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Iron impregnated carbon materials with improved physicochemical characteristics

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ABSTRACT

This paper highlights the effect of iron impregnation and surface oxidation on the physicochemical characteristics of iron impregnated carbon materials. These materials were characterized by various techniques like surface area, pore size distribution, SEM/EDX, CHN, XRD, FTIR, TG/DT, VSM and XPS analyses. The increase in the surface functionalities and pores diameter (3.51–5.49 nm) of the iron-impregnated carbon materials was observed with the increase in iron contents and surface oxidation. The saturated magnetization values (0.029–0.034 emu/g) for the iron-impregnated carbon materials reflected the magnetic tendency due to the development of small size iron oxides on their surfaces. The XPS spectra revealed the existence of different oxidation states of the corresponding metals on the iron impregnated carbon materials. The percentage removal of model dyes (Methylene Blue and Methyl Orange) by iron-impregnated carbon materials was enhanced (>90%) with the increase in iron contents and pores diameters.

1. Introduction

Carbon supported materials are widely used and well known for their surface characteristics such as high surface area, porous structure, surface reactivity due to the presence of different functional groups (i.e. hydroxyl, carbonyl, carboxylic acid, etc.) and chemical stability [1]. Activated carbon (AC) materials have a wide range of porosity, i.e., micro-, meso- and macro-pores with the surface areas ranging from hundreds to thousands m^2/g [2]. These parameters not only make AC a versatile adsorbent but also has led to its various applications such as catalyst supports for processes like pollutants removal, water purification and the regeneration of chemicals [3,4]. Although, some low cost adsorbents such as peat, wood, resin, chitosan fibers, coir pith, etc., have been tested as an alternative for AC, their toxin (organic and inorganic pollutants) removal efficiencies were found to be lower than AC itself [5].

In order to further enhance its efficiency, activated carbons are constantly modified [6–8]. In common practice, chemical or thermal treatment on AC is capable to increase the number and types of functional groups which will be crucial in creating more active sites responsible for its surface activity. Particularly, oxidation process plays an important role during the modification of the surfaces [9]. Usually, oxidation in the gas phase increases the carbonyl and hydroxyl groups on the surface while liquid phase oxidation enhances the number of carboxylic acid groups [10]. Acid radicals such as NO_3^- and SO_4^{2-} can be used to oxidize the surface of the carbon materials as they can enhance the acidic property and improve the hydrophilicity of the surface. Acids with oxidizing nature such as H_2SO_4 and HNO_3 can act as oxidizing agents and hence increase the concentration of surface oxygen functional groups and surface acidity [11]. Jian et al. [3] have reported the enhanced number of active surface functional groups on the AC surface upon oxidation. The synthesis of ordered mesoporous carbon (OMCs) materials is attracting the attention of researchers globally due to their enlarged porosity, electrical conductivity and thermal stability which are crucial for catalysis, energy storage, separation and adsorption [12–15]. Since last two decades, researchers have been attempting different pathways to prepare OMCs by using organometallic compounds [16], carbonization of polymer blends [17] carbon gels [18] and phenolic resin [19]. Some detailed reviews have been reported in literature describing the importance, synthesis and applications of the micro- and/or mesoporous materials [20–23]. These studies shed light on the basics of porous materials and their connection to the future technologies. In another study, it has been demonstrated that the mesoporous materials with pore size greater than 10 nm can be obtained by introducing a transition metal into the substrate, which can impart catalytic character to the inert porous material [24].

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Water pollution is one of the biggest challenges faced by the society these days. Many data are available describing the attempts by the various researchers to combat this problem [25–29]. Out of the many techniques, adsorption is considered to be an easily viable and a low cost technique with promising results [30–33]. The aim of our study was to prepare an eco-friendly, non-toxic and effective adsorbent materials based on activated carbon such that, the materials are reusable, low cost and applicable for a wide range of pollutants. Herein, we report a simple pathway to synthesize template free micro/mesoporous iron-impregnated carbon materials. In the current investigations we focused on the modification of powdered activated carbon (raw AC) with an oxidizing agent (potassium permanganate) and a metal precursor (ferrous sulfate) using a wet deposition method followed by foreign material's impregnation to develop new iron-impregnated carbon materials. The impregnated carbon materials were prepared by varying the molar ratios of ferrous sulfate to potassium permanganate. The raw AC and the newly synthesized iron-impregnated carbon materials were then characterized to examine the effects of iron impregnation and oxidizing agent on the spectral, thermal and surface characteristics of the AC matrix. Furthermore, to examine the influence of surface oxidation and iron impregnation on the chemical characteristics of iron impregnated carbon materials, the uptake of Methylene Blue (MB) and Methyl Orange (MO) dyes were selected as probe reactions, because the contamination of dyes in the wastewaters is drastically polluting the environment and is harmful for the life cycle [34].

2. Experimental

2.1. Materials

Activated carbon (labeled as raw AC) was supplied by R&M Chemicals, Essex (UK) while the potassium permanganate ($KMnO_4$) was obtained from Amresco, USA. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and sodium bicarbonate ($NaHCO_3$) were purchased from ACROS Organics. Methylene Blue and Methyl Orange were purchased from QReC (New Zealand) and Ajax Chemicals Ltd. (Australia), respectively. All the chemicals were used as received without further purification.

2.2. Synthesis of iron-impregnated carbon materials

The synthesis of iron impregnated carbon materials was carried out using the procedure described in our recently reported work [35]. In general, the aqueous solutions of the oxidizing agent and ferrous sulfate (0.1–1 M) were prepared. Initially, 5 g AC was stirred with 0.5 M $KMnO_4$ solution at 200 rpm for 20 min. Afterwards distilled water was added to dilute the suspension before it was filtered. The residue obtained was then mixed with 0.1 M $FeSO_4 \cdot 7H_2O$ and stirred using magnetic stirrer (WiseStir, DAIHAN Scientific Co. Ltd.), up to 8 h at the same rate. The suspension was filtered again, washed with 1% $NaHCO_3$ and soaked in $NaHCO_3$ solution overnight. Later, the suspension was washed with distilled water and filtered. The solid residue was air dried and then kept in an oven for complete drying. This modified carbon material was labeled as M1. A similar procedure was followed to synthesize the other two iron-impregnated carbon materials by keeping the amount of AC constant (5 g) while changing the molar ratios of $FeSO_4 \cdot 7H_2O$ to $KMnO_4$, i.e., 0.5 M:0.1 M (labeled as M2) and 1 M:1 M (labeled as M3).

2.3. Characterization of the powdered materials

The raw AC and iron-impregnated carbon materials were characterized by using the N_2 adsorption–desorption surface area analysis, scanning electron microscopy (SEM), energy dispersive X-ray (EDX), carbon/hydrogen/nitrogen (CHN), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric (TG/DTA) analyses, magnetization effect (VSM) and X-ray photoelectron spectroscopy (XPS). The specific surface area and pore size distribution of the raw AC and iron–carbon hybrid materials were determined by measuring the Nitrogen (N_2) adsorption–desorption isotherms using surface area analyzer (Model ASAP 2020 V4.01). Micromeritics has incorporated a built in density functional theory model using DFT Version 1.00 software with the surface area analyzers family Model ASAP 2000. The software is able to extract the data from micro-pore through mesopore region and compute the pore volumes against the pore size distribution. In the current study, the built-in software incorporating the DFT model with the surface area analyzer was used to investigate the adsorption of N_2 gas on the materials and examine the pore size distribution along with the surface area and pore volume determination. The data obtained from the instrument was used to draw the plot for cumulative pore volume against the pore size distribution. Prior to the analysis, all the samples were degassed to remove any pre-sorbed material or moisture in the sample matrix. To investigate the surface morphology of raw AC, M1, M2 and M3, a field emission scanning electron microscope (FESEM) (Carl Zeiss Leo Supra 50 VP Field Emission equipped with Oxford INCA-X energy dispersive microanalysis system) was used. Finely grinded powdered samples were mounted on a specimen stub with sticky tape. Moreover, the platinum coating on specimen was applied to make them conductive for appropriate visibility at higher magnification.

The X-ray analysis of the powdered materials were conducted by using BRUKER AXS D8 Advance X-ray diffractometer in 2θ range from 10° to 90° at a step size of 0.05° with Cu Kα X-rays and NaI scintillator type detector. For C/H/N/O analysis, approximately 15 mg dried powdered samples were taken and analyzed on a Perkin Elmer 2400 Series II CHN analyzer. The presence of surface functional groups on the solid materials was investigated by using Perkin Elmer Spotlight 200 FTIR microscope in the range of 650–4000 cm^{-1}. To do this, small fragments of powdered materials were viewed through a highly sensitive mercury cadmium telluride (MCT) detector. Thermal stability of the iron-impregnated carbon materials was examined by using Perkin Elmer (TGA)/Pyris 1 thermal analyzer under Nitrogen (N_2) gas flow with a temperature variation step of 10 °C/min from ambient temperature up to 900 °C. For the magnetic susceptibility of the iron modified carbon materials, Vibrating Sample Magnetometer (VSM) (Model 7400 Series VSM System) equipped with the IDEAS-VSM Version 4 software was used. The magnetization was examined in the applied magnetic field of −10 to 10 kOe, for iron impregnated carbon materials. The hysteresis loops, coercivity and magnetic saturation values for M1, M2 and M3 were figured out for comparison. For detailed elemental composition and oxidation states of elements on the surface, XPS studies were conducted on Shimadzu XPS Axis Ultra DLD instrument.

To investigate the dyes (MB and MO) removal potential of the newly synthesized materials, 0.1 g solid sample was reacted each time with 20 mL dyes solution (1–25 mg/L) for 3 h on an orbital shaker (IKA 260 basic) at an agitation speed of 250 rpm at 298 K. The initial and final concentrations of MB and MO in the analyte were determined by using Shimadzu UV–vis 2600 spectrophotometer at a wavelength of 660 and 464 nm, respectively. To determine the dyes removal potential of iron impregnated carbon materials, the following equations were used as reported elsewhere [35]:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

$$\text{Removal}\,(\%) = \frac{(C_o - C_e)100}{C_o} \tag{2}$$