Determining adsorption ability of bio-magnetic nanocomposites for lead (II) ion

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Abstract

The objectives of this work were to prepare bio-magnetic nanocomposites from magnetite nanoparticles combined with bacterial cellulose and to determine the Pb^{2+} ion adsorption. The results shown that the bio-magnetic nanocomposites presented a magnetic property, which investigated by Vibrating sample magnetometry (VSM) measurement, which showed a great saturated magnetization (M_S) value at 29.86 emu/g. Field-emission scanning electron microscopy (FE-SEM) was used for determined the morphology of samples, which exhibited the Fe_3O_4 nanoparticles entrapped on BC network structure. The adsorption of bio-magnetic nanocomposites for lead (II) (Pb^{2+}) ion was evaluated. The results indicated that the bio-magnetic nanocomposites exhibited high adsorption ability that can reduce the Pb^{2+} ion concentration up to 80%. The great M_S value and high adsorption ability of bio-magnetic nanocomposites could be of considerable interests for bio-separation and waste water treatment.

Keywords: magnetic nanocomposites, bacterial cellulose, heavy metal absorption

Introduction

Water is one of the most precious needs for life on earth. All plants and animals must have water to survive. It is also essential for the human activities. Water pollution is increasing worldwide because rapid growth of industry, increase human population, and domestic and agricultural activities. Water pollution containing heavy metal ions such as chromium, cadmium, copper, lead, nickel, mercury and zinc from industrial and domestic is becoming one of the most serious environment problems globally (Karami, 2013). Because of the low concentration of heavy metals in various resources could be several damages to the environment and adversely affecting the human health. The treatment of heavy metals is so important owing to persistence in the environment. The conventional technologies for the removal of heavy metal ions from aqueous solution include ion exchange, chemical precipitation, electrochemical treatment, reverse osmosis and adsorption. Among the different treatments described above, adsorption technology is generally considered to be a simple operation, relatively low cost and effective method (Ji *et al.*, 2012). The common adsorbents primarily include activated carbons, zeolite, clays, biomass and metal oxides. Magnetic iron oxide (Fe_3O_4) nanoparticles belong to metal oxide. This particle presents a cubic inverse spinel structure, which is specific subset of smart materials and are made usually in the size range of 1-100 nm, and are highly reactive because of their large specific surface areas (Dave *et al.*, 2014). Fe_3O_4 nanoparticles are inexpensive, easily scalable and highly reactive towards a wide array of organic and inorganic pollutants. Bacterial cellulose consist of cellulose

nanofibrils, is one of biopolymer. It can be biosynthesize by *Gluconacetobacter xylinum*. The remarkable features of BC, such as high water holding capacity, a fine fiber network, high tensile strength, no secondary pollution, high specific surface, pores and many hydroxyl groups in the chains that can be incorporated with other materials with fascinating structures and properties. However, BC is unsuitable for heavy metal ions adsorption because of lower adsorption capacity and poorer selectivity (Lu *et al.*, 2014).

Therefore, the objectives of this study were to synthesize Fe_3O_4/BC nanocomposites and explore the possibility of using Fe_3O_4/BC nanocomposites as adsorbents for the removal of heavy metal ions from aqueous solution.

Methodology

Biosynthesis of bacterial cellulose

Acetobacter xylinum strain TISTR No. 975 purchased from TISTR (Thailand Institute of Scientific and Technological Research, Thailand) was transferred to the nata de coco medium (containing coconut water 1000 ml, sucrose 50 g and $(NH_4)_2SO_4$ 25 g, pH of culture medium was adjusted to 4.5 by 5% (v/v) acetic acid) and incubated at 30 °C for 5 days under static condition. After that, obtained BC membrane were washed and boiled in deionized water for 2 h, to remove any residues on their surfaces and then boiled with 1% (w/v) NaOH solution for 2 h and thoroughly washed in deionized water until neutral pH.

Synthesis of bio-magnetic nanocomposites

The BC membranes were used to fabricate the bio-magnetic nanocomposites through in situ synthesis under ultrasonic treatment. Briefly, mixed solution of $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ (a molar ratio of the Fe^{3+} to Fe^{2+} ions to be fixed at 2:1 stoichiometric) (Katepetch *et al.*, 2011) were mixed in 200 ml of deionized water. The mixture solution was heated at 50 °C until $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ dissolved completely, called iron salt solution. Then, BC membranes (0.1 cm) were immersed in an aqueous irons salts solution for 12 h. After that, BC membranes were rinsed with deionized water. Iron-absorbed BC membranes were immersed in 200 ml of NH_4OH solution (pH 11) under a high intensity ultrasonic bath (Elmasonic S 80H; 50/60 Hz, 760 W) for 1 h, to obtain Fe_3O_4-bounded BC membranes. Then, iron-absorbed BC membranes were washed with a large amount of deionized water and resonicated for 30 min, to remove any loosely bound Fe_3O_4 nanoparticles. Finally, the BC/ Fe_3O_4 membranes were freeze dried and kept in desiccators for further use.

Field-emission scanning electron microscopy (FE-SEM)

Morphology of samples was determined by FE-SEM (Hitachi, Model SU8020, Japan). The surface were sputtered with carbon and analyzed with the aid of the secondary electron detector (SEI).

Vibrating sample magnetometry (VSM)

The magnetic property was detected by VSM methods. Samples was inserted into a sample holder and vibrated within a magnetic field of up to 8000G and the results were reported in term of a magnetic hysteresis loop.

Determination of lead (II) ions absorption

The lead (II) ions absorption was prepared by 4000 mg of $Pb(NO_3)_2$ was dissolved in 1,000 ml of deionized water, to obtain 4000mg/l of Pb^{2+} solution and diluted to 10 ml with various concentrations. The final concentrations of Pb^{2+} were 20, 60 and 100 mg/l. Then, 25 mg of BC/Fe_3O_4 nanocomposite sheets were load in Pb^{2+} solution in various Pb^{2+} concentrations at 25 °C, to test the adsorption of Pb^{2+}. After that, the BC/Fe_3O_4 nanocomposite sheets were removed out of the tube and the solution was taken and diluted properly to test the concentrations of Pb^{2+} by atomic absorption spectrophotometer (PerkinElmer, Model AAnalyst 800, USA).

Results and Discussion

Synthesis of bio-magnetic nanocomposites and its characteristics

Bio-magnetic nanocomposites were synthesized by co-precipitation combined with ultrasonic treatment from a mixture solution of Fe(II) and Fe(III) salts that is a common method for synthesize magnetite nanoparticles (Katepetch *et al.*, 2013; Zheng *et al.*, 2013). In this study was studied about the utilization of bacterial cellulose (BC) as bio-template for entrapped magnetite nanoparticles on BC network structure via ultrasonic-assisted in situ synthesis method. This method is simple and easy to control. When never dried BC sheets immersed in iron salt solution, Fe(II) and Fe(III) ion were diffused to inside of BC networks structure due to the difference of ions concentration. After BC was saturated by aqueous iron ions, Fe-absorbed BC was transferred to immersion in NH_4OH solution under ultrasonic condition to catalyst the Fe_3O_4 nanoparticles formation (Katepetch *et al.*, 2013). Then, Fe_3O_4 nanoparticles were generated and entrapped on BC network structure, which confirmed by FE-SEM micrographs as showed in Fig. 1(a-b).

Fig. 1 shows the FE-SEM micrographs of native BC (Fig. 1a) and bio-magnetic nanocomposite (Fig. 1b). In native BC, Fig. 1a presented ultra-fine network structure with size of diameter around 70-100 nm and length in several micrometers. After Fe_3O_4 nanoparticles formed on BC nanofibers, Fig. 1b exhibited Fe_3O_4 nanoparticles aggregated on BC fibers and also presented a good distribution.

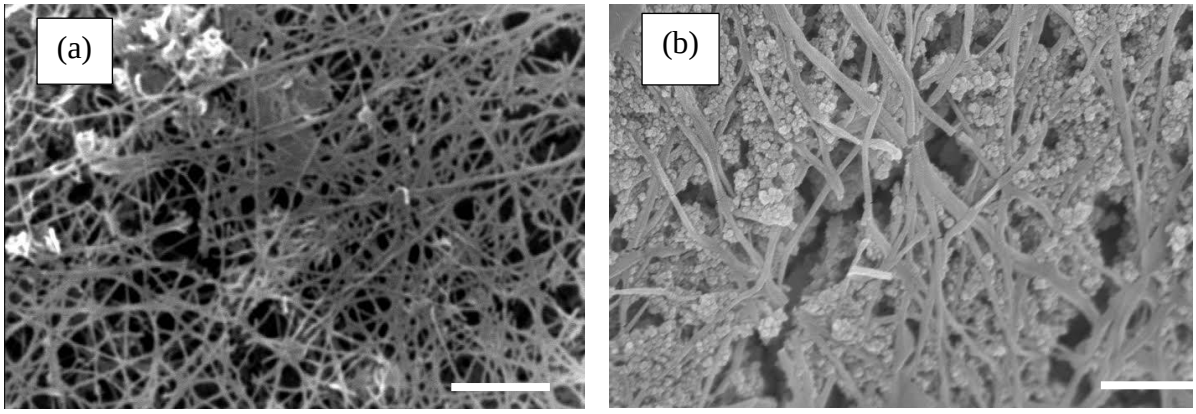

Figure 1: FE-SEM micrographs of native BC (a) and bio-magnetic nanocomposite (b) (scale bar = 1 micrometer)

The magnetic property of BC/magnetite nanocomposites or bio-magnetic nanocomposites were determined by VSM measurement that referred as the magnetic hysteresis curves and the saturated magnetization (M_S) value, as shown in Fig 2. Under the magnetic field, the bio-magnetic nanocomposites showed good magnetic responsiveness. When the applied magnetic field is removed, their magnetization disappears. The results showed that the magnetic hysteresis loop of bio-magnetic nanocomposites showed in Fig. 2 and M_S value was found to be 29.86 emu/g. Moreover, M_S value of native BC also was investigated, which was not presented the magnetization behavior (data not shown), which indicated that native BC has not magnetic property. From suggest results, the in situ synthesis combined with ultrasonic treatment can be prepared the bio-magnetic nanocomposites from BC and Fe_3O_4 nanoparticles. In addition, the obtained bio-magnetic nanocomposites presented the high M_S value was found to be 29.86 emu/g. These results were significantly higher than other studies in BC/Fe_3O_4 nanocomposites. Sourty *et al.* (1998) reported a M_S value of 3.5 emu/g and Katepetch *et al.* (2011) reached a M_S around 26 emu/g. The difference of M_S value may be probably due to the difference of processes, iron salts and the dimensional-structure of BC.

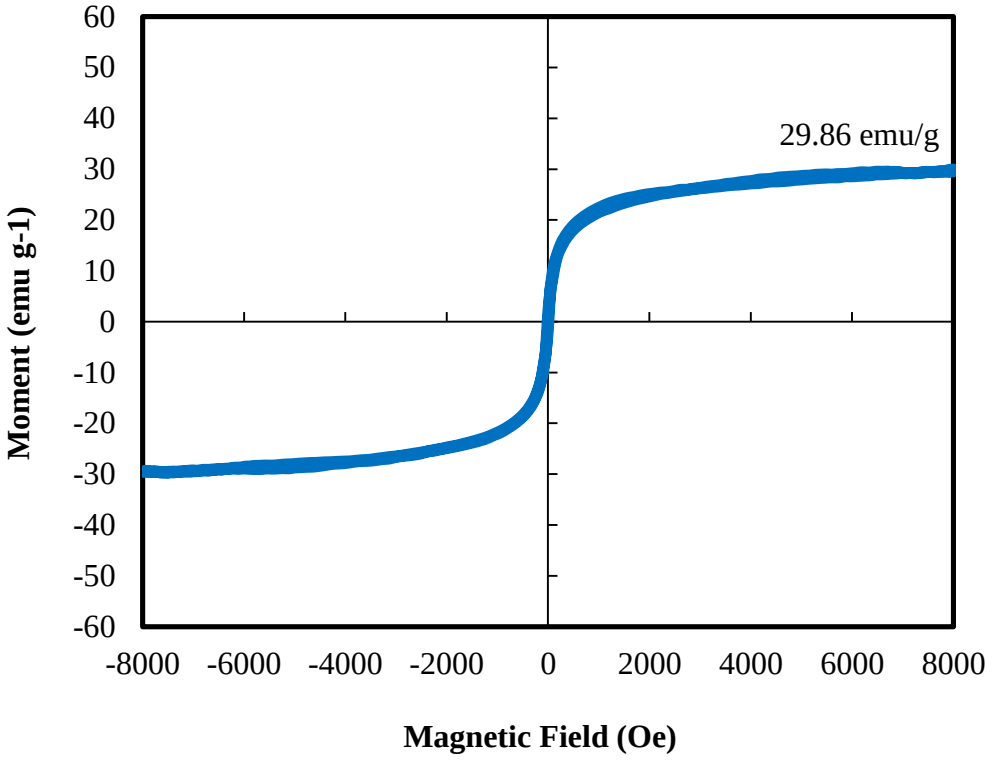

Figure 2: The hysteresis loops for the bio-magnetic nanocomposites

Determination of bio-magnetic nanocomposite for lead (II) ion absorption

Fig. 3 shows the adsorption ability of bio-magnetic nanocomposites for different Pb^{2+} concentration (20, 60 and 100 mg/ml) for 0-400 min. From Fig. 3, the increasing of Pb^{2+} adsorption with ion concentrations shows a trend of initial rapid rising and then mild change, while the native BC films does not showed the Pb^{2+} absorption (data not shown).

Initially (30 min), the Pb^{2+} concentration of mixture solution were great decreased around 80% when compared with the mixture Pb^{2+} solution without bio-magnetic nanocomposites. After 30 min, the Pb^{2+} concentration at 20, 60 and 100 mg/ml were approaches a constant around 2, 9 and 16 mg/ml, respectively. This is due to the interaction between hydroxyl groups of cellulose and Pb^{2+} ion by hydrogen and covalent bonding, resulting in the Pb^{2+} ions were fixed or entrapped on BC/Fe_3O_4 structure (Zhu *et al.*, 2011). These results can be confirmed about the bio-magnetic nanocomposites can significantly adsorbed Pb^{2+} ion in mixture solution. The great adsorption rate of bio-magnetic nanocomposites exhibited that they have promising applications in the industrial sewage treatment because it can adsorb Pb^{2+} ion efficiently. In addition, the bio-magnetic nanocomposites can be used not only to reduce the cost of the sewage treatment, but also to avoid secondary pollution to the environment (Donia *et al.*, 2012; Wu *et al.*, 2008; Zhu *et al.*, 2011).

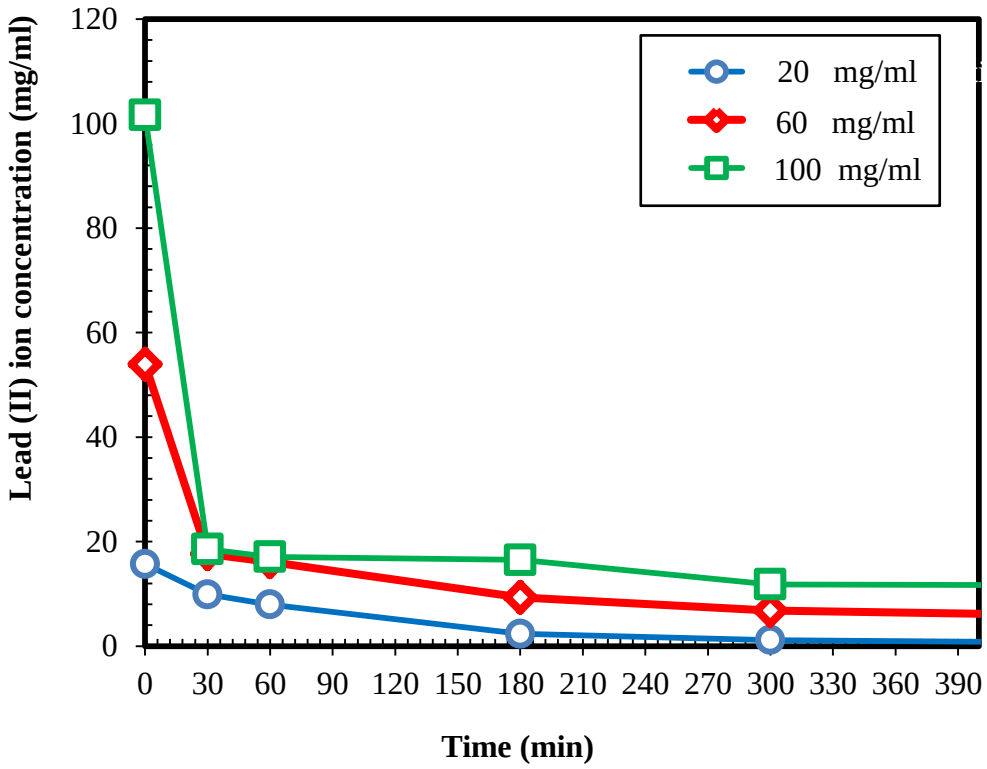

Figure 3: The adsorption ability of bio-magnetic nanocomposites for different Pb^{2+} concentration (20, 60 and 100 mg/ml)

Conclusion

In this study, the bio-magnetic nanocomposites were prepared from the incorporation between bacterial cellulose and magnetite nanoparticles. The results shown that the bio-magnetic nanocomposites presented a magnetic property presented high saturated magnetization (M_S) value at 29.86 emu/g and FE-SEM results also supported about the Fe_3O_4 nanoparticles entrapped on BC network structure. The adsorption of bio-magnetic nanocomposites for Pb^{2+} ion exhibited an increasing of Pb^{2+} adsorption with ion concentrations shows a trend of initial rapid rising and then mild change, which showed Pb^{2+} concentration decrease up to 80% when compared with control condition (without bio-magnetic nanocomposites). The great M_S value and high adsorption ability of bio-magnetic nanocomposites are suitable for applied as a kind of polymers for waste water treatment.

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