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Full Length Article

Preparation and characterization of sulfonated polystyrene/magnetite nanocomposites for organic dye adsorption ☆

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A B S T R A C T

Magnetite nanoparticles (MNPs) were prepared by co-precipitation method and were found to have average size of 5 nm with spherical shape crystalline structure with super-magnetic properties. Commercial polystyrene (PS) was sulfonated through the reaction with freshly prepared acetyl sulfate. Three different degrees of sulfonation, based on the ratio of the acetyl sulfate to polystyrene, were prepared (1:1, 1:3 and 1:5). Nanocomposites of the prepared magnetite nanoparticles 1:3 sulfonated polystyrene were prepared at different magnetite content (1, 5 and 10%). The produced materials were characterized by dynamic light scattering (DLS), transmittance electron microscope (TEM) X-ray diffraction (XRD) and vibrating sample magnetometer (VSM). PS, MNPs and the prepared nanocomposites were investigated as adsorbents for Congo Red (CR). The variables influencing the adsorption capacity, such as solution pH, contact time and the initial dye concentration were systematically investigated. The adsorption for CR by the previous adsorbents show maximum experimental uptake capacity of 26.78, 33.15, 53.35, 64.73, and 76.29 mg/g for PS, MNPs, SPS/MNPs 1%, SPS/MNPs 5% and SPS/MNPs 10%, respectively. The adsorption process was found to follow the pseudo second order kinetic model and fit quite well with Langmuir adsorption isotherm.

1. Introduction

For the greater part of human history, water has been in abundant supply in most regions of the world and therefore was an accessible resource for the vast majority of humanity. Sadly, this is no longer the case; in 2015, according to the United Nations, close to 800 million people have no access to safe, clean water sources and the number continues to climb [1]. Water pollution is defined as any chemical, biological, or physical change in water quality that has a harmful effect on living organisms or makes water unsuitable for desired usage. One of the major water contaminants is organic compounds, such as pesticides, organochlorines, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and organic dyes. Organic dyes are extensively used in various industries including dyestuff, paper, leather, cosmetic and textile [2]. Nevertheless, dye effluents are the most significant identified contaminant amongst the various pollutants of wastewater, because the presence of these dyes in water even at very low concentration is highly observable. At the same time, they may cause allergic dermatitis or skin irritation, may be carcinogenic and mutagenic to humans and aquatic organisms [3]. Azo dyes are the largest group of synthetic colorants known and have given rise to many water and soil environmental problems, especially Congo red (CR), the most widely used azo dye in textile industry. Because of the high stability against light, temperature, chemicals and microbial attack, azo dyes were difficult to decompose and remove from water using traditional wastewater treatment methods [4]. Recently, several techniques have been developed and implemented for the removal of CR molecules from dye effluents among which adsorption, as versatile technique, is preferred compared to others in terms of high efficiency, easy handling and cost-effectiveness [5]. Most commercial systems currently use zeolites, activated carbons, industrial by-products, agricultural wastes, clays, biomass and polymeric materials as adsorbents for this target [6,7]. However, the application of these adsorbents is limited because of their low adsorption capacities and separation inconvenience. Thus, great efforts are needed to exploit new promising adsorbents [2]. Recently, magnetic nanomaterials have attracted much interest, because they not only have a large removal

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capacity, fast kinetics and reactivity for contaminant removal, but also have high separation efficiency and reusability [8,9]. In recent years, many magnetic nanomaterials modified surface functionality have been studied for the removal of dyes and their adsorption conducts have been studied under moderate condition [10].

Zhang et al. studied the removal of both cationic dye (malachite green) and anionic dye (CR) by magnetic $Sr_5xBa_3x\ (PO_4)_3(OH)/Fe_3O_4$ nanopowder (namely SBPF) from aqueous solution under variables influencing the adsorption capacity, such as solution pH, temperature, adsorbent dosage, adsorption time and initial concentration, were systematically investigated. The adsorption process was found to be pH and temperature dependent and follow the pseudo-first-order and pseudo-second-order kinetic model for MG and CR, respectively and adsorption behaviors fit quite well with the Langmuir model for both dyes [11].

Zhang et al. prepared $Fe_3O_4/nSiO_2/mSiO_2$ and studied the contact time, CR initial concentration, temperature and pH on the adsorption capacity. The adsorbent shows highly efficient adsorption properties with adsorption kinetics and isotherm well fitted to pseudo-second-order kinetic and Langmuir isotherm models [12].

Beyki et al. prepared magnetic $MnFe_2O_4$ nanoparticles and $MnFe_2O_4$ reinforced polyamide resin. Prepared magnetic resin was employed as a green adsorbent for removing CR from aqueous solution with equilibrium obtained within one minute [13].

Beyki et al. synthesized Fe_3O_4-cellulose nanohybrid, epichlorohydrin and 1-methylimidazole and employed as a green sorbent for efficient biosorption of CR with fast equilibrium time described by Langmuir adsorption model [14].

The first objective of this work is to prepare the magnetite nanoparticles by co-precipitation method. The second objective is to prepare sulfonated polystyrene via sulfonation of commercial polystyrene by freshly prepared acetyl sulfate. From the product of first and second objectives the nanocomposite should be prepared. The third main objective of this study is to use these nanocomposites for adsorbing the CR from water and our attention is extended to study the adsorption kinetic and isotherm.

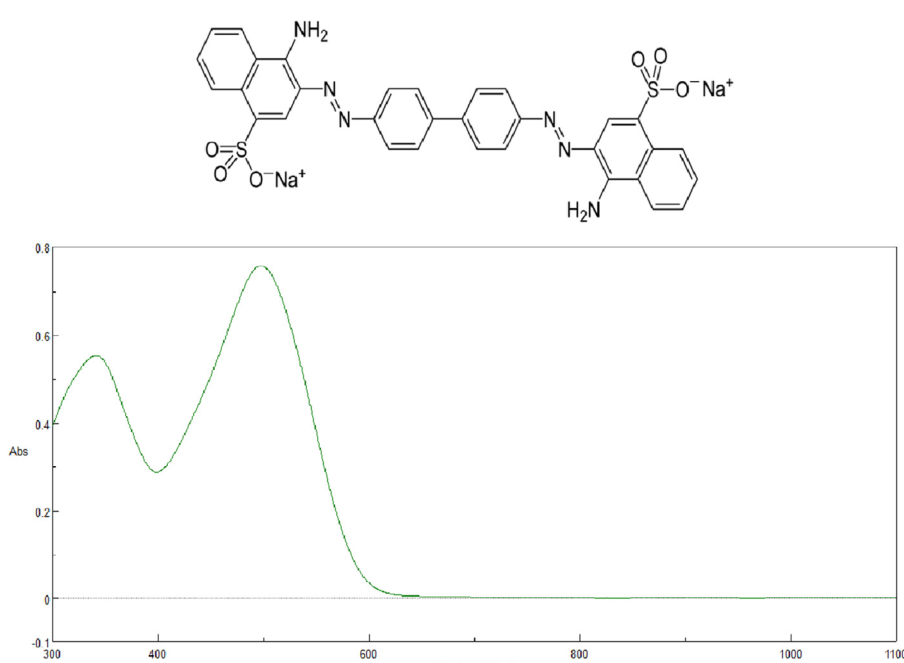
2. Material and methods

2.1. Materials

Commercial polystyrene wastes were collected from the local market, washed several times, divided into small pieces, grinded, dissolved in toluene and re-precipitated in ethanol. $FeCl_3{\cdot}6H_2O$, $FeCl_2{\cdot}4H_2O$, ammonium hydroxide, dichloromethane, acetic anhydride, sulfuric acid and tetrahydrofuran were of analytical grade and were used as received without further purification. CR was used a model dye where a stock solution was prepared by dissolution in deionized water and different concentrations were prepared by dilution. All other reagents were of analytical grade and were used as received without further purification.

2.2. Instrumentations

FT-IR spectra were recorded on a Nicolet Is-10 FT-IR Thermofisher scientific spectrometer. The prepared samples were examined using X-ray powder diffractometer, PANalytical X, PERT PRO MPD (Netherland), with Cu Kα radiation at a rating of 40 kV, 40 mA. The diffraction patterns were recorded at room temperature in the angular range of 40–80° (2θ) with step size 0.02 and scan step time 0.4 (s). The crystalline phases formed on the carbon steel surface were identifying using the ICDD-PDF database. Magnetic properties were tested by magnetometer using VSM Unit (LakeShore 7410) with the filed sweeping from −20000 to +20000 O_e at room temperature. High Resolution Transmission Electron Microscopy (HR-TEM) imaging was performed using a Jeol-TEM Japan 2100 operating at 200 kV. The samples for TEM were prepared by sonication of the samples in ethyl alcohol and depositing onto a copper coated carbon grid and then let the solvent to evaporate. Field Emission Scanning Electron Microscopy (FE-SEM) images were obtained using Quanta FEG 250, FEI C_o, Netherlands. The samples were loaded on a cupper tab then placed in the device for monitoring the surface morphology. Particles size, particles size



Scheme 1. Chemical structure of Congo red dye (upper) and its UV–Vis spectrum (lower).