions, remarkable properties, and great application potential.

Nanocomposite materials which exploded in recent research in material inorganic chemistry processes not only represent a creative alternative to design new materials and compounds for modern/small scale research, but also their improved or usual features allow the development of innovative industrial applications. Nanocomposites have attracted tremendous attention due to their potential applications in biomedical, catalytic, separation, chemical sensing, fuel cell, capacitor, micro-fabrication, tribological, resonant coupling, and high flux gas transport.

Alumina is a porous material and widely used as a catalyst. Its properties differ substantially from those of other porous material. Alumina is extensively used in chemical applications due to its high specific surface and is much cleared pore structure. Ceria (CeO_2) is one of the oxides which are mostly used to progress the performance of alumina. CeO_2 is a multifunctional rare earth oxide with various physics and chemical properties. Ceria can affect the structural stability and thermal stability of alumina, the degree of dispersion of a metal catalyst supported on an alumina catalyst carrier. Thus $\text{CeO}_2\text{-Al}_2\text{O}_3$ is used in many ways of catalytic process.

The present study builds on several area of research comprising methyl red dye degradation; malachite green dye removal using surfactant-modified alumina; $\text{Sn/Nb}_2\text{O}_5$ composite for methyl blue dye removing; Azo dye removal using CuFe_2O_4 ; Dye removal using metal doped alumina catalysts; $\text{Fe}_2\text{O}_3\text{-CeO}_2\text{-TiO}_2/\gamma\text{-Al}_2\text{O}_3$ as catalyst for methyl orange azo dye; porous CeO_2 nanowires/nanoarrays $\text{CeO}_2\text{-Al}_2\text{O}_3$ composite for high temperature catalytic process.

Gupta et al. (2006) in their study they have used untreated TiO_2 and Ag^+ doped TiO_2 for photo catalytic degradation of mixture of crystal violet and methyl red dye under UV irradiation. Das et al. (2009) have tested surfactant-modified alumina adsorbent for malachite green removal from water environment. More recently, Cantao et al. (2010) have reported on the removal of methyl blue using $\text{Sn/Nb}_2\text{O}_5$ composite. Lu et al. (2010), have presented a template and surfactant-free electrochemical method for the fabrication of hierarchical porous CeO_2 NWs have and NWAs, 50-200 nm of diameters and various micrometers of lengths of porous NWs/NWAs have used in removing of congo red in treatment of wastewater. Gao et al. (2009) have prepared and

characterized of spherical CeO₂-Al₂O₃ composites supporting for high temperature catalytic processes.

In this present research we have synthesized Al₂O₃-CeO₂ composites nanomaterials by combustion synthesis method. Al₂O₃-CeO₂ composites are characterized and are used as adsorbent materials for removal of organic dye molecule from aqueous system.

EXPERIMENT DETAILS

MATERIALS

The following chemicals were used for the synthesis of Al₂O₃-CeO₂ nanocomposites in all our experiment without further purifications. They are Al (NO₃)₃•9H₂O (purchased from S. D. Fine chemical Ltd. India, Ce (NO₃)₃•6H₂O (Loba Chemie. Ltd. India) and Urea (NH₂CONH₂) obtained from Loba Chemie. India. Double distilled water was used during the whole experiment.

METHODS

Al₂O₃-CeO₂ composites were prepared by combustion synthesis method. Al₂O₃-CeO₂ nanocomposites were synthesized by taking the oxidizers (Al (NO₃)₃•9H₂O;Ce (NO₃)₃•6H₂O) and fuel(urea) ratio at 1:1. However we have taken the ratio between Al (NO₃)₃•9H₂O and Ce(NO₃)₃•6H₂O in different manner such as 1:1 and 2:8. For this synthesis we have mixed the required amount of Al (NO₃)₃•9H₂O, Ce (NO₃)₃•6H₂O and urea (NH₂CONH₂) with continuous stirring and the ration of oxidizer fuel was maintained at 1:1. Thus 5 ml of doubled distilled water added to the mixed solution and stirring until complete transparent solution appears. Then it was heated in a preheated furnace for half an hour at 400°C to obtain the desire mixed nanocomposite sample.

We have also varied the molar ratio of aluminium nitrate and cerium nitrate precursors to prepared different molar ratio of Al₂O₃ - CeO₂ nanocomposites by combustion synthetic method.

ADSORPTION STUDIES

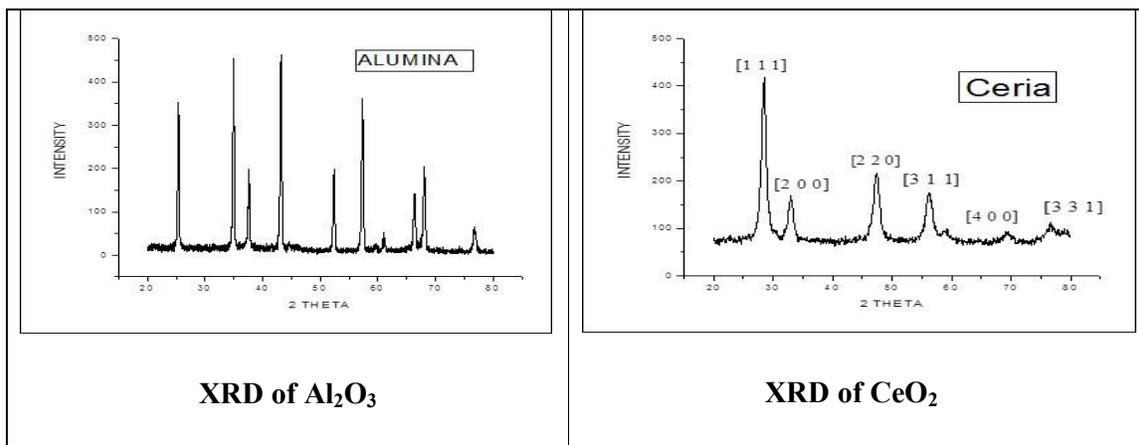
Adsorption measurements for selected organic pollutants were performed by batch experiments adding 0.1 gm of prepared sample into 20 ml of congo red (C₃₂H₂₂N₆O₆S₂Na₂) solution (100 mgL⁻¹) and 20 ml of methyl orange solution (100mL⁻¹) under stirring condition. This procedure continued at different time intervals, at different pH and at different dose/amount of sample. After the appropriate time of stirring, the solution was filtered by F-40 filter paper, and finally analyzed by UV-Visible spectrophotometer (UV- 2450).

RESULTS AND DISCUSSIONS

Aluminium oxide, Cerium oxide and Alumina/Ceria mixed nanocomposite prepared by combustion synthesis method are characterized by XRD Analysis, SEM, and EDAX Analysis.

XRD ANALYSIS

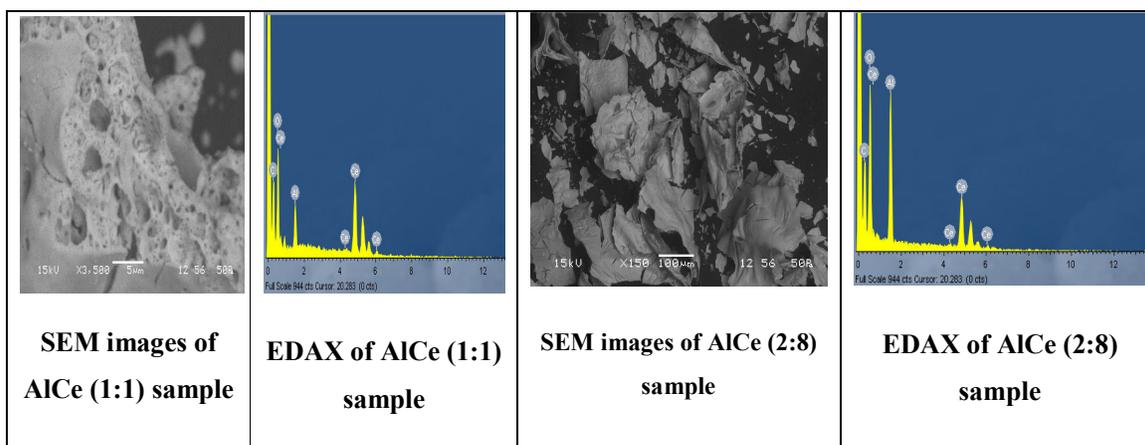
XRD of Al_2O_3 represents the X-Ray diffraction spectra of alumina and ceria particles prepared by combustion synthesis method.



The 2θ value of alumina sample was found to match with JCPDS - 42-1468 confirming the formation of alumina. The 2θ value of ceria sample was found to match with JCPDS - 81-0792 confirming the formation of ceria. X-Ray diffraction pattern also confirms the formation of alumina-ceria mixed sample.

SEM ANALYSIS

The surface morphology of alumina, ceria and alumina ceria mixed sample particles have been studied by scanning electron microscopy method. The below images represent SEM and EDAX images of Al_2O_3 , CeO_2 and mixed sample ($\text{AlCe}2:8$ and $\text{AlCe}1:1$). The EDAX analysis of alumina ceria nanocomposite suggests the presence of Al, O, Ce in the composite. The pore structure and flake like structure found in mixed sample.



Here we used alumina, ceria and mixed samples for removal of congo red and methyl orange dye from solutions. The adsorption of congo red is more in case of ceria and less in alumina. In case of mixed samples, in which amount of cerium nitrate is more i.e. AlCe2:8, the adsorption is slight increase in comparison to AlCe1:1 sample.

DYE REMOVAL

Dye removal efficiency (%R) in according to time variation (min.) was calculated from UV-Vis absorbance spectra. Here we observed that the dye removal efficiency is higher in case of pure (CeO₂) ceria nanopowder i.e. about 100%. The mixed sample AlCe 2:8 show the removal efficiency is in between 80-90%. However, incase of pure alumina (Al₂O₃) nanopowder the removal efficiency is very less. The congo red removal efficiency of the mixed composite increases with increasing is ceria doping to alumina materials. It is also observed that methyl orange dye removal efficiency in ceria is about 95%. But in other two mixed sample there is irregular dye removal efficiency in according to time variation, the range is about 32-65%. It is seen that lower pH gives high value of dye removal efficiency. In both cases pH 6 is the optimum value adsorption. After pH 6, the percentage removal efficiency maintains an equilibrium value. The graph of %R in different sample amount (sample is AlCe2:8) shows, as the amount of sample increases, the dye removal efficiency is also increases. We have varied the adsorbent doses from 0.025, to 0.1 gm for adsorption studies of both Congo red and Methyl orange dye. It is seen that the adsorption capacity of Al₂O₃-CeO₂ nanocomposite adsorbent materials is more in case of Congo red than that of methyl orange dye.

CONCLUSION

The following are some points for conclusion derived from the study.

- ❖ We have successfully prepared Al₂O₃-CeO₂ nanocomposite materials using combustion synthesis method.
- ❖ XRD studies confirmed the formation of nanocomposite materials.
- ❖ SEM micrographs suggest the ceria particles are spherical in shape and the Al₂O₃-CeO₂ nanocomposites are of flake like morphology with porous structure.
- ❖ Adsorption studies indicates that CeO₂ particles are good adsorbent materials for removal of Congo-red and Methyl Orange dyes and the adsorption capacity of alumina can be improve by doping with CeO₂.

FUTURE WORK

- ❖ This work can be extended by removing other dyes using Al_2O_3 - CeO_2 hybrid nanocomposite.
- ❖ To study adsorption performance of those dyes and comparison between them.

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