



Developing of a magnetite film of carboxymethyl cellulose grafted carboxymethyl polyvinyl alcohol (CMC-g-CMPVA) for copper removal



Nuraina Anisa Dahlan^a, Anand Kumar Veeramachineni^a, Steven James Langford^{a,b}, Janarthanan Pushpamalar^{a,*}

^a School of Science, Monash University Malaysia, Jalan Lagoon Selatan, 47500 Bandar Sunway, Selangor, Malaysia

^b School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

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ABSTRACT

Crosslinked carboxymethyl cellulose grafted carboxymethyl polyvinyl alcohol (CMC-g-CMPVA) was loaded with modified magnetite iron oxide (Fe₃O₄) nanoparticles to synthesise a new and easily separable adsorbent for the removal of copper (II) ions from water. The novel adsorbents were characterised by the presence of the functional group, surface morphology, crystallinity and magnetic property. The equilibrium time from the adsorption studies was found to be less than 240 min for both film and bead forms while the rate of Cu²⁺ removal decreased as the initial Cu²⁺ concentration increased. In addition, CMC-g-CMPVA film loaded with Fe₃O₄/SiO₂ nanoparticles was the best adsorbent with maximum adsorption capacity of 35.34 mg/g and exhibited a reusable potential. The properties exhibited by the new heterogeneous material is a promising adsorbent for the removal and recovery of copper (II) from wastewater.

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1. Introduction

The increase in population and industrialisation expansion has contributed to the contamination of wastewater in which various heavy metals and contaminants are released into the municipal water sources. Heavy metals are elements with density exceeding 5 g per cubic centimetre (Tchounwou, Yedjou, Patlolla, & Sutton, 2012). According to Fu and Wang (2011), an excessive release of heavy metals from industries such as the batteries, pesticides, metal plating and fertilisers industries into the wastewaters is due to the result of rapid industrialisation leading to devastating effects on the environment. In agriculture, the uptake of heavy metals by crops due to contaminated irrigation water will eventually cause the hazardous effect to human as heavy metals are typically non-degradable and highly toxic therefore they tend to be accumulated through food chains upon exposure (Huang et al., 2016; Valipour, 2015b). The hazardous effects of these heavy metals to both living organisms and environment have indirectly caused people to perceive the treatment of wastewater contaminated with heavy metals as a top priority (Wang, Lu & Li, 2016). For example, prolonged ingestion of copper(II) ions with a concentration higher than 1 mg/L will eventually cause serious complications such as vomit-

ing, fatigue, convulsions and even death (Paulino et al., 2006; Tan & Ting, 2014). To date, there are at least 20 types of common heavy metals identified that are released into the environment in the form of industrial waste.

As mentioned, the treatment of wastewater containing heavy metals is crucial before the release of the water into the environment. Besides, the treated water can be an alternative water source for selected crop irrigation. Therefore, it could be an economical way to reduce the dependence on surface waters and groundwater which can be used for other applications (Abdel-Raouf, Al-Homaidan, & Ibraheem, 2012; Valipour, 2015a, 2016). Various treatment techniques, such as chemical precipitation, biological method, ion exchange and adsorption, have been developed to remove the heavy metals from aqueous solution (Haiyan, Qiuxiang, & Ying, 2016; Khandanlou et al., 2016). Amongst these treatment techniques, adsorption is regarded as more superior in term of flexibility, initial cost, insensitive to toxic pollutants and convenience of operation (Akpomie, Dawodu, & Adebowale, 2015).

However, the main problem in wastewater management is to find a suitable, cost effective adsorbents to remove the metal contaminants. Adsorbents such as zeolites, clays and activated carbon have been used to remove the heavy metals (Biškup & Subotić, 2004; Gier & Johns, 2000; Karnib, Kabbani, Holail, & Olama, 2014). The main limitations faced by these adsorbents include weak interactions with metal ions, difficulty in separating during post-

* Corresponding author.

E-mail addresses: pushvenga@hotmail.com, pushpa.janarthanan@monash.edu (J. Pushpamalar).

treatment and some of them are non-reusable (Samiey, Cheng, & Wu, 2014). On the other hand, polymers are industrially attractive because they have higher adsorption capacity compared to other types of adsorbents due to the presence of different functional groups such as hydroxyl (-OH) and amino (-NH₂) groups which are responsible for the uptake of metal ions (Barakat, 2011; Zhang, Zeng, & Cheng, 2016). Also, these polymers are biodegradable, modifiable and renewable in certain situations (Abdulkhani, Daliri Sousefi, Ashori, & Ebrahimi, 2016).

In our previous work, a new graft copolymer consisting of carboxymethyl polyvinyl alcohol grafted to carboxymethyl cellulose (CMC-g-CMPVA) was prepared. CMC-g-CMPVA showed excellent swelling under various pH conditions, high thermal stability and biocompatibility (paper 1 under review). Furthermore, CMC-g-CMPVA expressed potential as a promising adsorbent for wastewater management as it could effectively adsorb Cu²⁺, Pb²⁺ and Cd²⁺ ions (paper 2 under review). However, most reported adsorbents have limitation for industrial applications as they are difficult to be separated after adsorption process. Therefore, magnetic nanoparticles can be incorporated into the adsorbents, which allows an easy separation by a magnetic field. Magnetite iron oxide nanoparticles are synthesised through co-precipitation method by mixing ferric and ferrous ions in a molar ratio 1:3 in distilled water (Daraei et al., 2012). Magnetic Fe₃O₄ nanoparticles are considered as potential adsorbents in removing heavy metals due to their high surface area and unique property of easy separation under external magnetic field (Wang et al., 2010). Furthermore, surface modification on the magnetic Fe₃O₄ nanoparticles through physical coating or introduction of functional groups can be performed to enhance adsorption performance. For example, the coating of Fe₃O₄ nanoparticles by chitosan was reported to be effective for adsorption of Cu²⁺ ions (Chang & Chen, 2005). Another study showed that the grafting of amino groups onto the surface of Fe₃O₄@SiO₂ nanoparticles could be used to remove Cu²⁺, Pb²⁺ and Cd²⁺ ions (Wang et al., 2010). Although magnetic Fe₃O₄ nanoparticles showed excellent adsorptive performance, these nanoparticles can easily agglomeration in aqueous solution, thus hindering their application in wastewater treatment. Furthermore, agglomeration causes a reduced magnetic property (Laurent et al., 2008). Many techniques can be used to solve the agglomeration problem such as using the polymers for encapsulating or coating materials to maintain the original function of the magnetic nanoparticles. Furthermore, in several literature, carboxymethyl cellulose (CMC) acted as coating materials or encapsulating medium for the magnetic nanoparticles in various biomedical applications such as drug delivery systems and magnetic resonance imaging (Butun, Ince, Erdugan, & Sahiner, 2011; Guo et al., 2015; Sivakumar et al., 2013).

In this work, we propose the incorporation of various types of Fe₃O₄ nanoparticles into CMC-g-CMPVA co-polymers as a novel adsorbent for copper removal. Therefore, this study aims to enhance the adsorption of heavy metals by incorporating various types of Fe₃O₄ magnetite nanoparticles into our prepared co-polymers. The types of magnetite Fe₃O₄ nanoparticles that were used are iron oxide (Fe₃O₄) nanoparticles, silica coated iron oxide (Fe₃O₄/SiO₂) nanoparticles, metformin modified silica coated iron oxide (Fe₃O₄/SiO₂-Met) nanoparticles and amine-modified silica coated iron oxide (Fe₃O₄/SiO₂-NH₂) nanoparticles. The novel adsorbents with magnetic property could be potential adsorbents for the treatment of wastewater in the industry. Two physical forms of CMC-g-CMPVA loaded with various magnetite Fe₃O₄ nanoparticles were prepared, namely film and beads and the surface morphology, presence of functional groups, crystallinity and magnetite properties of the adsorbents characterised. Additionally, the reusability property of the adsorbents is also studied.

2. Experimental

2.1. Materials

In this work, all reagents and solvents were used directly without further purification. Polyvinyl alcohol (PVA) was purchased from Central Drug House (P) Ltd., India. Carboxymethyl cellulose sodium salt (CMC), adipodihydrazide (ADH), (3-Aminopropyl) triethoxysilane (APTES), iron (II) chloride tetrahydrate, (FeCl₂·4H₂O), iron (III) chloride hexahydrate, (FeCl₃·6H₂O), N-hydroxysuccinimide (NHS), potassium iodide (KI), potassium carbonate (K₂CO₃), and tetraethyl orthosilicate (TEOS) were purchased from Nacalai Tesque, Inc, Japan. The chloroacetic acid and N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) were purchased from Sigma-Aldrich, USA. On the other hand, 3-trimethoxysilylpropyl chloride (CPTS) and metformin hydrochloride were purchased from TCI America while ammonia solution (25%), acetonitrile, toluene and aluminium chloride hexahydrate (AlCl₃·6H₂O) were purchased from Reindeman Schimdt Chemical. Sodium chloride (NaCl) was purchased from R&M Materials while copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O) was purchased from Merck, Germany. Lastly, ethanol (95%) was purchased from Kofa Chemical Works (M) Sdn Bhd., Malaysia. The pH of solutions was adjusted using 1 M NaOH and 1 M HCl.

2.2. Method

2.2.1. Preparation of CMC-g-CMPVA

The preparation procedure was described in our previous work (Dahlan et al., 2016 under review). Briefly, the carboxymethyl polyvinyl alcohol (CMPVA) was achieved through the reaction between alkali PVA and monochloroacetic acid under controlled conditions (Yu & Li, 2008). Then, 1% w/v of CMPVA was dissolved in distilled water at 95 °C in a water bath. In a separate 250 mL Schott bottle, 3% CMC was dissolved in distilled water at room temperature. Upon dissolution of CMC, 0.35 g of ADH, 0.31 g of 1-ethyl-3-(3-dimethylaminopropyl) (EDC) and 0.12 g of N-hydroxysuccinimide (NHS) were added to the CMC solution. Lastly, CMPVA was added to the CMC-ADH mixture and stirred at room temperature overnight. The product, CMC-g-CMPVA was dialysed in distilled water with NaCl to remove uncross-linked materials. The pure product was dried in the oven to constant weight and sieved to obtain fine powders for further analysis.

2.2.2. Synthesis of functionalized magnetite iron oxide (Fe₃O₄) nanoparticles

The different kinds of modified magnetite Fe₃O₄ nanoparticles were synthesised according to a published method by Ghaemi et al. (2015).

2.2.2.1. Synthesis of iron oxide (Fe₃O₄) nanoparticles. Iron oxide nanoparticles were synthesised using co-precipitation method. Briefly, 2.7 g of iron (III) hexahydrate (FeCl₃·6H₂O) and 1 g of iron (II) chloride tetrahydrate (FeCl₂·4H₂O) were dissolved in 130 mL distilled water. Then, ammonia solution was added to the orange-brown solution to adjust pH to 9.5 under rapid mechanical stirring. The solution was then heated up to 60 °C and vigorously stirred for 1 h. The resultant nanoparticles were collected using a magnet. The obtained nanoparticles were washed several times with acetone and distilled water followed by drying in an oven at 60 °C.

2.2.2.2. Synthesis of silica-coated iron oxide (Fe₃O₄/SiO₂) nanoparticles. Firstly, 1 g of Fe₃O₄ nanoparticles were dispersed in 50 mL of distilled water by ultrasonic treatment. The dispersed nanoparticles were washed with distilled water and later precipitated with

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