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Preparation and characterization of porous fly ash/$NiFe_2O_4$ composite: Promising adsorbent for the removal of Congo red dye from aqueous solution

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HIGHLIGHTS

- Fly ash/$NiFe_2O_4$ composite was prepared and characterized to remove Congo red dye.
- Higher adsorption facilitated by surface area, spinel structure and porous nature of composite.
- Composite with 50% $NiFe_2O_4$ was found to be optimum for maximum CR removal.
- The sorption data were evaluated by sorption isotherm.
- Dye adsorbed composite can be regenerated by thermal decomposition and used repeatedly.

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ABSTRACT

A series of fly ash/$NiFe_2O_4$ composites were prepared using fly ash and aqueous solutions of Ni, Fe nitrate salts and NaOH by co-precipitation followed by calcination method. The % mass ratio of fly ash: $NiFe_2O_4$ was varied in the range of 0:100 to 100:0. Samples were characterized by powder XRD, SEM, FTIR and N_2 adsorption–desorption measurements. These samples were further evaluated for their adsorptive performance in removal of Congo red (CR) dye from an aqueous solution. In all the composites, spinel nickel ferrite phase was found to be capable to get anchored with the fly ash surface and exhibited more crystalline nature as compared to pure $NiFe_2O_4$ phase. The BET surface area and porous character of the composite were found to increase with the decrease in the contribution of the fly ash, reach to maximum and then decreases on further decrease in fly ash. The composite having % mass ratio of fly ash: $NiFe_2O_4 = 50:50$ exhibited maximum CR adsorption from the aqueous solution on account of the higher BET surface area, more porous character, favorable condition for diffusion of dye molecules and combined effect of chemisorption and physisorption. Under optimum conditions, it has shown the recyclability with adsorption capacity of the magnitude 23.33 mg g^{-1}, which is much higher than individual fly ash, $NiFe_2O_4$ and other composites. The sorption data provided good fit with pseudo-second order kinetic model. The analyses of the adsorption data indicated that, the Langmuir model provides better correlation with the experimental data.

1. Introduction

Synthetic dyes are widely used for coloring purposes in textile, cosmetic, printing, food, leather and plastic industries. Worldwide, more than 70,000 t of dyes are produced per year out of which, approximately 100 t of dyes discharge in the form of effluent by these industries [1]. Due to the toxic and/or carcinogenic nature and the tendency of consuming the dissolved oxygen required by aquatic life, presence of even trace quantity of some of the dyes in the colored waste-water is considered as eco-toxic hazard, an objectionable type pollutant [2–4]. Congo red (CR), a sodium salt of benzidinediazobis-1-naphthylamine-4-sulfonic acid is one of such dyes. CR is benzidine-based anionic dye and hence it is human carcinogen as it metabolizes to benzidine [5]. Due to its structural stability and low-biodegradability, CR resist fade when exposed to

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light, water and many chemicals and hence it becomes difficult to remove once it is released into the aquatic environment [6].

Various methods of dye removal, like adsorption [7–10], nanofiltration [11], membrane separation [12], coagulation [13–15], aerobic and anaerobic microbial degradation [16] and chemical oxidation [17] have been reported. Among these techniques, adsorption has been found to be superior with high potential for the removal and recovery of dyes from wastewater. To remove CR from waste effluents, different adsorbents like activated carbons [18], modified papaya seed [19,20], surfactant-modified montmorillonite [21], aminopropyl silica xerogel [22], organo-attapulgite [23], acid activated red mud [24], iron oxide nanoparticles [25], mesoporous nanocomposite $Al_2O_3/Ni_{0.5}Zn_{0.5}Fe_2O_4$ microfibers [26], graphene oxide [27], etc. have been studied. Among these adsorbents, activated carbon is most widely used because of its high efficiency and high sorption capacity. However, its use is limited by high cost of production and regeneration. Thus, the development of alternative low cost and efficient adsorbent for removal CR from aqueous solution remains an important problem and attracting growing attention.

The increase in demand for power in domestic, agricultural, and industrial sectors has increased the pressure on the electricity generation units. Consequently, generation of electricity through thermal route involving combustion of pulverized coal has been increased. Coal fly ash (CFA) is a solid waste residue produced by combustion coal in bulk quantities. As a result, the research targeting effective utilization or recycle of fly ash has been gaining momentum [28–30]. On account of a very high adsorption capacity for variety of metals and organic compounds, fly ash has been used as adsorbent to remove water contaminants like as phenolic compounds, pesticides, and dyes [31]. CFA has been employed as an adsorbent for removal of dyes like methylene blue, crystal violet, rhodamine B, rosaniline hydrochloride, acid blue, acid red/black-1, etc [32,33], suggesting that, fly ash is a potential absorbent for dye removal of different types. However, fly ash performance for the dye removal depends strongly on origin, type, and treatment [34–36]. Mall et al. [6] reported that the adsorption of CR on fly ash collected from bagasse fired boiler is most favorable in comparison to the activated carbons. Bilal Acemioğlu reported adsorption of CR onto type C fly ash with 23.66% CaO [37]. However, no report on utilization of CFA to remove CR from water is available. Our preliminary study using CFA exhibits low absorption of CR from aqueous solution. Therefore, we thought that modification of CFA is needed to enhance the CR adsorption.

In recent years, spinel oxides have attracted a growing attention in wide range of applications because of their interesting structural features and physico-chemical properties [38]. These materials have a general formula AB_2O_4, in which A and B sites are occupied by di- and tri-valent cations respectively. Magnetic spinel ferrites (MFe_2O_4, M = Cu, Ni, Mn, etc.) have been studied to evaluate their performance in the removal of aqueous pollutants as they possess high surface area and the advantage of easy separation under external magnetic fields [39–41]. However, application of these materials is hindered by high cost, low adsorption capacity and narrow application range. For example, $CuFe_2O_4$, and $MnFe_2O_4$ could only be used to adsorb ionic organic pollutant. To overcome these disadvantages, several attempts such as impregnation over activated carbon [42], ball milling [43], and chemical coprecipitation with activated carbon [44,45] have been made. By virtue of its simplicity and no demand for special chemicals and procedures, chemical coprecipitation method seems to be most promising. Previous studies mainly focused on preparation of adsorbents containing carbon and iron oxide aiming at making magnetically separable activated carbon and regeneration of spent magnetic composites. Although, CFA and MFe_2O_4 individually have shown promising adsorption capacity, no systematic studies have been reported on the possibility of using CFA/MFe_2O_4 composites for maximizing the dye removal capacity. To best of our knowledge, no information is available about the preparation and application of CFA/spinel ferrites composites in adsorptive removal of CR from aqueous system. Therefore, the research work dealing with the feasibility and efficacy of CFA/$NiFe_2O_4$ composites for adsorption of CR from aqueous solution was undertaken.

The present study focuses on the preparation of fly ash/$NiFe_2O_4$ wherein the % mass ratio of fly ash/$NiFe_2O_4$ was varied in the range of 0:100 to 100:0. All the samples were characterized by powder XRD, SEM, FTIR and N_2 adsorption–desorption measurements. Their efficiency in adsorptive removal of CR dye from an aqueous solution was investigated in batch experiments. The influence of various parameters such as contact time, adsorbent dosage, initial dye concentration and temperature on the adsorption capacity has been investigated. The recyclability of the optimum adsorbent after its regeneration has also been studied using optimum adsorption conditions. The adsorption data were also analyzed in detail and discussed in the present communication.

2. Experimental

2.1. Preparation of fly ash/$NiFe_2O_4$ composites

Stock solutions were prepared by dissolving $Ni(NO_3)_2 \cdot 6H_2O$ (98% Thomas Beaker, India) and $Fe(NO_3)_3 \cdot 9H_2O$ (98% Thomas Beaker, India) in distilled water to obtain 3 and 2 M solutions respectively. A solution with a Fe:Ni mole ratio of 2:1 was prepared by mixing Ni and Fe stock solutions at room temperature with constant stirring. To this, an appropriate amount of fine powder of coal fly ash (Parli Thermal Power Station Ambajogai, Maharashtra, India) was added in such a way that, the Fly ash/$NiFe_2O_4$ % mass ratios equals to 90:10, 70:30, 50:50, 30:70 and 0:100. Aq. NaOH solution (5 mol) was added to this slurry slowly with constant stirring until the pH becomes 10 ± 0.2 and stirring was further continued for 1 h. The solid was recovered by filtration and then washed thoroughly with distilled water. The wet cake was dried in an air oven at 90 °C for 12 h. The dried material was ground to fine powder and then calcined at 400 °C for 6 h. The final products thus obtained were designated as $FANiFe_{10}$, $FANiFe_{30}$, $FANiFe_{50}$ and $FANiFe_{70}$ where the numbers indicate the percentage mass of $NiFe_2O_4$ in the sample. The individual fly ash (% mass ratio of fly ash/$NiFe_2O_4$ = 100:0) and $NiFe_2O_4$ (% mass ratio of Fly ash/$NiFe_2O_4$ = 0:100) were designated as $FANiFe_0$ and $FANiFe_{100}$ respectively.

2.2. Characterization

The phase identification and purity were examined by powder X-ray diffraction (XRD), (P Analytical PXRD system, Model X-Pert PRO-1712) using nickel-filtered CuKα radiations and employing scanning rate of 0.0671°/s in the 2θ range from 10 to 80°. The Scanning Electron Microscope (SEM) images were obtained by using microscope (LEICA Stereo Scan 440) after coating the sample with Au–Pd evaporated film. Nitrogen adsorption–desorption isotherms were obtained using a conventional volumetric nitrogen adsorption apparatus (Micromeritics ASAP 2010 system). The calcined sample was activated by degassing it at 250 °C for 10 h at 0.00133 Pa, prior to the measurements. The sample was then cooled to −196 °C using liquid nitrogen and the sorption of nitrogen was carried out at different equilibrium pressures. The specific surface area of the sample was calculated using Brunauer, Emmett, and Teller (BET) method. The FTIR spectra were recorded on a