Journal of Molecular Liquids 230 (2017) 152–162

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Synthesis, characterization and using at the copper adsorption of chitosan/polyvinyl alcohol magnetic composite

Hatice Karaer [a,b,*], İsmet Kaya [a,**]

[a] Çanakkale Onsekiz Mart University, Department of Chemistry, Polymer Synthesis and Analysis Lab, 17020 Çanakkale, Turkey
[b] Dicle University, Faculty of Science, Department of Chemistry, 21280 Diyarbakır, Turkey

ARTICLE INFO

Article history:
Received 18 November 2016
Received in revised form 6 January 2017
Accepted 9 January 2017
Available online 11 January 2017

Keywords:
Chitosan
Magnetic chitosan
Magnetic composite
Adsorption
Copper adsorption

ABSTRACT

A chitosan/polyvinyl alcohol (CTN/PVA–Fe_3O_4) magnetic composite was prepared in one step and examined by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX), transmission electron microscopy (TEM), dynamic light scattering (DLS), Brunauer-Emmett-Teller (BET), thermal gravimetric analysis/differential thermal analysis (TGA-DTA) and differential scanning calorimetry (DSC). Effects of several parameters, such as temperature, pH, and initial concentration on removal of Cu(II) from aqueous solution by the CTN/PVA magnetic composite were studied as a function of contact time. Equilibrium data obtained from sorption of Cu(II) solutions having initial concentrations of 25 to 400 mg L^{-1} by sorption of the CTN/PVA magnetic composite at different temperatures (25, 35 and 45 °C) were applied to Langmuir and Freundlich adsorption isotherms. Maximum adsorption capacity (Q_{max}) was found to be 143 mg g^{-1} by using Langmuir isotherm model, by which thermodynamic parameters (ΔH^o, ΔG^o and ΔS^o) were also calculated. Activation energy was calculated by using rate constants for this model and its value was found 26.52 kJ mol^{-1}.

1. Introduction

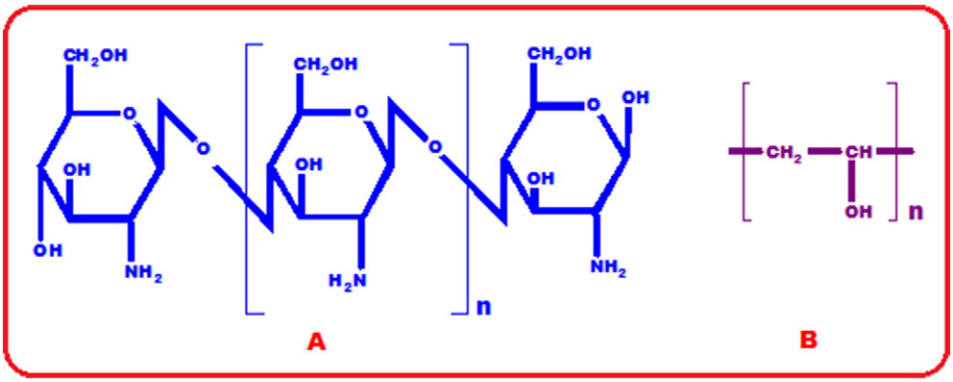
Removal of heavy metal from ground water and industrial waste water is presently a significant environmental concern. Heavy metals have been released into the environment because of rapid industrialization and have created a major global fear. The removal of their from drinking water is a real challenge owing to their trace quantities, formation of complexes with natural organic matter and toxicity even at very low concentrations [1]. Heavy metal ions in the environment arise from both natural and industrial emissions. Not only they can be non-degradable, but also will be bio-accumulated in animals, plants and human body, causing serious disorders [2–4]. The techniques that have been commonly used to remove toxic metals from industrial waste are coagulation/precipitation, ion exchange, reduction–oxidation process, liquid–liquid extraction, reverse osmosis, evaporation, adsorption and membrane separation. These methods are not cheap and effective. Adsorption is economical, efficient and greatly used methods for elimination toxic metals from aqueous environment. Researchers have been interested in the modification of chitosan for more effective adsorption recently [5]. Chitosan is one of the most plenty biopolymer in nature and has been widely used as bio sorbent for removal of metal ions from wastewater [6]. Chitosan has NH_2 and OH side groups which may act as active parts for chelating metal ions. The mechanisms of adsorption depend on the type of heavy metal and radionuclide ions, the solution composition and the pH of the aqueous solutions [7]. To increase its adsorption capacity and increase the adsorption rate, the design and exploration of novel adsorbents are still necessary [8].

Poly (vinyl alcohol) (PVA) is a water-soluble matter containing large amounts of —OH groups and it has a lot of advantages such as low price, chemical stability, biocompatibility, high durability and non-toxicity [9,10]. CTN/PVA polymer has received increasing attention because of its good mechanical stability, high hydrophilicity and good biocompatibility. CTN/PVA beads have been commonly used for the removal of heavy metal ions by many researchers [7]. Copper is one of the most common contaminants in industrial residues. Several industries, such as dyeing, paper, petroleum, copper/brass plating and copper–ammonium rayon, release Cu(II) containing wastewater. It has been a major concern owing to its toxicity to aquatic life, human beings and the environment [6]. Though Cu^{2+} and Zn^{2+} are known to be the essential trace elements to humans, higher Cu^{2+} and Zn^{2+} intake can be reason adverse effects. The maximum acceptable concentration of Pb^{2+}, Cd^{2+} and Cu^{2+} advised by the World Health Organization (WHO) for drinking water is <0.01, 0.003 and 2 mg L^{-1}, respectively [11].

The co-precipitation method is efficient route to synthesize magnetic particles. Iron oxides (FeO, Fe_3O_4 or γ-Fe_2O_3) are precipitated from aqueous solution of Fe(II) and/or Fe(III) salts with alkali along with

* Correspondence to: H. Karaer, Dicle University, Faculty of Science, Department of Chemistry, 21280 Diyarbakır, Turkey.
** Corresponding author.
E-mail addresses: profhatice23@hotmail.com (H. Karaer), kayaismet@hotmail.com (İ. Kaya).

http://dx.doi.org/10.1016/j.molliq.2017.01.030
0167-7322/



Scheme 1. Structure of chitosan (A) and poly (vinyl alcohol) (B).

proper ageing time. Fe_3O_4 can be constituted by a chemical reaction as follows [12]:

$$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O \quad (1)$$

Song et al. had been prepared to magnetic chitosan beads using a methodology inspired by the rolling of water droplets over lotus leaves. They had been examined application in biomedicine and biotechnology, including in cell expansion for tissue engineering or for the production of therapeutic proteins [13].

Synthesis and characterization of Core–shell magnetic chitosan particles [14] and spectrochemical characterization and catalytic activity of transition metal complexes derived from Schiff base had been examined in literature [15].

In this paper, magnetic CTN/PVA–Fe_3O_4 composite was prepared through a simple one-step in situ co-precipitation process. Furthermore, its sorption property for removing Cu(II) from aqueous media was investigated as kinetically and thermodynamically.

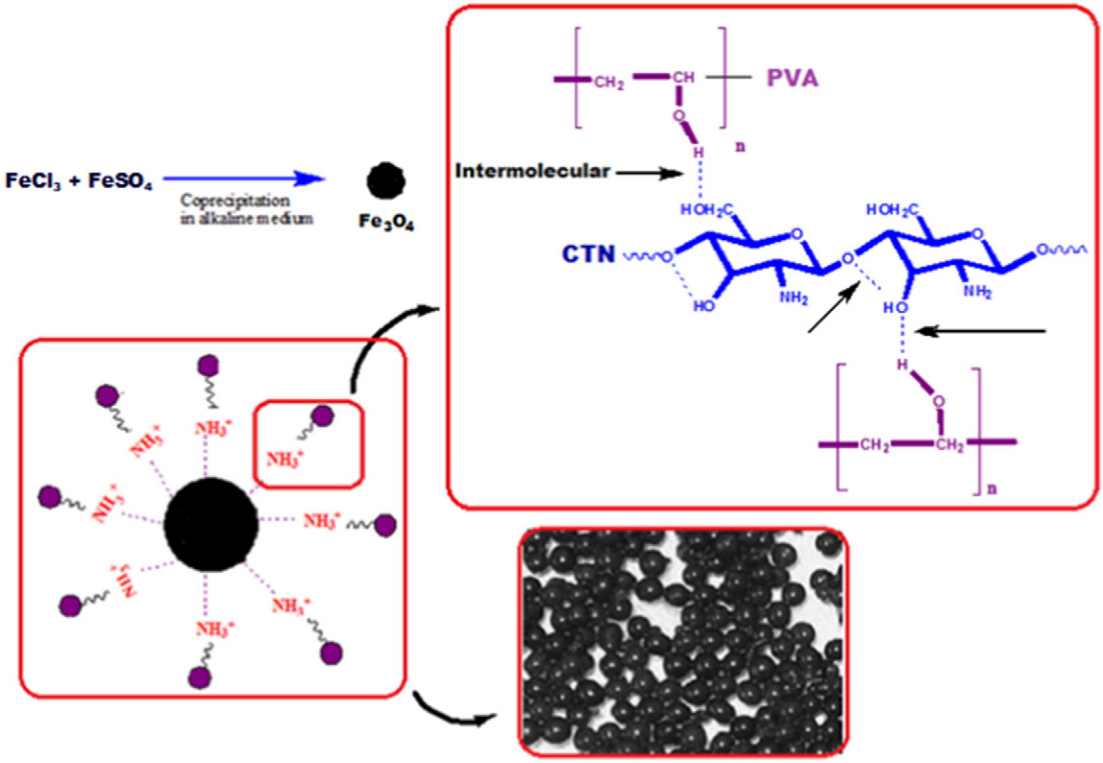
2. Material and method

2.1. Chemicals

Low molecular weight chitosan was used from Sigma–Aldrich. Poly (vinyl alcohol) (Sigma–Aldrich) has an average M_W: 30,000–70,000 g mol^{-1} and 90% hydrolyzed. $CuSO_4 \cdot 5H_2O$ was purchased from Merck. Sodium hydroxide (NaOH), $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ were purchased from Sigma–Aldrich.

2.2. Synthesis of the CTN/PVA magnetic composite

The CTN/PVA magnetic composite was prepared according to literature [7]. Chitosan (4 g) was dissolved in 100 mL acetic acid (3%, v/v). Poly (vinyl alcohol) (4 g) was entirely dissolved in deionized water (100 mL) overnight at 70 °C. The solutions were mixed together at 70 °C and stirred for 30 min. Fe(III) (as $FeCl_3$) and Fe(II) (as $FeSO_4$) (0.02 mol:0.01 mol) were added into the mixed solution. The solution was kept stirring for 60 min and then added into 500 mL NaOH solution



Scheme 2. Synthesis of CTN/PVA magnetic composite.