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# Experimental study on efficient removal of total iron from wastewater using magnetic-modified multi-walled carbon nanotubes

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ABSTRACT

Magnetic multi-walled carbon nanotubes (MMWCNTs) were used for the removal of total iron from wastewater samples. X-ray diffraction (XRD), transmission electron microscope (TEM), Fourier transform infrared (FT-IR) and vibrating sample magnetometry (VSM) measurements were used as characterization techniques. The prepared magnetic adsorbent can be well dispersed in the water and easily separated magnetically from the medium after loaded with adsorbate. Response surface methodology (RSM) coupled with central composite design (CCD) was used to investigate the effects of operating parameters, namely $D/C$ (adsorbent dosage per initial concentration of pollutant ($(mg)_{adsorbent}/(mg/l)_{initial}$)) and pH, on total iron removal (%). Using RSM model shows that the optimum removal of total iron was 98.97% at pH = 8.2 and $D/C = 5$. The experimental data were analyzed by the Langmuir and Freundlich adsorption models. The maximum adsorption capacity for total iron removal was obtained as 200 mg/g from Langmuir isotherm model. The present study shows the novel nature of the nanocomposite, which can remove total iron from wastewater.



## 1. Introduction

With two-thirds of the earth's surface covered by water and the water is important to the mechanics of the human body, it is evidently clear that water is one of the prime elements responsible and vital source for life on earth. Water circulates through the land just as it does through the human body, transporting, dissolving, replenishing nutrients and organic matter, while carrying away waste material. Groundwater is an important source of drinking water (Ellis et al., 2000; Alimohammadi et al., 2016). Wastewater treatment serves two main objectives, protecting the environment and conserving freshwater resources. Two major resources of water (industrial wastewater and brackish water) have been truly considered as waste and were mostly thrown away and not used as a water source (Bukhari, 2008; Ghasemi et al., 2016). Iron is a substrate for the growth of bacteria in the water mains. When iron bacteria die and slough off, bad odors and unpleasant tastes may be caused (Michalakos et al., 1997). It is important to treat wastewaters and COD to reduce contaminants to the environment because of generating a great volume of urban and industrial wastewaters in industrialized countries, and also the risk of dumping these effluents into rivers, lakes or the sea, (Rasoul-Amini et al., 2014; Mayahi et al., 2015). Total iron concentration in treated effluents from municipal and industrial sources is usually less than 3.0 mg/l, and for drinking water is less than 0.3 mg/l (Xiong and Mahmood, 2010). What is more, the intensive development of industry is causing the deterioration of the environmental quality. Within this context, the removal of metal ions from industrial wastewaters is vital for the development of industries. Contamination due to the presence of iron species can be found currently in natural waters (Víctor-Ortega et al., 2016). Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Iron is a potentially toxic heavy metal. In excess, it can cause cancer, heart disease, and other illnesses. Iron compounds may have a more serious effect upon health than the relatively harmless element itself.

Total iron removal technologies and percent removal including electro-coagulation (EC) 95–99%, oxidation/filtration 80–90%, ion exchange 90%, adsorption–oxidation 84–92%, activated carbon filtration 75–90%, subsurface iron removal more than 50%, aerated granular filter 80–90%, bioremediation 70%, supercritical fluid extraction 80% have been developed for removal of total iron from municipal and industrial effluents (Chaturvedi and Dave, 2012). Adsorption, on the other hand, is one of the most recommended physical–chemical treatment processes that is commonly used and

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applied for heavy metals removal from water samples and aqueous solutions (Mahmoud et al., 2010). The large specific surface area, small size, and hollow and layered structures that MWCNTs propose more than other nanoparticles, help with the total iron removal (Zhang et al., 2012). Among the various technologies as microbial fuel cell (MFC), magnetic adsorption methods are the new method of the removal of total iron from industrials' wastewaters, since they can produce high-quality water by a process that is economically feasible (Madrakian et al., 2011; Ghasemi et al., 2013). Multi-walled carbon nanotubes (MWCNTs) have engrossed more and more consideration for their unique structure and excellent mechanical, electrical, and thermal properties. MWCNTs have attracted researchers' interest as a new type of powerful solid-phase extraction adsorbent (Qu et al., 2008). The $Fe_3O_4$/MWNTs nanocomposites could respond rapidly to the permanent magnet, and after adsorption, the nanocomposites could be separated from solution easily by an external magnet (Song et al., 2011). Although there are some researches on the adsorption of pollutants by MWCNTs magnetic composites, there is no report about the detailed investigation of MWCNTs magnetic composites on the adsorption of total iron with response surface methodology. Response surface methodology (RSM) design is a collection of statistical and mathematical techniques which are useful for analyzing the effects of several independent variables on the response design and optimization process (Sedighi et al., 2012). In this paper, we presented a method to easily prepare $Fe_3O_4$/MWCNTs NPs composite nanotubes. It was to synthesize nearly monodispersed $Fe_3O_4$ NPs on the surface of MWCNTs by an in situ method, and we could get better morphology. The objective of this work is to explore the magnetic nanoparticle efficiency on the removal of total iron. To generate systematic experimental data for covering a wide the range of operating conditions and to predict the maximum percent of iron removal, response surface methodology was used as a systematic experimental design method.

## 2. Materials and methods

The carbon nanotubes used here had an inner diameter of about 10 nm and the average outer diameter of MWCNTs was between 30 and 50 nm (the length was up to a few micrometers), which were purchased from Nano port Co. Ltd. (Shenzhen, China). Other reagents were analytical grade and used without further purification including $FeCl_3{\cdot}6H_2O$, $FeCl_2{\cdot}4H_2O$, and $NH_3{\cdot}H_2O$. All glassware were soaked in dilute nitric acid for 24 h and finally rinsed for three times with distilled water prior to use (Zhang et al., 2016). The neodymium-iron-boron block magnet used in generating the magnetic field for total iron-water separation was used (maximum theoretical field strength: 13.2 kg) (Wang et al., 2013). Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, analytically pure), ferrous chloride ($FeCl_2$, analytically pure), ammonia solution (28 wt.%) and $FeSO_4{\cdot}7H_2O$ were all purchased from Merck and Fluka. A Metrohm model 713 pH-meter was used for pH measurements. The Design Expert 7.5 software was used for the regression and the graphical analyses of the experimental data.

### 2.1. Synthesis of $Fe_3O_4$/MWCNTs nano composite

In a typical synthesis, firstly, the MWCNTs were purified in a solution of concentrated sulfuric acid and concentrated nitric acid (a 4:1 volume ratio). The samples were sonicated in a typical ultrasound bath for 4 h. This acid mixture containing MWCNTs was diluted to 20% of its original concentration. The oxidized MWCNTs were filtered with a PTFE filter membrane (Alltech, 0.45 μm pore size) with the aid of vacuum pump then it was washed by DDW until the filtrate is neutral. MWCNTs were dried in the oven at 100 °C for 6 h. 30 mg of functionalized MWNTs was dissolved in 19 ml of distilled water by ultrasonic irradiation for 25 min. Then 20 mg of $FeCl_3{\cdot}6H_2O$ was added under stirring. After the mixture was stirred vigorously for 30 min under $N_2$ atmosphere, 30 mg of $FeCl_2{\cdot}4H_2O$ was added and keep stirring under $N_2$ atmosphere for 20 min. 5 ml of concentrated $NH_3{\cdot}H_2O$ diluted with 14 ml of distilled water was added to the mixture drop by drop. The adding of $NH_3{\cdot}H_2O$ aqueous solution was finished in 120 min and then the solution was heated to 70 °C and reacted for 2 h. The whole process must be under $N_2$ atmosphere. The reaction mixture was then centrifuged, washed with distilled water and dried at 70 °C for 12 h.

### 2.2. Solution preparation

Iron stock solution containing 598 mg of $FeSO_4{\cdot}7H_2O$/l was prepared by dissolving $FeSO_4{\cdot}7H_2O$ salt (analytical reagent grade) in distilled water that contains 100 ppm of Fe. The pH value of the total iron working solution was adjusted with 1 M HCl and 1 M NaOH solutions before adsorption experiments.

### 2.3. Adsorption study

The adsorption of total iron on MWCNT-γ-$Fe_3O_4$ was studied under batch conditions. For this aim, a series of 12 solutions of 50 ml wastewater samples each, and of various concentrations varying from 10 to 20 ppm of total iron, with 5 mg of the nanocomposite was agitated for 120 min in 100 ml bottles kept in a shaker rotating at rpm of 200. The temperature was kept at 25 °C in preliminary experiments. After magnetic separation using the permanent magnet, a single beam UV–VIS spectrophotometer (UV-DR5000, Hach) was used for determination of total iron concentration in the solutions. The absorbance was read at 510 nm. The total iron removal efficiency was determined using the following expression:

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

where $C_0$ and $C_t$ represent the initial and final concentrations in mg/l. All experiments were performed in triplicate to ensure the repeatability of the results the supernatant solutions were analyzed spectrophotometrically at 510 nm wavelength. The effect of pH value on adsorption was investigated by taking the initial pH value varied in the range 3–10. The Langmuir and Freundlich isotherm were studied to calculate the concentrations of adsorbed total iron.

### 2.4. Characterization

Chemical structure of γ-$Fe_3O_4$ nanoparticle functionalized with MWCNT was determined by X-ray diffraction (XRD). XRD traces were recorded from $2\theta$ of 20–70° with a 0.02° step size. Phase identification was done by the powder XRD pattern Rigaku D/max-cB automatic X-ray with Cu Ka irradiation ($k$ = 0.154056 nm). Transmission electron microscope (TEM) images were collected using a Hitachi 8100 electron microscope (Tokyo, Japan). Fourier transform infrared (FT-IR) spectra of KBr powder-pressed pellets were recorded on an Agilent Cary 600 series FT-IR spectrometer. Magnetic characterization was conducted on a vibrating sample magnetometry (PPMS VSM, Model 6000). The specific surface area and the pore size distribution of acid treated MWCNTs and MMWCNTs were determined by nitrogen adsorption/desorption porosimetry at (77.4 K) using a porosimeter (Bel Japan, Inc.).