Journal of Saudi Chemical Society (2015) 19, 511–520

King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Ferric oxide nanoparticles decorated carbon nanotubes and carbon nanofibers: From synthesis to enhanced removal of phenol

Hamza A. Asmaly [a], **Basim Abussaud** [b,*], **Ihsanullah** [b], **Tawfik A. Saleh** [c], **Vinod Kumar Gupta** [d,e,f], **Muataz Ali Atieh** [g,*]

[a] *King Abdulaziz City for Science and Technology – Technical Innovation Center on Carbon Capture and Sequestration, King Fahd University of Petroleum and Minerals, Saudi Arabia*
[b] *Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*
[c] *Chemistry Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*
[d] *Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India*
[e] *Centre for Environment and Water, The Research Institute, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia*
[f] *Department of Applied Chemistry, University of Johannesburg, Johannesburg, South Africa*
[g] *Qatar Environment and Energy Research Institute, Qatar Foundation, PO Box 5825, Doha, Qatar*

Received 17 February 2015; revised 4 June 2015; accepted 8 June 2015
Available online 16 June 2015

KEYWORDS

Carbon fibers;
Carbon nanotubes;
Ferric oxide impregnation;
Phenol;
Removal

Abstract In this work, ferric oxide nanoparticle decorated carbon fibers and carbon nanotubes (CNF/Fe_2O_3 and CNT/Fe_2O_3) were synthesized and characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), X-ray diffraction (XRD), zeta potential and BET surface area analyzer. The prepared nanocomposites were evaluated or the removal of phenol ions from aqueous solution. The effects of experimental parameters, such as shaking speed, pH, contact time, adsorbent dosage and initial concentration, were evaluated for the phenol removal efficiency. The adsorption experimental data were represented by both the Langmuir and Freundlich isotherm models. The Langmuir isotherm model best fitted the data on the adsorption of phenol, with a high correlation coefficient. The adsorption capacities, as determined by the Langmuir isotherm model were

* Corresponding authors. Tel.: +966 1 38602205; fax: +966 1 38604234.
E-mail address: motazali@kfupm.edu.sa (M.A. Atieh).
Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jscs.2015.06.002

0.842, 1.098, 1.684 and 2.778 mg/g for raw CNFs, raw CNTs, CNF–Fe_2O_3 and CNT–Fe_2O_3, respectively.

1. Introduction

Phenolic compounds are generated in pulp and paper, petroleum refinery, dye synthesis, coal gasification and pharmaceutical industries and have been identified as common contaminants in wastewaters. Phenols have found application in the production of wide varieties of phenolic resins, used in construction of automobiles and appliances, adhesives and epoxy resins, as well other various applications [1]. Due to the harmful nature of phenols and their potential hazardous effects on human health, they have been classified as toxic pollutants. Hence, it is required by the US Environmental Protection Agency (EPA) regulations to lower phenol content of wastewater below 1 ppm [2].

Various techniques have been developed for the phenol removal from wastewater, such as electrochemical oxidation [5], adsorption [3–6], wet air oxidation [7,8], chemical coagulation [9], solvent extraction [10], membrane separation [11,12], bioremediation [13,14] and photo catalytic degradation [15,16]. Traditionally, activated sludge has been widely employed for the removal of phenol from wastewater because of its relatively low cost and straightforward process [17]. However, this method is not efficient for the treatment of wastewater with high concentration of phenol due to low biodegradability. In addition, the regeneration process of the adsorbent is not only expensive, but also very complex [3,18].

The application of adsorption for phenol treatment in wastewater is favored by its potential to remove both organic and inorganic constituents, even at low concentrations. Adsorption has the advantage of its relative ease of operation both in batch and continuous operation, the absence of sludge formation, potential of regenerative reuse of adsorbent and availability of low cost adsorbent materials [12]. Carbon-based adsorbent materials, which are hydrophobic and non-polar, have good potential for phenol removal in wastewater. Their large surface area, well developed porosity and tunable surface-containing functional groups are features that enhanced their adsorption efficiency [12,13].

Various nanomaterials have been investigated recently for prudential applications in various fields. Carbon nanotubes have been employed for the removal of heavy metals [18] and organic compounds [19] from water. Metal oxides decorated with metal particles have shown photocatalytic, optical and visible light photoelectrochemical performance [20–23].

In this work, ferric oxide impregnated carbon fibers and carbon nanotubes were employed for the removal of phenol from water. Surface of the CNFs and CNTs were modified with ferric oxide, to study its effect on phenol adsorption. The physicochemical properties of the modified and unmodified CNFs and CNTs were determined using SEM, EDS, TEM, XRD, zeta potential, BET surface area analysis and TGA. The effects of experimental parameters, such as adsorbent dosage, contact time, pH, initial phenol concentration and shaking speed on the removal of phenol, were investigated.

2. Experimental

2.1. Adsorbent impregnation

Carbon fibers (CNFs) and carbon nanotubes (CNTs) used in this study were purchased from Nanostructured and Amorphous Materials, Inc. USA. The CNFs had 95% purity, outside diameter of 200–500 nm and length ranging from 10 to 40 µm, while the CNTs had 95% purity, outside diameter of 10–20 nm and length ranging from 1 to 10 µm.

Ferric oxide (Fe_2O_3) from ferric nitrate Fe $(NO_3)_2{\cdot}6H_2O$ was impregnated onto 5 g of the CNFs and CNTs in ethanol (98% purity), followed by sonication (110 V at 40% amplitude) and calcination at 350 °C for 3 h. For 10% iron oxide 1.443 g of pure ferric nitrate [Fe $(NO_3)_3{\cdot}9H_2O$] was dissolved in 300 mL ethanol. An amount of 1.8 of CNTs/CNFs was also dissolved in 400 mL of absolute ethanol. Both solutions were sonicated for 45 min separately and then mixed together. The resultant mixture was again sonicated for 1 h at room temperature. The mixture was then kept in an oven to evaporate the ethanol. The aim of ultrasonication is to have a complete and homogeneous wetting of the particles during impregnation and hence decreasing the possibility of agglomeration due to the formation of clumps of liquid [9]. The residue was then calcinated for 3.5 h at 350 °C in furnace to get CNTs/CNFs impregnated with 1% iron oxide.

2.2. Characterization

The prepared materials have been characterized using scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS), Back scattering FE-SEM, TEM, thermogravimetric analysis (TGA), BET surface area analyzer Micrometrics ASAP 2020, zeta potential, and X-ray diffraction (XRD).

2.3. Preparation of stock solution

Stock solution of phenol with initial concentration of 2 ppm was prepared by serial dilution of 1000 ppm solution. First 1000 mg of phenol was dissolved in 1 L deionized water. Solvents (1.0 M nitric acid and 1.0 M sodium) were used to adjust pH of the stock solution. Solution pH was maintained during the experiments by the addition of buffer solutions.

2.4. Batch adsorption studies

Batch adsorption experiments were performed at room temperature to study the effects of pH, contact time, adsorbent dosage and shaking speed on the phenol adsorption efficiency by the raw and decorated ones with ferric oxide (CNF–Fe_2O_3). The concentrations of phenol were analyzed using UV–VIS and the percentage removal was calculated as: