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Kinetic and equilibrium investigation of Cu(II) removal by Co(II)-doped iron oxide nanoparticle-immobilized in PVA–alginate recyclable adsorbent under dark and photo condition

Ee Ting Wong, Kian Hwa Chan, Ani Idris *

Department of Bioprocess Engineering, Faculty of Chemical Engineering, c/o Institute of Bioproduct Development, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

HIGHLIGHTS

- Immobilization of Co(II)-doped iron oxide nanoparticle in PVA–alginate matrix.
- Improvement of Cu(II) adsorption under photo condition.
- The experimental data can be fitted well by Langmuir–Hinshelwood kinetic model.
- Excellence recyclability.

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ABSTRACT

Magnetic nanoparticles of cobalt(II)-doped iron oxide (Co-Fe_2O_3) were synthesized by co-precipitation method using stable ferric and cobalt salts coated with different surfactants (citrate, acetate and polyetheylene glycol (PEG)) and water as the carrier. X-ray diffraction (XRD) and transmission electron microscope (TEM) confirmed the formation of single phase cobalt iron oxide nanoparticles while Fourier transform infrared (FTIR) was performed so as to ensure successful coating process. The nanoparticles were then immobilized in polyvinyl alcohol (PVA)-alginate gel matrix for the removal of Cu(II). X-ray photoelectron spectroscopy (XPS) was then used to validate the Cu(II) removal mechanism under photo condition. Langmuir equation was used to simulate the adsorption isotherms while Weber–Morris model and Langmuir–Hinshelwood model were then used to describe diffusion and adsorption kinetics. Adsorption–desorption results depicted that the PEG coated Co-Fe_2O_3 PVA–alginate adsorbent experienced only a 2.7% drop in removal efficiency after 5 cycles which made it a potential photoadsorbent to be used for Cu(II) removal.

1. Introduction

Heavy metal contaminated water threatens not only the aquatic lives but also human health due to their ability to accumulate in the food chains [1]. Among various heavy metals, copper application covers a variety of industry such as architecture, tube, pipe, electrical, automotive, seawater industrial, machined products, fuel gas and etc [2].

Due to its wide range of application, the effect of Cu(II) contamination to the environment has become more significant than other metals ion. Copper is an important trace element required by humans for enzyme synthesis, tissue and bone development [3,4]. However, the divalent copper is toxic and carcinogenic when excessive consumption occurs through ingestion. Moreover, intake of excessively large doses of Cu(II) by human leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage and central nervous system irritation followed by depression [5].

Traditional metal ion treatment processes includes chemical precipitation, ion exchange, electrolysis, reverse osmosis, adsorption, etc. Among those treatment methods, adsorption is still considered to be an economical, simple, efficient, recyclable, and promising method for treating metal-ion-contaminated water [6]. Recently, the use of nanoparticles have been of great interest especially in the waste water treatment. Many studies [7,8] reported that the metal oxide nanoparticles such as ferric oxide and non-metal oxide such as silica exhibit favorable sorption to heavy metal

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* Corresponding author. Tel.: +60 7 5535603; fax: +60 7 5588166.
E-mail address: ani@cheme.utm.my (A. Idris).

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ions. However, these nanoparticles when in suspension tend to agglomerate and therefore lose their performance efficiency overtime. Consequently, to improve the applicability of the nanoparticles in real waste water treatment, the nanoparticles were always impregnated into the polymeric support or encapsulated with shell to improve its dispersion and minimize the tendency of agglomeration and inactivation [9]. In this study, the nanoparticles were immobilized in the PVA–alginate polymeric matrix to form a recyclable and practical adsorbent for Cu(II) removal.

Studies have shown doping is one of the common ways to increase the performance of the semiconductor nanoparticles such as TiO_2 or iron oxide [10,11]. The substitution of iron (Fe^{2+}) in an iron oxide with other transition metals or metal ions such as nickel, cobalt, silicon and aluminum was found to improve the photoactivity of the semiconductor nanoparticles through the enlargement of the light absorption density and thereby enhancing the harvesting efficiency of sunlight during the photo treatment process [12,13]. So in this study, the Co(II) was used as the dopant to form the semiconductor nanoparticles which has better performance than the native iron oxide nanoparticles. In most of the literature, most of the Cu(II) was removed through simple adsorption process, the enhancement of Cu(II) removal process under photo condition by semiconductor Co-Fe_2O_3 nanoparticles immobilized PVA–alginate matrix has yet to be reported. Therefore, in this study, the removal mechanism of Cu(II) by Co-Fe_2O_3 nanoparticles loaded adsorbent was studied and verified by surface characterization instrument. Since different types of coated surfactants were reported to affect the adsorption capability of the adsorbent [14–16], adsorption isotherm and kinetic adsorption model were also studied for different surfactants coated adsorbents. Besides acting as surfactants to prevent the agglomeration of nanoparticles, the coated PEG, acetate and citrate shell also function as organic hole scavengers which could help to stabilize the positive hole created during photo-excitation process [17–19].

In addition to the adsorption isotherm, the photo adsorption was also investigated by using the modified Langmuir–Hinshelwood model to describe its photo-removal kinetic. The experiment data was also fitted into Weber–Morris model so as to determine the rate limiting step of the diffusion mechanism during the photo removal process. The recyclability of the adsorbents which is one of the major concern in practical adsorption process was also investigated in this study.

2. Methodology

2.1. Materials

Cobalt chloride and ferric chloride salts (reagent grade; purity >98%) were purchased from Sigma Aldrich and Riedel–deHaen respectively. Sodium hydroxide, PEG MW600, sodium acetate and sodium citrate (ACS reagent, PhEur; purity >97%) were supplied by Merck. Nitric acid (HNO_3, 65%, v/v), acetone, and PVA MW184000 were supplied from Aldrich Chemicals whereas sodium alginate, boric acid and calcium chloride (ACS Reag. PhEur) were provided by Fluka Chemie GMGH. The chemicals used for preparing standard Cu(II) solution were copper(II) sulfate salt (ACS reagent, purity >98%) from Sigma Aldrich. All the chemicals used are ACS reagent grade and used without further purification.

2.2. Synthesis of doped Co-Fe_2O_3 nanoparticles coated with PEG, citrate and acetate

In this study, the cobalt(II)-doped iron oxide was synthesized through co-precipitation method. Nanoparticles of Co-Fe_2O_3 were synthesized using high purity salts of $CoCl_2{\cdot}6H_2O$ and $FeCl_3{\cdot}9H_2O$ in 1:2 ratios and 0.6 M sodium hydroxide solution was added by drops. The magnetic precipitate was formed and washed with distilled water and acetone to remove unwanted residual of salts.

Next, the precipitate obtained was acidified by nitric acid so that a reversion of the surface charges can be provoked and oxidized into Co-Fe_2O_3 at 90 °C [20]. The wet slurry was dispersed in 15 ml of 3 different surfactants; PEG (50%w/v), acetate (50%w/v), and citrate (50%w/v), respectively at 80 °C. Coating of the nanoparticle with these organic surfactants would improve the dispersion and prevent the agglomeration of the nanoparticles in PVA–alginate matrix.

2.3. Characterization of Co-Fe_2O_3 nanoparticles

EELS and energy dispersion X-rays (EDX) were performed to determine the electronic structure and composition analysis for the nanoparticle specimen [21]. The nanoparticle size was characterized by TEM (JEM-2010F). XRD (Rigaku D/Max 2500) was used to identify the crystal composition of coated nanoparticles while FT-IR (PerkinElmer IR Spectoscopy v 5.3) was used to confirm that the PEG, acetate and citrate coating were successful.

2.4. PVA–alginate spherical matric preparation

A mixed solution of PVA and sodium alginate was used to synthesize the PVA–alginate polymeric matrix using the method reported by Zain et al. [22] with 8% v/v of nanoparticles loading.

2.5. Effect of pH on Cu(II) removal

The pH of solution is the one of the critical parameters which influences the removal of Cu(II) from the aqueous solutions. The solution pH was adjusted from 2 to 10 using either HCl (1%v/v) and NaOH (1%v/v) solution. The experiments were conducted under light irradiation of 1000Ft-Cd with the adsorbent (10.0 g) with 100 ml of 50 ppm Cu(II) solution in beaker at the temperature of 29 ± 2 °C. The Cu(II) concentration was then determined after 2 h of contact time. The Cu(II) concentration was determined by the modified method which was described by Aksu and Oglu [23] and then determined at 460 nm using the UV-spectrophotometer (Shimadzu UVmini-1240).

2.6. Kinetic experiments for adsorption process of Cu(II)

The adsorption isotherm of PEG-coated Co-Fe_2O_3 PVA–alginate adsorbent, acetate-coated Co-Fe_2O_3 PVA–alginate adsorbent and citrate-coated Co-Fe_2O_3 PVA–alginate adsorbent were described by fitting the experimental data obtained into the Langmuir model. Weber–Morris model was used to characterize the diffusion model of the photo adsorption process. Finally, modified Langmuir–Hinshelwood kinetic model was used to describe the rate of photo generation active site for all the photoadsorbents.

2.7. Recyclability of the photoadsorbent

Adsorption–desorption cycles were used to evaluate the reusability of the different surfactants (PEG, acetate or citrate) coated Co-Fe_2O_3 PVA–alginate adsorbent. The adsorption experiments were conducted by putting the 5.0 g of adsorbent into the separate beakers with each beaker contained 50 ml of 50 mg/L of Cu(II) synthetic solution. After 3 h of light illumination (1000Ft-Cd), the adsorbent (5.0 g) from each beaker was stirred moderately with desorbing agent (HCl 50 ml of 0.1 M) in 250 ml Erlenmeyer flasks for 12 h at room temperature and the concentration of Cu(II) desorbed was then measured. The adsorbents were then washed with distilled water for 60 min in room temperature and were recycled