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Ceramics International 39 (2013) 5443–5451

CERAMICS INTERNATIONAL

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Adsorptive removal of Congo red dye from wastewater by mixed iron oxide–alumina nanocomposites

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Received 30 November 2012; received in revised form 3 December 2012; accepted 15 December 2012
Available online 26 December 2012

Abstract

Nanocomposites composed of mixed iron and aluminium oxide (Fe_2O_3–Al_2O_3), have been synthesized by hydrothermal method, and further used as adsorbent for the adsorptive decolorization of Congo red dye from an aqueous system. The as-prepared nanomaterials were sintered at 500 °C and 1000 °C, to obtain pure Fe_2O_3–Al_2O_3 mixed composites. The XRD studies confirmed the formation of pure and crystalline FeOOH–AlOOH (as-prepared), γ-Fe_2O_3–Al_2O_3 at 500 °C and α-Fe_2O_3–Al_2O_3 phases at 1000 °C. The morphology and size of the obtained nanocomposites were characterized by SEM and TEM. Effects of pH, contact time, initial concentration of adsorbate have been studied. The optimum pH for maximum removal of Congo red in all the three phases of nanocomposites was found to be 7. The maximum removal capacity was 498 mg/g for γ-Fe_2O_3–Al_2O_3 phases. Among the three different adsorbents, γ-Fe_2O_3–Al_2O_3 shows complete removal within 15 min of contact time.

Keywords: Nanocomposites; Hydrothermal method; Congo red; Adsorbent

1. Introduction

Composites where nanoscale inclusions are imbedded within matrix of a material have attracted increasing research attention in recent years. Nanocomposites refer to materials consisting of at least two phases with one dispersed in another that is called matrix and thus forms a three dimensional network [1]. Nanocomposites exhibit properties different from that of the bulk material. A small inclusion of nano sized particle produces a great change in the properties [2]. As the nano-scale morphology plays an important role in achieving desired macroscopic properties, it is important to characterize the interaction of the nanoscale samples with the intrinsically immiscible phases [3]. Nanocomposite with fine uniform domains is challenging because we need to control both the micro structural length scales as well as the elemental distributions. Now-a-days, researchers are much more interested in mixed metal oxide nanoparticle because of its broad class of catalytic, electronic, magnetic properties and also for its heterogeneous catalysis [4]. Recently, Dong et al., have synthesized iron oxide and alumina nanocomposite (Fe_2O_3–Al_2O_3) with a unique structure, which shows a remarkable catalytic performance in Fischer–Tropsch synthesis [5]. These nanoparticles often exhibit superior properties and performance; it is because of its large specific surface area. Among various metal oxides the oxides of aluminium (Al) and iron (Fe) have large advantages because of their low cost, extensive availability, thermal stability and remarkable adsorption capacity [6,7]. Violante et al. have studied on the adsorption of heavy metal ions on mixed Fe–Al oxides in absence or presence of increasing concentrations of oxalate or tartrate [8]. Ground water and surface water pollution is a serious problem due to its high toxicity for the presence of dyes and organic waste. Among them Congo red dye is an important source of water pollution and a known human carcinogen. Congo red dye is a benzidine-based azo dye with a complex chemical structure and is highly soluble in aqueous solution. It is generated from textiles, printing and dyeing, paper, rubber, plastics

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0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2012.12.052

industries etc [9]. Therefore, it is very important to remove the remaining Congo red before it mixed up with any water resource. Structural stability of Congo red is the major challenge for its removal from wastewater treatment [10]. Different process have been used to remove Congo red from colored effluents but among all, adsorption has been recognized as the most popular treatment process due to its simplicity, high efficiency, easy recovery and the reusability of the adsorbent [11–13]. Similarly, Gong et al., studied the removal of cationic dyes from aqueous solution using magnetic multi-wall composite carbon nanotube as adsorbent. Adsorption characteristics of the nanocomposite adsorbent were examined using methylene blue, neutral red and brilliant cresyl blue as adsorbates [14].

In the present study, iron oxide–alumina mixed nanocomposite was prepared by hydrothermal method and their adsorption characteristic for the removal of Congo red dye from aqueous solution was studied. The synthesized mixed oxy-hydroxide sample was sintered at different temperatures to obtain mixed oxides nanocomposites. The adsorption experiments such as effect of contact time, pH, adsorbent dose and initial concentration variation were explored in batch experiments. The adsorption isotherm and kinetic studies were also carried out to elucidate the adsorption mechanism. A comparative study for maximum removal capacity of using different mixed oxide nanocomposite adsorbents was also reported here.

2. Experimental section

2.1. Materials

Ferrous sulphate ($FeSO_4 \cdot 7H_2O$) and Aluminium nitrate ($Al\ (NO_3)_3 \cdot 9H_2O$) of analytical grade with purity 99.0% was obtained from Merck, India. Both NaOH pellets and NH_3 solution were also obtained from Merck, India. All chemicals were used without further purifications. Double distilled water was used throughout the experiments for preparation and dilution of the solutions.

2.2. Synthesis of Fe_2O_3–Al_2O_3 nanocomposites

In this work, Fe_2O_3–Al_2O_3 nanocomposites were prepared by hydrothermal method. The $Al\ (NO_3)_3 \cdot 9H_2O$ and $FeSO_4 \cdot 7H_2O$ salts were taken in a molar ratio of 1:1 and were mixed in 50 mL distilled water. Then the mixed solution was stirred vigorously. At the same time, a mixed precipitant was prepared by adding 25 mL of 2 M 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. The formation of precipitate in the whole mixture solution was transferred into a 100 mL Teflon cupped pressure pot. The pressure pot was sealed and kept in an electric oven at 180 °C for 6 h. After that the pressure pot 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 h followed by grinding. The obtained deep yellow powder was further calcined at 500 °C and 1000 °C, to form mixed Fe_2O_3–Al_2O_3 nanocomposite.

2.3. Characterization

The surface morphology of iron oxide–alumina mixed nanocomposite was characterized by using a SEM JEOL JSM- 5300 and was operated at 15 kV. In order to increase the conductivity of the samples, they were gold coated using a JEOL FRC 1200 fine coater before taking SEM. The powder X-ray diffraction patterns were obtained on a Pan analytical X-ray diffractometer (PW1830) using Cu K_α ($\lambda = 1.541$ Å) radiation. A JEOL 200 HRTEM was used to characterize the iron oxide–alumina mixed nanocomposite materials and was operated at 200 kV. The mixed nanocomposites were dispersed in ethanol and then a drop of the above dispersion was taken on a carbon coated copper grid (300 meshes) for HR-TEM imaging. A digital pH meter (Satorius Model PB-11) combined with glass electrode was used for all experiments. A Shimadzu UV–visible spectrophotometer (Shimadzu-2450) was used for adsorption study of Congo red dye.

2.4. Adsorption experiments for Congo red dye by batch process

The un sintered and sintered mixed iron oxide–alumina nanocomposites samples were used as adsorbent for removal of organic dye pollutants. The adsorption study was carried out by taking 100 mg of powder samples into 10 mL of Congo red ($C_{32}H_{22}N_6O_6S_2Na_2$) solution (100 mg/L) under stirring condition. The adsorption study was carried out with change in different parameters viz. change in time, pH, and initial concentration of Congo red. After appropriate time of stirring, the solution was filtered using whatman-40 filter paper, and finally analyzed by UV–visible spectrophotometer.

3. Result and discussion

3.1. Structural properties

We have used hydrothermal method for preparation of iron–aluminium oxide mixed nanocomposites powder. The obtained powder was sintered at different temperatures and the formation of different phases was confirmed by XRD study. Fig. 1 shows the XRD pattern of iron oxide–alumina mixed nanocomposites. This result revealed that the formed materials are crystalline in nature. Fig. 1(a) shows XRD pattern of the as prepared mixed nanocomposites. It is observed from the XRD data that the hydrothermal mediated synthesis of as prepared samples consists of mixture of boehmite (γ-AlOOH) and lepidocrocite (γ-FeOOH) phases, which is confirmed from the JCPDS Files (File no.84-0175) and (File no. 77-0247),