SYNTHESIS OF EMERALDINE BASE – *PHRAGMITES AUSTRALIS* BIOCOMPOSITE AND ITS APPLICATION FOR Cu²⁺ IONS REMOVAL FROM AQUEOUS SOLUTIONS

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Abstract

In this paper the influence of *in situ* synthesized biocomposite of emeraldine base and *Phragmites australis* (Cav.) Trin. ex Steud (Common reed) on the removal of copper ions from aqueous media is discussed. Physico-chemical parameters such as initial copper ion concentration, composite dosage and contact time between composite and Cu²⁺ ions in the water solution were studied. The removal efficiency of copper by biocomposite of emeraldine base and Common reed was determined. Two different quantities of Common reed in the biocomposite (Biocomposite I and Biocomposite II) were used. The results show, that the longer contact time leads to the increased removal efficiency. Maximum removal efficiency of 99.9 % and 98.3 % was achieved using Biocomposite I and Biocomposite II, respectively.

Key words: Common reed, copper ions removal, Emeraldine base, *in situ* polymerization.

Introduction

The wastewaters generated during the non-ferrous metals production and their processing like electroplating and other industrial processes are the main sources of environmental pollution with heavy metals (Yong-hua et al. 2007). The most commonly found include copper, cadmium, chromium, arsenic, etc., all of which cause risks for the environment and humans (Lambet et al. 2000, Jaishankar et al. 2014). The heavy metals are difficult to remove from the environment and often cause secondary pollution (Pan et al. 2002). The most commonly used methods for removing them from wastewater are chemical precipitation, extraction, reverse osmosis, adsorption, ion exchange, membrane separation, electrodialysis, coagulation, biological treatment, etc. (Fu and Wang 2011). The high cost of most of these methods is a limitation for their widespread usage. Development of innovative and cost-effective processes for treating waters with low concentration of heavy metals is needed. Some new materials with polymeric nature, which are alternative to conventional sorbents, were used recently. In most cases, these substances are used in combination with other materials in order to increase their treatment efficiency. This effect is due to the enlarged surface area and greater electron donor

property, derived synergistically from both components of the composite material (Bhaumik et al. 2014). There are some composite materials such as polyaniline/polystyrene, aniline/sulfoanisidine, poly-aniline/metallic iron nanoparticles, etc. (Gupta et al. 2004, Li et al. 2009, Sharma et al. 2014, Kang et al. 2015, Mittal et al. 2016, Naushad et al. 2016, Pathania et al. 2016, Sharma et al. 2016, Sharma et al. 2017, Sharma et al. 2015, Sharma et al. 2015). On the other hand it is well known that *Phragmites australis* (Cav.) Trin. ex Steud (Common reed) and other macrophytes play significant role in water purification as they accumulate in their tissue various organic and inorganic pollutants as well as metal compounds (Lavrova and Koumanova 2006, Lavrova and Koumanova 2008, Vymazal and Březinová 2016). The preparation of composites of polyaniline and vegetation waste, the so called biocomposites, is of interest for many researchers. In their scientific studies they use sawdust, rice husks, jute fibers, kapok fibers, etc. (Mansour et al. 2011, Ghorbani and Eisazadeh 2013, Kumar et al. 2008, Zheng et al. 2015). Such biocomposites showed high removal efficiency of heavy metal ions from aqueous media. Due to biocomposites selectivity and efficiency, easy preparation and cost effectiveness they are a good alternative to conventional sorbents which are used in practice.

The aim of this study was to investigate the possibility of *Phragmites australis*/Emeraldine base biocomposites to remove copper ions from a model aqueous media. The influence of the experimental conditions – metal ion concentration, polymer dosage and contact time on the Cu^{2+} ions removal from aqueous media was studied.

Material and Methods

Reagents

Aniline ($C_6H_5NH_2$), hydrochloric acid (HCl), ammonium persulfate (($NH_4)_2S_2O_8$), sodium hydroxide (NaOH), copper sulphate pentahydrate ($CuSO_4.5H_2O$), sodium acetate ($C_2H_3NaO_2$) and acetic acid (CH_3COOH) pure for analysis were used in the experiments. Distilled water was also used. Leaves of *P. australis* from comparatively clean area in this study were used. After collection they were washed first with tap water, then with distilled water to remove any dust particles. The washed crops were dried for 2 h at 60 °C. The dried material was rinsed with acetone and then with 0.3 M NaOH and was again dried at the same temperature to constant weight (Mo et al. 2009). After its pre-treatment the dried material was finely grinded.

Preparation of the biocomposites

The preparation of the biocomposites was carried out in standard conditions and two different solid/solution ratios were used. In the first case *P. australis*/aniline ratio (Biocomposite I) was 1:15 and in the second case (Biocomposite II) it was 1:4. The preliminary weighed amounts of Common reed (leaves) were mixed with 1938.6 mL of 1 M HCl under continuous stirring at 800 rpm for 24 h. After that 61.4 mL of aniline was added to the reaction mixture and the suspension was stirred for 24 h at room temperature. The solution of the oxidant, which was necessary for the preparation of polyaniline from aniline monomer, was prepared by dilution of ammonium persulfate (($NH_4)_2S_2O_8$) with distilled water to volume of 800 mL. This solution was add-

ed to the reaction mixture and the resulting suspension was stirred continuously for another 24 h. The suspension was filtered and washed with distilled water. In order to remove the impurities and possible residual monomers the suspension was washed several times with mixture of water and methanol at ratio 80:20. At the end of the process the polymerized aniline monomer in the biocomposites composition was under protonated form – emeraldine salt. It is well-known that it is not particularly efficient for removal of ions from an aqueous media and it has to be converted into more effective form – emeraldine base. The conversion of emeraldine salt into emeraldine base was carried out via washing the resulting precipitate with 1 M NaOH to pH 10.0–11.0. Thus deprotonation was achieved, consisting in the release of electron pairs on the nitrogen atoms in the amine groups of the emeraldine base polymer chain. These free electron pairs are the places where the metal ions, contained in the aqueous media, can be trapped. The washed precipitate was dried at 60 °C to a constant weight. Well-dried biocomposite was ground to a homogeneous powder.

Preparation of standard solutions of copper ions

Solution of copper ions with concentration of 1 g·L^{-1} was prepared, using 3.93 g $CuSO_4 \cdot 5H_2O$ and distilled water. Then standard solutions with concentrations of 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 30.0, and 50.0 mg·L^{-1} were prepared.

Experimental

In order to establish the influence of the contact time on the removal of copper ions from aqueous media by *P. australis*/Emeraldine base biocomposites, individual samples with initial copper ions concentration of 50.0 mg·L^{-1} (C_o) were prepared. The volume of each sample was 50 mL and certain amount of the biocomposites (0.1, 0.5, 1.0 and 1.5 g) was added to each of them. To adjust pH to 5.0, proper for the copper ions removal (Srithongkham et al. 2012), acetate buffer was added to each solution. The samples were placed in iodine flasks and were shaken with a plate shaker for 1, 3, 5, 7, 10, 15, 30, 60 and 360 min, respectively. Samples with volume 20 mL were taken and filtered through a blue ribbon filter paper to remove suspended biocomposite particles. The filtrates were analysed by ISP–OES ('Prodigy' High dispersion ICP-OES, Telledyne Leeman Labs) in order to determine copper ions concentration.

In order to establish the influence of initial copper ions concentration individual samples with certain initial Cu^{2+} concentration (C_o = 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 30.0, 50.0 mg·L^{-1}) were prepared. The volume of each sample was 50 mL. Certain amount of the biocomposites (0.1 g) was added to each of them. To adjust the pH to 5.0, acetate buffer was added to each solution. The samples were placed in iodine flasks and were shaken with a plate shaker for 30 min. Samples with volume 20 mL were taken and after filtration through a blue ribbon filter paper were analysed for Cu^{2+} ions concentration.

The removal efficiency was determined according to the formula (1):

$$RE = 100 - \left(\frac{C_t}{C_o}\right) \cdot 100 \qquad (1),$$

where: RE is removal efficiency (%), C_o is the initial concentration (mg·dm^{-3}), and C_t is the concentration at time t (mg·dm^{-3}).

Results and Discussion

Influence of the contact time and biocomposite dose on copper ions removal

The results show that with increasing of the contact time between biocomposites and the standard solutions, Cu^{2+} ions concentration is decreasing (Figs. 1 and 2). For example, using 0.1 g of Biocomposite I (Fig. 1) decreased initial copper ions concentration as follows: at 1st min – with 1.3 times, at 10th min – with 1.9 and at 360th min – with 2.2. When using the same amount of Biocomposite II the initial copper ions concentration was decreased as follows: at 1st min – 1.1 times, at the 10th min – 1.4, and at 360th min – 1.6.
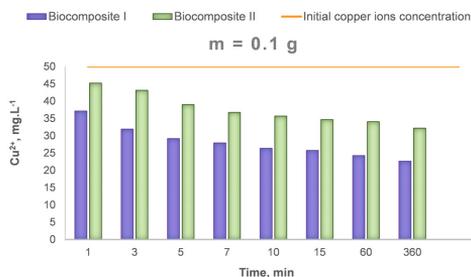

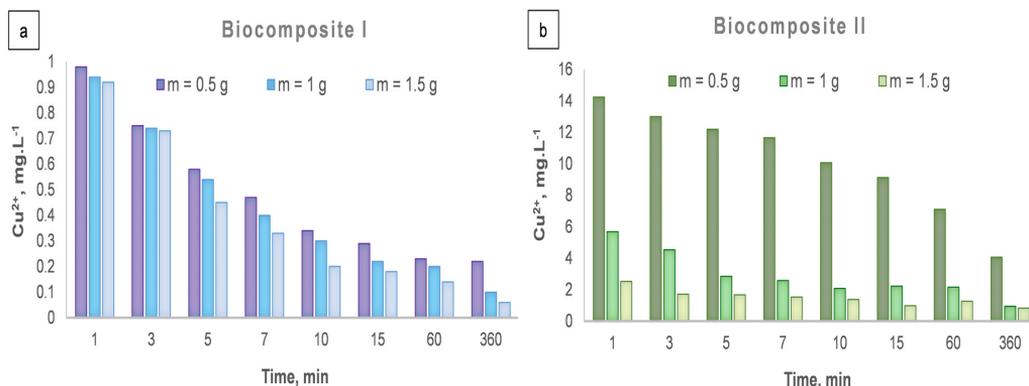Fig. 1. Influence of contact time on copper ions removal by 0.1 g of biocomposites.

Fig. 2. Influence of the contact time on the copper ions removal at different Composite I (a) and Composite II dose (b).

Figure 2 (a, b) shows that the concentration of copper ions decreased with the time and the biocomposite dose increased toward their initial concentration. For example, for a period of one minute and usage of 0.5 g, 1 g and 1.5 g of Biocomposite I, the concentration of copper ions was reduced to 0.98 mg·L^{-1}, 0.92 mg·L^{-1} and 0.94 mg·L^{-1}, respectively. Using the same quantities of Biocomposite II and same period of time, it decreased up to 14.24 mg·L^{-1}, 5.69 mg·L^{-1} and 2.53 mg·L^{-1}, respectively.

The results show that the process of bonding between metal ions and biocomposite material occured immediately after mixing of the composite with the solution of copper ions. After that the process slowed down and at the 360th min the concentrations of Cu^{2+} which were achieved are 0.22 mg·L^{-1}, 0.1 mg·L^{-1} and 0.06 mg·L^{-1}, using 0.5 g, 1 g and 1.5 g of Biocomposite I and 4.06 mg·L^{-1}, 0.94 mg·L^{-1} and 0.83 mg·L^{-1}, using the same quantities of Biocomposite II. Fig. 2-b shows that usage of higher dose leads to better results.

A big difference was observed when 0.5 g Biocomposite II and the other two quantities of the same material were used (1 g and 1.5 g).

Based on the results obtained from the analysis, the removal efficiency of Cu^{2+} was calculated (Table 1).

Table 1. Summary of removal efficiency achieved.

Time, min	Removal efficiency, %			
	Dose, g			
	0.1	0.5	1.0	1.5
	Biocomposite I			
1	25.7	98.0	98.1	98.2
360	54.7	99.6	99.8	99.9
	Biocomposite II			
1	9.5	71.5	88.6	94.9
360	35.5	91.9	98.1	98.3

The results show that Biocomposite I was more effective in comparison with Biocomposite II and there was no significant difference when using 1 g or 1.5 g of them. Comparing the removal efficiencies which were achieved it was seen that in both cases a high degree of purification was achieved. Obviously, when greater doses of the composite material were used, better results were obtained. The larger content of emeraldine base in Biocomposite I provided more available free electron pairs on the nitrogen atom structure, where positively charged metal ions can be bonded. Although the percentage content of emeraldine base in Biocomposite II is less than that in Biocomposite I, and the content of plant matter is greater than that in Biocomposite I, respectively, high removal efficiencies were achieved. This means that the biosorbent *P. australis* also contributes to the successful purification process.

Identification of copper ions initial concentration on their removal with biocomposite

From the results obtained it was observed that with increasing of initial copper ions concentration, the removal efficiency of 0.1 g biocomposites was reduced (Fig. 3). The lowest one was observed in the samples containing 30 $mg \cdot L^{-1}$ and 50 $mg \cdot L^{-1}$ copper ions. In the first case the removal efficiency was 82.8 %, using Biocomposite I and 58.3 % – using Biocomposite II and in the second case it was 49.4 %, using Biocomposite I and 31.0 % – using Biocomposite II. The higher removal efficiency at lower concentrations can be explained by existence of enough free nitrogen atoms in the polymer chain, which have higher electron density namely those involved in the complexing with copper ions. With increasing of metal ions concentration the possibility of their binding to polymer structure reduces.
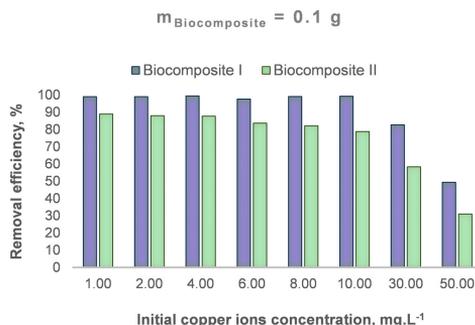

Fig. 3. Comparison between removal efficiency of 0.1 g Biocomposite I and Biocomposite II, using different initial copper ion concentrations.

Because of usage of $CuSO_4 \cdot 5H_2O$ for standard solutions preparation, the sulphuric ions concentration was measured too. It is well-known that the polyaniline is not suitable for negatively charged ions removal. This fact was confirmed and the results are shown in Figure 4.
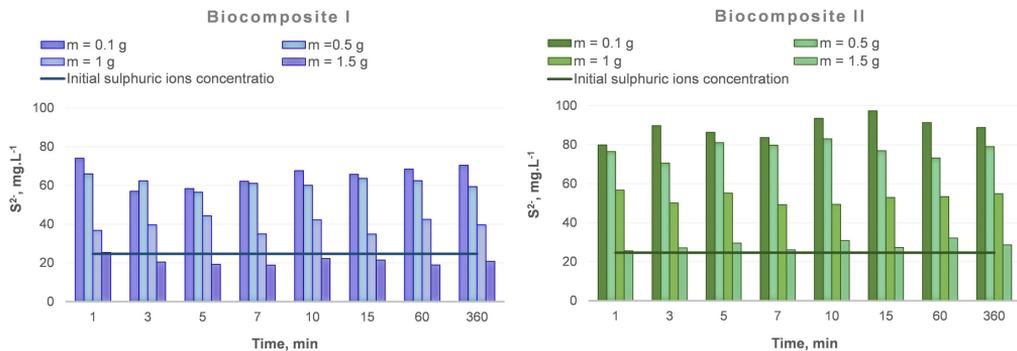
Fig. 4. Influence of the contact time on the concentration of sulphuric ions.

Their concentration was increased from 24.65 mg·L^{-1} to 97.38 mg·L^{-1} with time. Perhaps this increasing is due to the release of this element from *P. australis* joined in the biocomposite. Therefore, there was not observed water purification from sulphuric ions.

The mining industry causes aquatic environment contamination with sulphate ions in high concentrations, which are toxic for aquatic flora, influencing plants' growth and chlorophyll levels (Davies 2007). The animals are also susceptible to these ions and if young animals consume contaminated water they can get chronic diarrhea or in some cases it can cause their death. That is why effective removal of these ions from the wastewater is needed.

Conclusions

The possibility of *Phragmites australis*/Emeraldine base biocomposites to remove copper ions from model aqueous media was studied. For this purpose preparation of biocomposites consisted of emeraldine base and different quantities of *P. australis* was successfully performed by *in situ* polymerization of aniline. It was established that with increasing of the contact time greater removal efficiency was observed using both Biocomposites I and II. Maximum copper ions removal efficiency was achieved using 1.5 g of them for a period of 360 min. For Biocomposite I the obtained efficiency was 99.9 %, and for Biocomposite II – 98.3 %. The results show that Biocomposite I was more effective in comparison with Biocomposite II and there was no significant difference when using 1 g or 1.5 g of them. In the form that were used the synthesized *Phragmites australis*/Emeraldine base biocomposites are not suitable for removal of negatively charged ions, such as sulphuric ones.

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