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MWCNTs decorated with $Mn_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles for removal of crystal-violet dye from aqueous solutions

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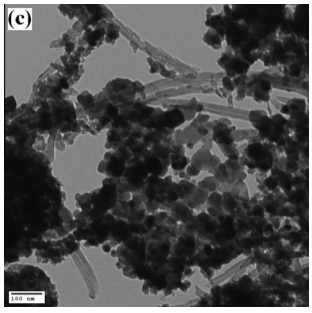
HIGHLIGHTS

- $Mn_{0.8}Zn_{0.2}Fe_2O_4$ was prepared using spent Zn–C batteries through sucrose method.
- MWCNTs/$Mn_{0.8}Zn_{0.2}Fe_2O_4$ nano-composite was prepared via same method.
- The nano-composite was characterized and investigated to remove crystal violet dye.
- After removal, the nano-composite can be easily separated using a normal magnet.
- The optimum condition for the efficient removal was investigated and discussed.

GRAPHICAL ABSTRACT

TEM image showed that MWCNTs are homogeneously decorated with $Mn_{0.8}Zn_{0.2}Fe_2O_4$ particles. The interaction seems to be sufficiently strong, as demonstrated by the absence of any free ferrite particles especially after prolonged sonication subsequent to TEM measurement.



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ABSTRACT

In the present study, a simple, economic and environmentally friend method was utilized for the production of multi-walled carbon nanotubes (MWCNTs) decorated with $Mn_{0.8}Zn_{0.2}Fe_2O_4$ nanoparticles, synthesized via recycling process of Zn–C battery. The chemical composition and structure of the MWCNTs/$Mn_{0.8}Zn_{0.2}Fe_2O_4$ composite were confirmed by X-ray diffraction and Fourier transform infrared measurements. The morphology as well as the decoration process was characterized using transmission electron microscopy. The results showed that the MWCNTs are homogeneously decorated with cubic loosely agglomerated ferrite particles having mean crystallite size of 20 nm. An appropriate decoration mechanism was suggested and discussed. The hysteresis measurements exhibited reasonable magnetic characteristics for the obtained composite which facilitate its separation from their dispersed solution using normal magnet. Surface area measurement indicates relatively large specific surface enhances its use in adsorption process. The adsorption capacity of the entire composite was investigated using crystal violet dye. The effect of composite mass, contact time, solution pH and solution temperature on the adsorption process was investigated. The adsorption process was found to follow a pseudo-second-order model. The calculated adsorption thermodynamic parameters (ΔG, ΔH and ΔS) suggested the spontaneity of the thermodynamically favorable adsorption process.

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1. Introduction

Due to their unique structure, carbon nanotubes (CNTs) were found to exhibit many fascinating characteristics including mechanical, electronic and chemical properties [1,2]. Recently, they have been investigated as a promising adsorbent for many organic and inorganic pollutants depending on their large surface area, fibrous shape and layered structure [3–5]. The adsorption capacity can be easily modified through chemical treatment with some metal oxides [6,7]. In this category, unique magnetic characteristics can be obtained through magnetic modification of CNTs with iron oxides [8] as well as some ferrite materials [3], which enhances their uses as magnetic data storage [9], microwave-absorbing materials [10], magnetic composites for drug delivery [11], etc. besides their uses as adsorbents [12].

Many researchers in the literature were reported on the synthesis and characterization of multi-walled carbon nanotubes (MWCNTs)/ferrite nano-composite used for different applications [13–17] but on the other hand, very few works dealing with the adsorption capability of these nano-composites are presented.

Farghali et al. [18] presented a simple hydrothermal precipitation method for producing MWCNTs decorated with $CoFe_2O_4$ nanoparticles used to investigate the adsorption capability of methylene blue dye.

Abdel Salam et al. [12] synthesized MWCNTs/$NiFe_2O_4$ nano-composite and used it for the removal of aniline from aqueous solution.

Zhang et al. [16] synthesized $Mn_{1-x}Zn_xFe_2O_4$/MWCNTs ($0 < x < 1$) via solvothermal method. The obtained composites were characterized by XRD, TEM, SEM and vibrating sample magnetometry (VSM). An appropriate mechanism for the nano-composite formation was also investigated. To the best of our knowledge, this is the only work in the literature dealing with MWCNTs/Mn–$ZnFe_2O_4$ nano-composite. In the present work, we prepared similar nano-composite via an alternative simple, cheap, economic and environmentally friend method using sucrose [19]. The contents of the entire ferrite, viz. manganese, zinc and iron will be obtained through recycling process of Zn–C battery previously described [20]. The prepared nano-composite will be characterized and investigated to remove crystal violet (CV) dye from aqueous solutions as an example of organic pollutants.

2. Experimental

2.1. Preparation of the MWCNTs/ferrite magnetic nano-composite

MWCNTs with average diameters of 60–100 nm were obtained from Shenzhen Nano-Technologies, China, and were used as received.

A recycling process of Zn–C battery was carried out, as previously described [20] to extract Mn, Zn and Fe required for ferrite preparation. Then, the stoichiometric ratios of each metal to prepare $Mn_{0.8}Zn_{0.2}Fe_2O_4$ were achieved using analytical reagents metal nitrates. The procedure for the preparation of entire ferrites using sucrose method is followed as previously reported in [19]. Stoichiometric amounts of metal nitrates in 100 ml distilled water and sucrose aqueous solution (12 g dissolved in 50 ml distilled water) are mixed thoroughly and kept at 60 °C for 30 min under vigorous stirring. The pH was adjusted to 7 by the addition of ammonia solution. The sticky gel obtained was evaporated until the combustion process occurs. The obtained loose as-prepared powder was then grounded and stored in dessicator.

MWCNTs/ferrite magnetic nano-composite (containing 70% w/w MWCNTs) was prepared by thoroughly mixing of MWCNTs with the stoichiometric amount of the entire metal nitrates during the preparation of the respective ferrite nanoparticles. The suspension obtained was then subjected for 1 h sonication process after which the same above procedures are followed until obtaining nano-composite.

2.2. Characterization techniques

The chemical composition of the battery contents was determined using atomic absorption spectrophotometer (AAS). The crystal phase was characterized by XRD using a Bruker axs D8 high-resolution diffractometer employing Cu-Kα radiation (λ = 0.15418 nm). The morphology was characterized by transmission electron microscopy using a JEOL-2010 instrument running at an accelerating voltage of 100 kV. Fourier transform infrared spectra were measured using a FT-IR, Perkin–Elmer in the range of 600–200 cm^{-1} using KBr-pellet technique. Magnetic properties were measured at room temperature using a vibrating sample magnetometer (VSM-9600 M) at applied magnetic field up to 5 kOe. The specific surface area was determined from nitrogen adsorption/desorption isotherms measured at 77 K using a model NOVA 3200e automated gas sorption system (Quantachrome, USA).

2.3. Adsorption experiment

Adsorption experiments were performed to determine the effect of the MWCNTs/ferrite magnetic nano-composite mass, solution pH, time and temperature on the adsorption process. The experimental procedures were performed as follows: (1) 20 ml of 10.0 mg L^{-1} solution of CV was prepared; (2) the initial pH was measured, and a defined amount of the magnetic nano-composite was then added to the solution; (3) these solution was stirred on a magnetic stirrer for a certain period of time, at room temperature; (4) at definite time intervals, a certain volume of the solution was removed and immediately using ordinary magnet the clear supernatant was collected using a glass pasture pipette; and (5) the residual CV concentration in the supernatant was determined using Perkin Elmer Lambda 25 UV–Vis spectrophotometer, USA at wavelength 588 nm. The amount of CV removed was determined by measuring the difference in the concentrations of the samples that were obtained at two consecutive time intervals over the course of the adsorption experiment using the following equation:

$$\%\ \text{Crystal Violet Removed} = 100 - \frac{C_t}{C_0} \times 100 \quad (1)$$

where C_0 and C_t are the concentrations of CV in solution (mg L^{-1}) at time $t = 0$ and t, respectively.

2.4. Real water samples collection

The efficiency and applicability of MWCNTs/ferrite magnetic nano-composite for the removal of CV was explored using real water samples. A tap water sample (TWS); collected from our lab after allowing the tap water to flow for 10 min, and a wastewater sample, collected from the Waste Water Treatment Plant (Membrane Bio-Reactor Technology) – King Abdulaziz University (KAUWW), Jeddah City (Latitude deg. North 21.487954, Longitude deg. East 39.236748). Both samples were filtered through 0.45 μm Millipore filter paper and kept in Teflon® bottles at 5 °C in the dark.

3. Results and discussion

3.1. Characterization of MWCNTs/ferrite magnetic nano-composite

3.1.1. X-ray diffraction

Fig. 1 shows XRD patterns of the as-prepared $Mn_{0.8}Zn_{0.2}Fe_2O_4$, using Zn–C battery extract, and MWCNTs/$Mn_{0.8}Zn_{0.2}Fe_2O_4$ compo-