



Preparation of Fe₃O₄-chitosan hybrid nano-particles used for humic acid adsorption



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ABSTRACT

The adsorbent of Fe₃O₄-chitosan hybrid nano-particles have been prepared. In this process, these materials were initially synthesized by chemical co-precipitation and then cross-linked with chitosan to coat on the surface of Fe₃O₄ nano-particles. The characterization of the synthesized Fe₃O₄-chitosan hybrid nano-particles was performed using FTIR, XRD, TEM, EDX, BET and TGA. Finally, the Fe₃O₄-chitosan hybrid nano-particles were used for the adsorption of humic acid (HA) from aqueous solutions using batch adsorption technique. The influences of contact time, pH, adsorbent dosages, initial concentration of HA and temperatures on the adsorption process were studied. The adsorption isotherms were better fitted by Langmuir isotherm with the adsorption capacity was found to be 44.84 mg/g. The results of the kinetic study showed that the adsorption of HA onto Fe₃O₄-chitosan hybrid nano-particles could be described by the pseudo second order kinetic model with a rate constant in the range of 0.032–0.104 g mg⁻¹ min⁻¹, respectively. Thermodynamic parameters data indicated that the HA adsorption process was non spontaneous and endothermic under the experimental conditions, with the values of Gibbs free energy (ΔG°) were in the range of 2.92–4.65 kJ/mol; as well as the values of enthalpy (ΔH°), entropy (ΔS°) and the activation energy (E_a) were found to be 21.80 kJ/mol, 57.55 J/mol and 19.27 kJ/mol, respectively. The computational chemistry study showed that the interaction between adsorbent and HA was occurred through the interaction between amine groups of chitosan and phenol groups of HA. The adsorption of HA from real sample using the prepared adsorbents showed that the Fe₃O₄-chitosan hybrid nano-particles has higher adsorption percentages than both Fe₃O₄ nano-particles and pure chitosan.

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1. Introduction

Humic acid (HA) is a subclass of humic substances and accounts for a significant portion of the dissolved organic matter found in peat water. The chemical and physical characteristics of humic acid are strongly dependent on the source they originated. HA is natural occurring organic molecule formed by the breakdown of animal and vegetable matters and other biological activities of microorganisms in the environment. The presence of humic acids in water introduce a yellowish to brown color and pose a serious environmental problem, particularly in drinking water treatment because of their taste and odor. They also tend to react with a variety of oxidants and disinfectants used for the purification of drinking water forming carcinogenic disinfection byproducts (DBPs) such as tri-

halomethanes and haloacetic acids (Hamid et al., 2011; Park and Yoon, 2009; Rojas et al., 2011; Sonea et al., 2010).

Recently, there are several methods used to remove humic substance, especially humic acid as main component from peat water, such as coagulation-flocculation (Park and Yoon, 2009; Rojas et al., 2011), photocatalysis (Sonea et al., 2010), electro-coagulation processes (Gheraout et al., 2009) and membrane technology (Hamid et al., 2011; Park and Yoon, 2009; Rojas et al., 2011). However, these methods are not widely used due to their high cost and economic disadvantages.

Adsorption is a well-known separation process and is widely used to remove certain classes of chemical pollutants from water. It has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and high efficiency (Toor and Jin, 2012). Although the adsorption technique is versatile and is easy to adopt in practical forms, the adsorbent materials are either costly or cannot be regenerated in the large-scale applications.

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Chitosan is a natural adsorbent due to the presence of the amine ($-NH_2$) and hydroxyl ($-OH$) groups. These groups serve as the adsorption sites for many adsorbates (Chang and Juang, 2004). However, raw chitosan presents some major problems in adsorption process, i.e. (i) weak mechanical property, (ii) easy dissolution in acidic media, (iii) low specific gravity, (iv) high swelling ratios, which limits its use in either batch or column modes (Dong et al., 2014; Jiang et al., 2013). In addition, conventional bioadsorbents based on cellulose are difficult to be separated and recovered except by high speed centrifugation or filtration and this lead to limit the practical application of these bioadsorbents. For above-mentioned reasons, it is significant and necessary to explore environment-friendly bioadsorbents based on raw chitosan that possess higher adsorption capacities and excellent separation property.

Currently, magnetic metal oxides such as Fe_3O_4 nano-particles are in focus as powerful adsorbents due to their large specific surface area and small internal diffusion resistance (Mohammadi et al., 2014). As comparison, some researchers have also studied the magnetic carbon nanotubes as the pollutant removals (Ma et al., 2013; Yu et al., 2012a,b), which showed similar activity to magnetic metal oxides due to the large specific area and specific pore size suitable for the pollutant adsorbent. These magnetite nano-particles can adsorb pollutant from aqueous solutions and then be separated from the water with a simple magnetic process. However, such ultrafine particles face great challenges in their practical applications. The first challenge is how to separate Fe_3O_4 nano-particles from bulky solution in an effective and economical manner. It is generally known that the acting force of the magnetic field on the particles is directly proportional to particle size (Jiang et al., 2012) and cannot be effectively separated in a moderate magnetic field (Jiang et al., 2012; Yavuz et al., 2006). In addition, nano-sized Fe_3O_4 particles tend to aggregate into bulky particles and thus result in a significant decrease in adsorption capacity. Consequently, how to develop Fe_3O_4 -based adsorbents of high capacity and feasible separation is becoming an interesting but challenging topic in the field of environmentally functional materials.

Many researchers have been focused on modification of the Fe_3O_4 nano-particles to provide a better surface specificity for the removal of different pollutants from aqueous solutions. For this purpose, a wide range of chemicals, such as polyacrylic acid (Zhou et al., 2013), humic acid (Zhang et al., 2013), carboxymethylcyclodextrin (Badruddoza et al., 2010), graphene oxide (Chang et al., 2012; Xie et al., 2012), zinc oxide (Singh et al., 2013), multi-wall carbon nano-tube (Ai et al., 2011), graphite (Li et al., 2014), chitosan (Cao et al., 2014), activated carbon (Liu et al., 2010; Do et al., 2011), alginate (Mohammadi et al., 2014; Srivastava et al., 2012), surfactant (Shariati et al., 2011; Wang et al., 2012) and polymers (Bhaumik et al., 2013; Han et al., 2013; Shuang et al., 2013) have been used to modify the surface of Fe_3O_4 magnetic nano-particles.

This paper reports on the preparation of Fe_3O_4 -chitosan hybrid nano-particles using an in situ co-precipitation method, as a magnetic adsorbent for the removal of HA from aqueous solution. Effects of various experimental conditions such as contact time, initial concentration, pH and adsorbent dosages, on the adsorption were evaluated through a batch equilibrium technique. In addition, the adsorption of peat water (the real water sample) has also been performed.

2. Materials and methods

2.1. Materials

The reagents used for the preparation of Fe_3O_4 -chitosan hybrid nano-particles were $FeSO_4 \cdot 7H_2O$ (Aldrich), $FeCl_3 \cdot 6H_2O$ (Aldrich), ammonium hydroxide, 25% (Merck), epichlorohydrin (Merck),

Table 1

The characteristics of peat water (a real sampel).

Parameters	Unit	Result
Color	Pt-Co	475
Organic compounds	mg/L $KMnO_4$	238
pH	-	4.01
Conductivity	$\mu S/cm$	62
Turbidity	mg/L SiO_2	7.5
Iron	mg/L	0
Manganese	mg/L	0
Calcium	mg/L	0
Magnesium	mg/L	6.2

chitosan ($M_r = 500$ kDa) with 85% degree of deacetylation was obtained by Aldrich, acetic acid (Merck), and ethanol (Merck). Deionized water was used in all experiments. For the adsorption experiments, humic acid (Merck) was chosen as the model organic pollutant. The real sample, peat water was collected in November 2014 from Rimbo Panjang, a sub district of Kampar in Riau Province, Indonesia, which is a source for water supply. The peat water was collected in a cleaned plastic container and then delivered to the laboratory. After filtration through $0.45 \mu m$ hydrophilic PTFE membrane filters (Millipore, JHWP09025), the filtered water was stored in brown glass bottles at $4^\circ C$ to minimize changes of its properties, which is hereafter referred to as raw water and used in the experiments. The water quality of the peat water can be seen in Table 1.

2.2. Fe_3O_4 nano-particles preparation

The synthesis of the Fe_3O_4 nano-particles were based on the study carried out by Dong et al. (2014) with some modifications. In a typical procedure, a mixture of $FeCl_3 \cdot 6H_2O$ (0.046 mol) and $FeSO_4 \cdot 7H_2O$ (0.023 mol) was dissolved into 150 mL deionized water in 250 mL three-necked flask and N_2 was imported for 3 min to extrude the air. Then 20 mL ammonium hydroxide (25%) was added quickly into the iron solution under vigorous stirring. After 30 min, 3 mL epichlorohydrin was added into the mixture to modify the Fe_3O_4 nano-particles and the mixture was heated to $75^\circ C$ for 1 h under N_2 atmosphere then cooled to room temperature. The Fe_3O_4 nano-particles were collected through magnetic separation and washed with deionized water and ethanol three times, respectively, then dried at vacuum conditions.

2.3. Synthesis of Fe_3O_4 -chitosan hybrid nano-particles

Chitosan (0.5 g) in 100 mL of 1.0 wt% acetic acid solution, 1.5 g modified Fe_3O_4 nano-particles were added into a three-necked flask and then the mixture was refluxed for 4 h at $65^\circ C$ and pH 6. After the completion of the reaction, the composites were collected through magnetic separation and were washed by deionized water and ethanol for several times. The products were dried in vacuo.

2.4. Characterization

In order to confirm the coating of chitosan onto Fe_3O_4 -chitosan hybrid material, the compositions of the nano-particles were examined in dried KBr powder by recording the infrared spectra over the frequency range of $4000-400 \text{ cm}^{-1}$ using a Fourier transform infrared (FTIR) spectrophotometer model 8300 IR-TF (Shimadzu, Japan). The crystalline structure of the synthesized Fe_3O_4 -chitosan hybrid material was examined by X-ray diffraction (XRD) RINT 2000 (Rigaku Instrument Corp., Japan) with $Cu K\alpha$ ($\lambda = 0.15406 \text{ nm}$) radiation at 40 kV and 100 mA at room temperature. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to observe the morphology of the Fe_3O_4 -chitosan

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