COPPER IONS REMOVAL FROM AQUEOUS MEDIUM THROUGH EMERALDINE

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ABSTRACT. *In situ* synthesized emeraldine salt and emeraldine base were used for copper ions removal from aqueous medium. Physicochemical parameters such as initial copper ion concentration, polymer dosage and contact time between the emeraldine and the metal ions in aqueous solution were studied. Removal efficiency of copper using the obtained emeraldine forms was estimated. It was found that the emeraldine base extracts the Cu^{2+} from aqueous solutions better than emeraldine salt. The binding process between the metal ions and the polymer occurs immediately after their mixing and the main process occurs within 15 minutes in all the experiments. For this period of time and 50 mg/l initial copper ions concentration, removal efficiency of 76.8 % was achieved using 1.5 g emeraldine base. The maximal removal efficiency (98.3 %) of the ions was achieved for 1440 min.

Keywords: *In situ* polymerization; polyaniline; emeraldine; copper ions removal

ОТСТРАНЯВАНЕ НА МЕДНИ ЙОНИ ОТ ВОДНА СРЕДА ЧРЕЗ ЕМЕРАЛДИН

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РЕЗЮМЕ. За отстраняването на медни йони от водна среда са използвани емералдин сол и емералдин база, синтезирани чрез in situ полимеризация. Изследвани са физико-химични параметри като начална концентрация на медните йони, доза на полимера и време на контакт между емералдина и металните йони във водния разтвор. Изчислен е ефектът на пречистване на водната среда от медните йони чрез получените емералдинови форми. Установено е, че емералдин база извлича Cu^{2+} йони от водния разтвор по-добре от емералдин сол. Процесът на свързване между металните йони и полимера се случва веднага след смесването им, а основния процес протича в рамките на 15 минути при всички експерименти. За този период от време и 50 mg/l начална концентрация на медните йони, ефектът на пречистване, който се постига при използването на 1.5 g емералдин база е 76,8 %. Максималният ефект на отстраняване (98.3 %) на тези йони се постига за 1440 минути.

Ключови думи: In situ полимеризация; полианилин; емералдин; отстраняване на медни йони

Introduction

Because of the toxic effect of heavy metals they have to be removed from the wastewater before discharge in the aquatic environment. Among the most dangerous heavy metal ions are Cu, Cd, Cr, As, Pb, Ni, etc. During the production of copper from copper ores, manufacturing of printed circuit board, electronics plating, plating, printing operations, wire drawing, copper polishing, paint manufacturing and wood preservatives production, large amounts of wastewaters with high concentrations of copper ions are produced. Copper ions are very toxic for living organisms and therefore should not be released into the environment. Adsorption is a basic process for metal ions removal from wastewater and the scientists are looking for new materials which are alternative to the conventional sorbents, such as Polyaniline, Polypyrrole, Polythioamide, Chitosan, etc. [Hutchison et al., 2008; Henneberry et al., 2011; Wiatrowski et al., 2009; Urgun-Demirtas et al., 2012; Hamissa et al., 2010; Blázquez et al., 2011; Schiewer and Balaria, 2009; Yu et al., 2011]. Some of these materials have polymeric nature [Gupta et al., 2004; Li et al., 2009; Balarama et al., 2005; Kumar et al., 2008; Zhang et al., 2010; Wang et al., 2009; Chandra and Kim, 2011; Bhaumik et al., 2012; Vieira and Beppu, 2006; Kagaya et al, 2010; Qu et al., 2010], The usage of such substances is significant because of their high stability, selectivity, low cost, easy polymerization and effectiveness. It is well-known that the nitrogen atom in these amino-derivatives makes coordinate bond with positive charged metal ions, due to the free electron pairs. Thanks to this, the metal ions removal from treated wastewater is possible. The small particle size of the used adsorbent also increases the process effectiveness. The aniline monomer polymerization leads to production of polyaniline which can be found in one of these three idealized oxidation states – leucoemeraldine, which is white, clear or colorless $(C_6H_4NH)_n$, emeraldine – has dark green color for the emeraldine salt and dark blue color for the emeraldine base $([C_6H_4NH]_2[C_6H_4N]_2)_n$, and (per)nigraniline, which is blue/violet $(C_6H_4N)_n$ [Stejskal, 1995].

The aim of this study is to investigate the possibility of emeraldine to remove copper from model aqueous medium. This research consists of emeraldine synthesis and study of the experimental conditions like metal ion concentration, polymer dosage and contact time for copper ions removal from model aqueous solution. These investigations are needed to determine the removal efficiency.

Materials and methods

Chemicals and solvents

Pure for analysis Aniline ($C_6H_5NH_2$), Hydrochloric acid (HCl) and Ammonium persulfate ($(NH_4)_2S_2O_8$) were used for the polyaniline synthesis. Distilled water was also used. For the emeraldine salt conversion to emeraldine base, pure for analysis sodium hydroxide (NaOH) was used. $CuSO_4.5H_2O$, pure for analysis, with concentration of 1 g/l was used for the preparation of the model solution. Then standard solutions with concentrations of 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 30.0, 50.0, 70.0 and 100.0 mg/l were prepared. Sodium acetate and acetic acid, pure for analysis, were used for preparing acetate buffer for pH adjustment.

Emeraldine salt synthesis

Polyaniline was synthesized through oxidative polymerization using aniline monomer ($C_6H_5NH_2$) and ammonium persulphate ($(NH_4)_2S_2O_8$) as an oxidant. Distilled aniline (61.4 ml) was diluted with 1 M HCl to 2 liters in a volumetric flask. Ammonium persulphate (168.7 g) was diluted with distilled water to 800 ml. Both solutions were cooled in refrigerator at temperature of 5 ºC. After that the oxidant solution was added dropwise to the 0.5 M aniline solution. The mixture was stirred for 1 hour at room temperature and after that was left to polymerize. The greenish-black suspension of emeraldine salt was filtered through Buckner funnel using continuous stirring with mechanical agitator for better filtrate draining. The precipitate was washed repeatedly with distilled water and after its dewatering was dried in oven at 40 ºC to constant mass. The dried polymer was ground to a fine homogeneous powder.

Emeraldine base synthesis

Protonated emeraldine salt was converted to emeraldine base through washing with 1 M NaOH to pH 10.0 – 11.0. The polymer was dried at 40 ºC to constant mass and after that was ground to a fine homogeneous powder.

Removal technique

In order to establish the influence of the contact time on the copper ions removal as well as the influence of the polyaniline dosage, 50 ml individual samples with initial copper ion concentration of 50 mg/l were prepared. A pre-weighed on an analytical balance amount of polyaniline (m = 0.1 ÷ 1.5 g) and acetate buffer for adjustment of pH to 5 were added to each of the samples [Awual et al, 2014; Igberase et al., 2014; Mansour et al., 2011]. The water samples were poured in iodine flasks and agitated for 24 hours at temperature of 17±1 ºC. At the predetermined time intervals, 20 ml portions of each suspension were taken and filtered through blue ribbon filter paper to remove suspended polymer particles.

In order to establish the influence of the initial copper ions concentration on their removal, 50 ml aqueous samples with different initial copper ion concentration (C_o = 1 ÷ 100 mg/l) were prepared. A certain amount of polyaniline (m = 0.1 g) and acetate buffer for pH adjustment to 5 was added to each of the samples. The water samples were agitated at temperature of 17±1 ºC. At the end of the predetermined period of time, the 20 ml portions of each water samples were taken and filtered through blue ribbon filter paper to remove polymer particles.

Instrument and measurements

Atomic absorption spectrometry was used for copper concentration measurement in the precipitates (Perkin Elmer-323 apparatus).

Removal efficiency

The efficiency of Cu^{2+} removal by polyaniline was calculated according to the formula (1):

$$\text{RE}, \% = 100 - \left(\frac{C_t}{C_o}\right) \times 100 \quad (1)$$

where C_o is the initial Cu^{2+} concentration and the C_t is the concentration at time "t" in mg/l.

Results and discussion

Effect of contact time and polyaniline dosage on the removal efficiency.

The binding process between the copper ions and the polymer occurs immediately after mixing of the polymer and the aqueous media, containing copper ions, followed by a complexation reaction delay (Fig. 1). 28 % removal efficiency by 0.1 g emeraldine base was obtained in 15 minutes. After that the Cu^{2+} removal remains constant up to 24 hours. For comparison of the effectiveness of the two forms emeraldine – salt and base, at the same period of time 0.1 g emeraldine salt was used. It was established that the emeraldine salt removes 25 % of the initial 50 mg/l copper ions concentration and after that the removal efficiency also does not change until the 24th hour.

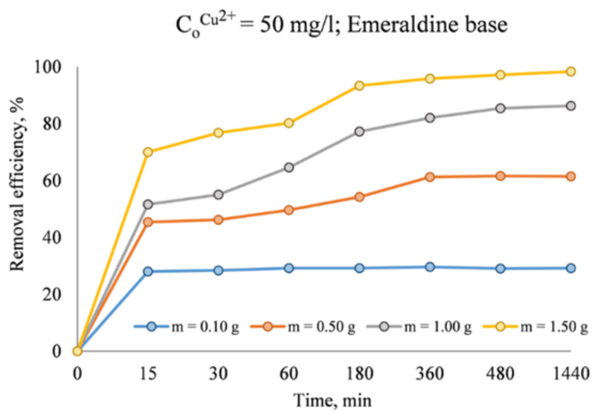

Fig. 1. Effect of the contact time and emeraldine base dosage on the removal efficiency.

In the experiments with the same initial copper ions concentration (50 mg/l) but greater emeraldine base dosage (0.5, 1.0 and 1.5 g), the removal efficiency, achieved in 15 minutes, was as follows: 45.4 %, 51.6 % and 70.0 %, respectively. At the 24^{th} hour the removal efficiency was increased up to 61.4 %, 86.2 % and 98.3 %, respectively for the above mentioned quantities of emeraldine base. The usage of 1.5 g emeraldine base leads to the highest removal efficiency - 98.3 % in 24 hours. It is well-known that the emeraldine base is more effective for metal ions removal due to the more available electron pairs in its structure, compared to the emeraldine salt, and the obtained results confirmed this statement. Despite that, the emeraldine salt succeeded to catch almost the same amount of copper ions as the emeraldine base in the identical technological conditions. Probably, the removal process with emeraldine salt is a combination of different mechanisms beside the complexation.

Effect of the initial Cu^{2+} concentration on the removal efficiency

The results show, that with initial copper ions concentration increasing, the effect of their removal with 0.1 g of polyaniline is decreasing (Fig. 2). For example, in a period of 30 minutes and the initial copper ions concentrations of 1 mg/l, 10 mg/l and 50 mg/l removal efficiency of 88 %, 60 % and 30 %, respectively, was achieved. The higher removal efficiency achieved in the experiments with lower copper concentration can be explained by the presence of a sufficient number of free electron pairs in the nitrogen atoms of the polymer chain, which have a higher electron density and that those are involved in the complexation with the copper ions. The increasing of the initial metal ions concentration leads to decreasing of the possibility for their attachment to the polymeric structure.

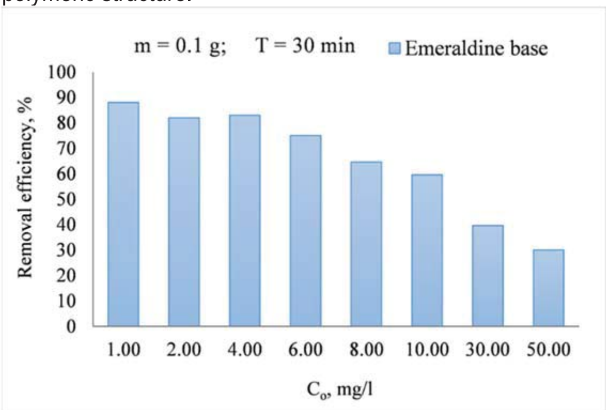

Fig. 2. Effect of the initial concentration of the copper ions on the emeraldine base removal efficiency.

The removal efficiency which was achieved in the experiments with emeraldine salt is lower in comparison with that in the experiments with emeraldine base. For example, in the 30 minute experiment with 10 mg/l initial copper ions concentration, the removal efficiency was 40 %, which is 1.5 times lower than that achieved in the experiment with emeraldine base at the same time and initial copper concentration. With copper ions concentration increasing, the removal efficiency of 0.1 g emeraldine salt is not higher than 27 % (Fig. 3).

Conclusions

The preparation of emeraldine salt and emeraldine base was successfully performed by *in situ* polymerization of aniline. The metal complexation reaction proceeds very quickly and in 15 minutes was achieved 70 % removal efficiency with initial copper ions concentration of 50 mg/l and 1.5 g emeraldine base. The removal efficiency of copper ions increased with the polymer dosage and the contact time increased. The emeraldine base removal efficiency was higher than that of the emeraldine salt.

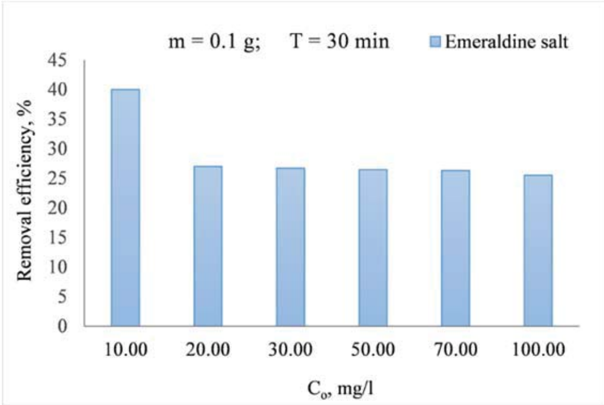

Fig. 3. Effect of the initial copper ions concentration on the removal efficiency of emeraldine salt.

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This article was reviewed by Prof. Dr. Maria Karsheva and Assoc. Prof. Dr. Svetlana Bratkova.