Journal of the Taiwan Institute of Chemical Engineers 61 (2016) 292–298

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Mussel-inspired synthesis of magnetic polydopamine–chitosan nanoparticles as biosorbent for dyes and metals removal

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ARTICLE INFO

Article history:
Received 7 July 2015
Revised 26 November 2015
Accepted 11 January 2016
Available online 6 February 2016

Keywords:
Biosorbent
Chitosan
Polydopamine
Adsorption
Multiple pollutants

ABSTRACT

A novel magnetic polydopamine (PDA) and chitosan (CS) hybrid nano-biosorbent was fabricated by assembling biomimetic polymer (PDA) and CS onto magnetic nanoparticles (NPs). The resulting PDA/CS/Fe_3O_4 nano-absorbent was characterized by means of the Fourier transform infrared spectra (FT-IR), transmission electron microscope (TEM), elemental analysis, vibrating sample magnetometer (VSM), and X-ray photoelectron (XPS). Based on the high surface area of nanoparticles and high-level active sites from polydopamine and chitosan, a multiple interactions to absorb pollutants with of resulted biosorbent can be anticipated. Demonstrated by batch tests, the nano-absorbent showed highly effective adsorption ability for target heavy metals and dyes, the maximum adsorption capacity was up to 245.6 mg g^{-1}, 47 mg g^{-1}, 151.6 mg g^{-1}, 204 mg g^{-1} and 61 mg g^{-1} and the removal percentage reached 98.4%, 92%, 95.8%, 96.9% and 92.5% for Hg(II), Pb(II), Cr(VI), Methylene blue and malachite green, respectively. Consequently, PDA/CS/Fe_3O_4 with excellent absorbability, stability and reusability could be used as a promising adsorbent for removal multiple pollutants in wastewaters.

1. Introduction

Heavy metals and toxic organic pollutants contaminated water could cause particular damage to aquatic life and humans through drinking, exposure, or food chain, the tragic example of water pollution in Minamata (Japan) profoundly reflects extremely hazardous effects to human health by mercury contamination water [1–3]. Because the important influence to human healthy, water pollution created the major global concern and extensive attention has been focused on it [4]. However, with the rapid industrialization and development of modern agriculture, multiple water pollution still has been continuously released into environment [5]. Therefore, effective removal of heavy metals and toxic organic pollutants from water environment has become urgent task to be resolve. A variety of methods have been adopted to eliminate water pollution, such as chemical precipitation, ion exchange, membrane filtration, electrochemical, flotation and adsorption [6,7]. Compared with other methods, the adsorption has been regarded as promising technology due to its simplicity, high efficiency and selectivity, wide-ranging availability and low cost [8].

Chitosan (CS), one of the nature bio-absorbents, has been widely regard as a promising bio-polymeric-material of great scientific interest because of its abundant nature resource, biocompatibility and biodegradability, strong adsorption properties and wide functionalized potential [9–11]. To overcome the recycle problem and facilitate operational technique, magnetic recyclable biomaterial has been extensively developed and received widespread attention. Therefore, lots of magnetic chitosan bio-adsorbents have been reported and shown unexceptionable removal ability for heavy metals and toxic organic pollutants in aqueous phase [12,13]. Since nano-materials with large specific surface area and high reactivate have been developed as excellent absorbents, nano sized magnetic chitosan bio-adsorbents have drawn extensive attentions in the field of environmental remediation and shown extraordinary adsorption capacity of pollutants because that they exhibit the advantages of combining both nano-materials and chitosan biosorbent [14].

Polydopamine (PDA) was moved into the spotlight as a novel coating material for primary advantage of facile and generic approach to form the film on various substrates *via* spontaneous oxidative polymerization of dopamine under mild conditions [15,16]. Spontaneous polymerization of dopamine onto surfaces

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http://dx.doi.org/10.1016/j.jtice.2016.01.008
1876-1070/

caused power of attraction in the field of membrane science, material and surface chemistry [17]. Due to abundant functional groups such as catechol groups, amine groups, and aromatic moieties, polydopamine is considered to be a new kind of potential biosorbent which can offer large numbers of active sites for adsorption heavy metal ions and toxic organic pollutants through chelation and π–π stacking interactions [18]. Furthermore, polydopamine could easily react with amine-containing polymers based on Michael-type addition and Schiff base reactions, which imparts to prepare diverse hybrid materials with specific functionalities [19]. As a result, polydopamine-based hybrid biosorbent could be synthesized under the mild condition and show potential applications on removal of environmental water pollutants [20].

In this work, a novel, facile and effective hybrid nano-biosorbent was fabricated by assembling biomimetic polymer (PDA) and chitosan onto magnetic nanoparticles based on Schiff base reaction. Combined the large surface area of nanoparticles and high-level active sites of polydopamine and chitosan, a strong adsorption capacity and efficiency of resulted biosorbent could be anticipated. PDA not only cross-linked the chitosan to increase the stability of sorbent and helped the hybrid bio-polymer strongly stuck on the surface of the nanoparticle, but also enhanced the binding ability for heavy metal ions and toxic organic pollutants. The composition and structure of the prepared PDA/CS/Fe_3O_4 hybrid nano-biosorbent was studied with the help of characterization methods. Three kinds of heavy metal ions (Hg(II), Pb(II), Cr(VI)) and two kinds of organic dyes (methylene blue and malachite green) were used as representative water pollutants to investigate the adsorption ability of PDA/CS/Fe_3O_4. Adsorption models as well as kinetic properties of removal process were also clarified.

2. Experiment

2.1. Materials

Dopamine hydrochloride (DA·HCl), Ethylene glycol, Sodium acetate (NaAc) and $FeCl_3{\cdot}6H_2O$ were purchased from AiHua Fine Chemicals Co., Ltd. (China); Chitosan with a degree of deacetylation of 90% (80 mesh) was purchased from Yuhuan Ocean Biology Company (Zhejiang, China). All other reagents were analytical grade and were used as received. Aqueous solutions at various concentrations were prepared from $HgCl_2$, were used as sources for Hg(II).

2.2. Apparatus

The FT-IR was recorded with a Nicolet Magna-IR spectrophotometer between 4000 and 450 cm^{-1} using the KBr pellet technique. Transmission electron microscopy (TEM, FEI Tecnai G20) was obtained to elucidate the dimensions of the nanoparticle. The concentration of ions in solution was determined by an inductively coupled plasma spectrometer (ICP/IRIS Advantage, Thermo, America). Magnetization measurements were performed on a vibrating sample magnetometry (VSM, LAKESHORE-7304, USA). The chemical analysis for the virgin and Hg(II)-loaded nano-biosorbent were conducted by X-ray photoelectron spectroscopy (XPS, ESCALAB210, VG, UK).

2.3. Preparation of magnetite Fe_3O_4 nanoparticle

Typically, 1.0 g of anhydrous $FeCl_3$ and 2.0 g of anhydrous sodium acetate were added to 30 mL of ethylene glycol, after that, 10 mL of 2-aminoethanol was added to give a transparent solution via reflux. This mixture was then transferred to a Teflon-lined autoclave and treated at 200 °C for 8 h [21]. Magnetite Fe_3O_4 nanoparticle was collected by magnetic decantation and washed with distilled water thoroughly. Finally, the nanoparticles were dried at 60 °C of 24 h under vacuum.

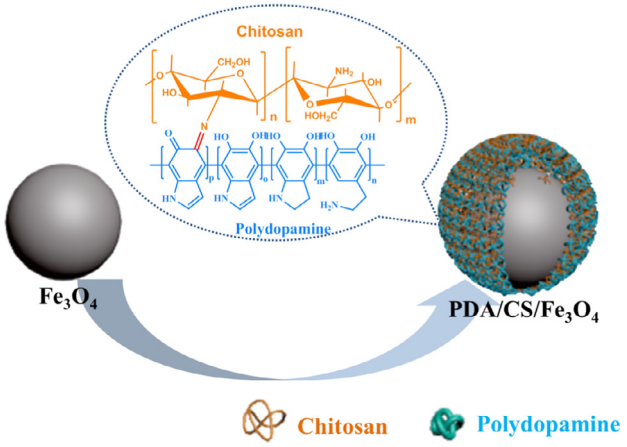

Fig. 1. Scheme for the synthesis route of the PDA/CS/Fe_3O_4 nano-biosorbent.

2.4. One-pot synthesis of PDA/CS/Fe_3O_4 nano-biosorbent

10 mL of the above magnetic nanoparticle suspension (contained 0.05 g Fe_3O_4) was added to three-neck bottle and sonicated for 10 min. 0.03 g chitosan was dissolved in 20 mL 1% acetic acid and the pH was adjusted to 7.0 by NaOH solution, then the chitosan solution was added to the above suspension under stir. 0.05 g of PDA was then added to the system, then the tris solution was dropwise added (10 mM, pH 10) until the pH reached 8.5. After sonication for 30 min, the reaction temperature was rose to 90 °C for 2 h to obtain the PDA/CS/Fe_3O_4 nano-biosorbent [20]. The product was washed with distilled water thoroughly and dried at 60 °C under the vacuum for 24 h. The synthesis routine of nano-biosorbent was shown in Fig. 1.

In order to take the comparative experiments, the magnetic chitosan nanoparticle (MCS) and PDA nanoparticle (MPDA) have been prepared. The synthesis process was in the same way like reported [3,20].

2.5. Adsorption experiment using batch methods

Batch adsorption studies were performed by placing 0.01 g PDA/CS/Fe_3O_4 in series of flasks containing pollutant aqueous solution (50 ml) with desired initial concentration and pH. After that, the flasks were shaken in a thermostat oscillator at specific temperature with constant rate 130 rpm for a given time under dark environment.

The effect of different solution pH on adsorption of heavy metal, adjusted the desired pH range was adjusted from 2 to 7 using HNO_3 and NaOH solutions, and for dye in the range of 3-10. The working concentration of pollutant was 30 mg L^{-1} for kinetic studies and 5–200 mg L^{-1} for isotherm studies. The concentration of heavy metal was determined with inductively coupled plasma spectrometer (ICP/IRIS Advantage, Thermo). Dyes were measured with a PERSEE TU-1810 UV–vis spectrophotometer. The amount of pollutant adsorbed per gram of the biosorbents was calculated on the basis of following equation [22].

$$Q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

$$\text{Adsorption efficient} = \frac{C_o - C_e}{C_o} \times 100\% \quad (2)$$

where Q_e is the adsorption capacity (mg g^{-1}); C_0 and C_e are initial and equilibrium concentrations of the Hg(II) (mg L^{-1}) in the testing