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Electrochemical Synthesis and their Photocatalytic Application of Mesoporous γ-Al2O3 Nanoparticles

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ABSTRACT

Electrochemical reduction method was used to synthesize gamma-alumina (γ-Al_2O_3) nanoparticles (NPs) by optimizing different parameters like electrolysis time, current density, concentration of stabilizer or electrolyte, separation between two electrode and solvent. The synthesized γ-Al_2O_3 NPs were characterized by analytical techniques like XRD, SEM and EDX. Moreover the γ-Al_2O_3 NPs were explored for photocatalytic degradation of cationic pollutant Rhodamine B (RhB) and anionic pollutant Congo red (CR) in aqueous solution under sunlight. The degradation was 55.06% and 63.9% for RhB and CR respectively. The rate constant for RhB and CR was found to be pseudo first-order with values 0.170 and 0.208 h^{-1} respectively.

Keywords: Electrochemical, Mesoporous γ-Al_2O_3 Nanoparticles, Photocatalytic, Rhodamine B, Congo red

INTRODUCTION

Research on synthesis of γ-Al_2O_3 NPs has received considerable attention due to their broad range of application in ceramics, adsorbents, catalysts, composite materials and molecular separation [1-5]. γ-AlOOH, γ-Al_2O_3 and α-Al_2O_3, among which γ-Al_2O_3 is the most important phase because of its remarkable properties like high insulation, high strength, high rigidity and transparency. There are several possible routes to obtain nano sized Al_2O_3 like chemical vapor deposition in flame [6], spark plasma sintering [7], hydrothermal [8,9], sol-gel [10], laser ablation [11], mercury mediated technique [12] and electrochemical reduction [13]. Variously nanostructured alumina have been synthesized such as mesoporous alumina [14,15], fiber, wires, belt, rod and tube [16-18]. Advantages of electrochemical reduction method are easy installation, time budget, high purity sample is obtained, easy isolation and no side product formation. The presence of organic waste created a serious problem to living being. The removal of organic pollutants from wastewater has been the matter of increasing interest in recent years. There are various methods for removal of RhB, CR and similar dyes from water system like coagulation, chemical oxidation, liquid-liquid extraction, electrochemical treatment, adsorption and photocatalysis [19-24].

MATERIALS AND METHODS

Chemicals and methods

All chemicals were of AR grade and purchased from Merck chemical suppliers. Distilled water was used as solvent.

γ-Al_2O_3 NPs were synthesized by electrochemical reduction method. In general procedure we have taken electrolysis cell which contains 25 mL aqueous solution of tetrapropylammonium bromide (0.01M) as the stabilizer cum electrolyte, aluminium plate (1 cm × 1 cm) and inert platinum (1 cm × 1 cm) were used as a sacrificial anode and cathode respectively. Formation of aluminium hydroxide precipitate was observed by monitoring the turbidity in solution by applying constant current density 10 mA/cm^2 for 2 h in nitrogen atmosphere. The aluminium hydroxide precipitate collected by decantation, washed with distilled water 3-4 times, dried under vacuum desiccator. This dried sample was annealed and at 900°C for 2 h to convert it to γ-Al_2O_3 NPs and stored in glass vials. The electrolytic cell can be represented as follows:

$Al_{(+)}$ | Solvent + E | $Pt_{(-)}$

Where E represents the electrolyte.

The crystal phase and crystallinity were determined by powder X-ray diffractometer with Cu-Kα radiation (λ=1.5406 Å) recorded using Bruker D8 Advance. The surface morphology of γ-Al_2O_3 NPs was studied by scanning electron microscopy carried out with JEOL-LED 2300 (LA) equipment. The chemical composition of the γ-Al_2O_3 NPs was determined by using an energy dispersive X-ray spectroscopy (EDS; combined spectrometer/SEM instrument) A UV-vis spectrophotometer (Shimadzu 1800) was used to determine the photocatalytic activities of the γ-Al_2O_3 NPs in the degradation of RhB and CR dye.

Photocatalytic activity test

The photocatalytic activities of the γ-Al_2O_3 NPs under sunlight irradiation were determined by measuring the photo degradation of RhB and CR aqueous solution (25 mg/lit). RhB and CR dyes have different molecular structure and different functional group (**Figure 1**). The RhB is a cationic dye with a methyl nitride group [$(C_2H_5)_2N^+$] and the CR is an anionic azo dye with sulfonate group (SO_3^-). For the reaction 100 mg of γ-Al_2O_3 NPs was dispersed in 250 mL 25 mg/lit dye solution in pyrex beaker, to establish the absorption/desorption equilibrium, Teflon coated magnetic stirrer used to stirred reaction mixture magnetically. After equilibrium was established, the suspension was exposed to sunlight with constant stirring. During the reaction 5 mL solution was withdrawn at specific time intervals and centrifuged. The absorbance maxima for RhB and CR were determined at 553 and 497 nm respectively using UV-vis spectrophotometer.

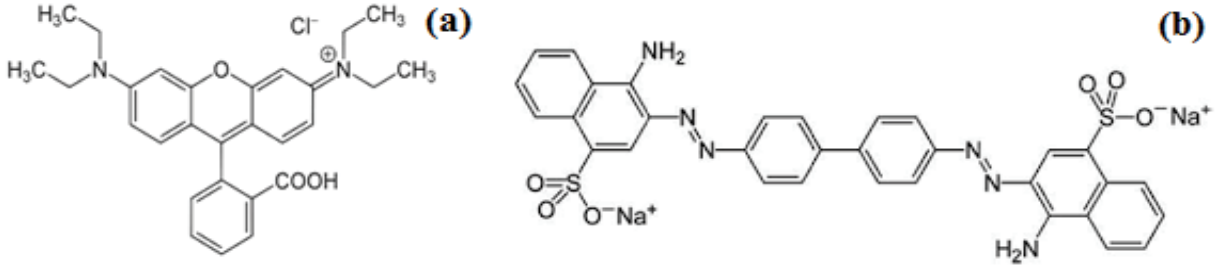

Figure 1: Structure of RhB (a) and CR (b).

RESULTS AND DISCUSSION

XRD studies

X-ray diffraction analysis (XRD) was used to confirm the crystal phase, purity and average grain size of NPs. (**Figure 2**) shows the XRD pattern of γ-Al_2O_3 NPs. The peaks that appeared at 2θ values of 32.60°, 38.49°, 46.71°, 56.76°, 61.37°, 67.94° and 77.29° correspond to the characteristic reflection of (220), (222), (400), (422), (511), (440) and (621) planes of the cubic γ-Al_2O_3 structure well-coordinated with JCPDS card no. 02-1420. The average grain of the γ-Al_2O_3 NPs is 18.15 nm.

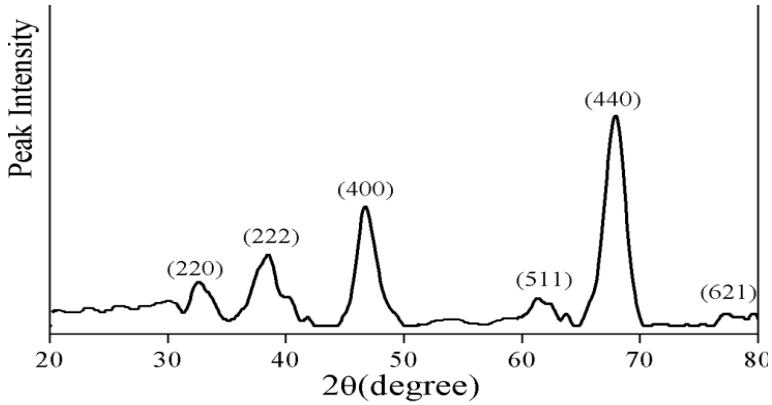

Figure 2: XRD pattern of a synthesized γ-Al_2O_3 NPs.

SEM - EDX studies

Figure 3a and **3b** are SEM micrograph and EDX spectrum of γ-Al_2O_3 NPs respectively. SEM image shows mesoporous structure of nanoparticles. EDX spectrum shows absence of elemental impurities in the prepared γ-Al_2O_3 NPs.

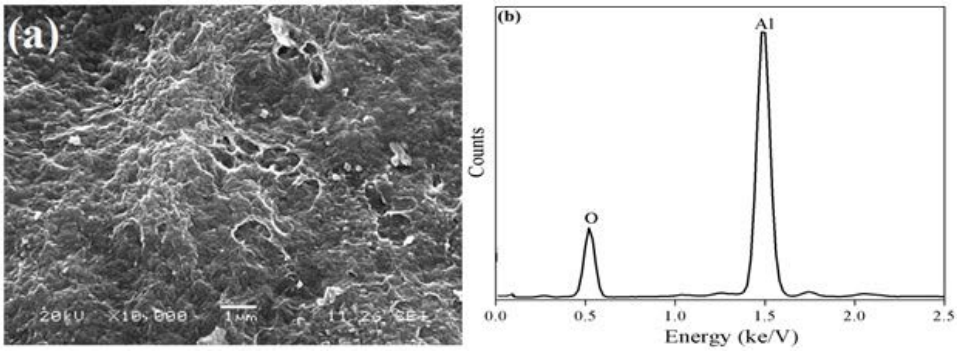

Figure 3: (a) SEM image of synthesized γ-Al_2O_3 NPs (b) EDX spectrum of synthesized γ-Al_2O_3 NPs.

Photocatalytic degradation studies

Photodegradation of RhB and CR using γ-Al_2O_3 NPs under sunlight irradiation was studied. The decrease in absorbance values in presence of γ-Al_2O_3 NPs with irradiation time, were observed for RhB and CR as indicated in **Figure 4a** and **4b**. It clearly revealed the efficient degradation of these dyes. The color of dyes solution faded within 6 h in sunlight irradiation in presence of γ-Al_2O_3 NPs. The % degradation was found to be 55.06% and 63.9% for RhB and CR respectively shown in **Figure 5a**. The rate of photocatalytic degradation for RhB (0.170 h^{-1}) was lower than CR (0.208 h^{-1}) exposed in sunlight (**Figure 5b**).

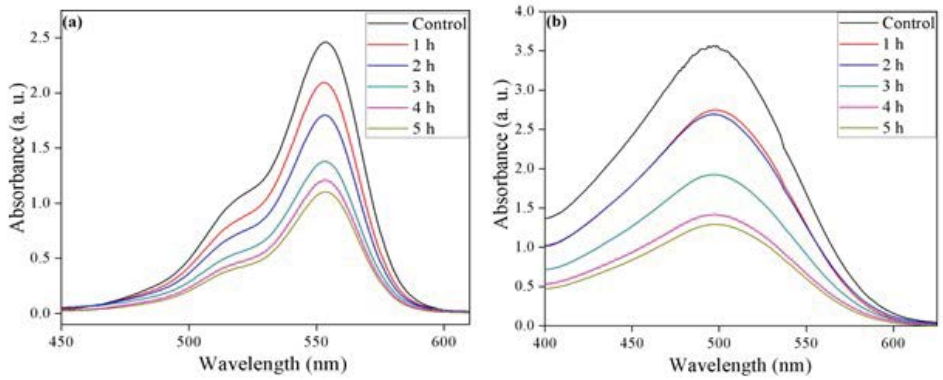

Figure 4: UV-vis absorption spectra of RhB (a) and CR (b) aqueous solution in the presence of γ-Al_2O_3 NPs at different irradiation times.

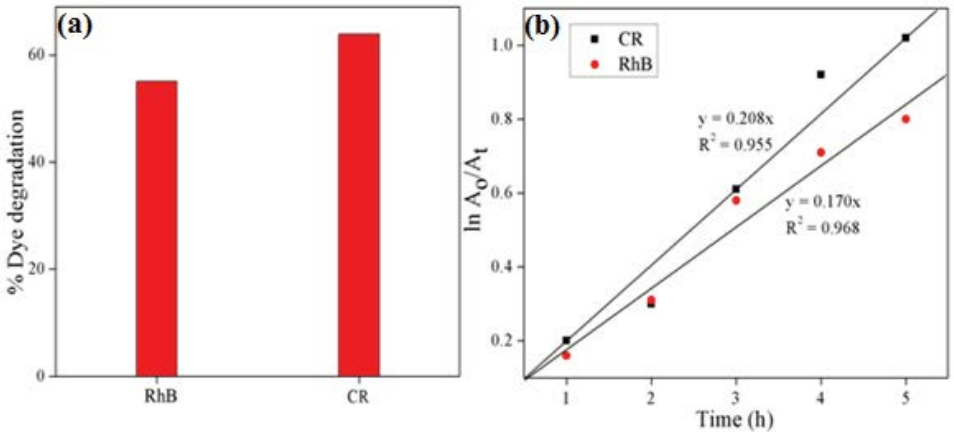

Figure 5: Percentage (%) dye degradation and pseudo first order kinetics respectively.

CONCLUSION

In this study γ-Al_2O_3 NPs were successfully synthesized by an electrochemical reduction method. The XRD pattern revealed that formation of cubic structure γ-Al_2O_3 NPs. The average grain size of synthesized NPs is 18.15 nm SEM image indicate mesoporous nature of NPs. EDX spectrum represent only Al and O that is complete removal of electrolyte. The prepared γ-Al_2O_3 NPs were used as a photocatalyst for the degradation of RhB and CR dye under sunlight irradiation. The higher degradation of CR was recorded 63.9% as compared to RhB dye. The rate constant for RhB and CR was found to be pseudo first-order with values 0.170 and 0.208 h^{-1} respectively.

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