

## Removal of Cu<sup>2+</sup> Ions from Aqueous Medium Using Clinoptilolite/Emeraldine Base Composite

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**Abstract.** The aim of this study was to investigate the removal efficiency of *in situ* synthesized composites consisted of emeraldine base and clinoptilolite on copper ions removal from aqueous medium. Two composite materials (*Composite I* and *Composite II*) with different quantity of clinoptilolite were synthesised. The influence of the composite dosage, the contact time and the initial copper ions concentration has been studied. The results show that the significant removal of the copper ions becomes at the first minute of the contact between the composite material and the aqueous medium and the longer contact time leads to increasing of the copper ions removal. The removal efficiency at the 1st minute was 57.5% and 77.3% using *Composite I* and *Composite II*, respectively. Maximum removal efficiency of 87.3% and 96.8% was achieved at the same dosage of *Composite I* and *Composite II*, respectively, at contact time of 360 minutes and temperature of 24 °C.

**Key words:** *in situ* polymerization, polyaniline composite, clinoptilolite, copper ions removal.

### Introduction

The wastewater streams, contaminated with heavy metals such as Cu, Pb, Hg, As, etc., are usually released from mining and metallurgical industry as well as from the galvanic production processes. The widely applied processes for their treatment are often either very expensive or cannot meet the health and environmental protection standards. Because of the accumulation of heavy metals in the environment and the newest environmental standards, a development of innovative and cost-effective techniques for their removal is important. Some of the materials such as polyaniline, polypyrrole, polythioamide, chitosan, etc. and their combinations, which have polymeric nature, were used. Combination of different polymeric compounds or their combination with

different sorbents leads to increasing of the treatment efficiency (WANG *et al.*, 2009; KAGAYA *et al.*, 2010; OLAD & NASERI, 2010; ZHANG *et al.*, 2010; MANSOUR *et al.*, 2011; BHAUMIK *et al.*, 2012; JIANG *et al.*, 2012; GHORBANIA & EISAZADEHB, 2013; RASHIDZADEH & OLAD, 2013; BEHBAHANI *et al.*, 2014; FAGHIHIAN & RASEKH, 2014; IGBERASE *et al.*, 2014; 2014; SHYAA *et al.*, 2015). This effect is due to the enlarged surface area and greater electron donor property (BHAUMIK *et al.*, 2014). The zeolites are microporous aluminosilicate minerals, commonly used as adsorbents and ion exchangers (SHERY, 1966; ĆURKOVIĆ *et al.*, 1997; ONTHONG & KAREMDABEH, 2010; TOROSYAN *et al.*, 2013; AWUAL *et al.*, 2014; YANEVA *et al.*, 2016). Their lattice structure contains interconnected voids which are filled with cations, usually of elements from

group I-A or II-A of the periodic system, which can be exchanged with other cations from the surrounding medium.

The aim of this study is to investigate the possibility of clinoptilolite/emeraldine base composites for the removal of copper ions from model aqueous medium. This research includes a synthesis of composites consisted of clinoptilolite and emeraldine base and study on the influence of the initial metal ion concentration, composite dosage and contact time.

### Materials and Methods

The experiments were carried out with pure for analysis aniline ( $C_6H_5NH_2$ ), hydrochloric acid (HCl), ammonium persulfate ( $(NH_4)_2S_2O_8$ ), sodium hydroxide (NaOH),  $CuSO_4 \cdot 5H_2O$ , sodium acetate ( $C_2H_3NaO_2$ ) and acetic acid ( $CH_3COOH$ ). Distilled water was also used. The zeolite used in the experiments is clinoptilolite ( $(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36} \cdot 12H_2O$ ) and was obtained from the eastern part of the Rhodope mountain in Bulgaria. The used material was with a particle size of 0.1-0.8 mm.

#### *Preparation of clinoptilolite/emeraldine base composite*

Two types of composites were obtained which were differ in the amount of the clinoptilolite used for their synthesis. In the first case the ratio clinoptilolite/aniline (*Composite I*) was 1:15 and in the second case (*Composite II*) it was 1:4. The preliminary weighted amounts of zeolite were mixed with 1M solution of hydrochloric acid (HCl) at continuous stirring (800 rpm) for 4 hours. After that the aniline was added to the reaction mixture and the stirring continued 24 hours. 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 a volume of 800 ml. This solution was added to the reaction mixture and the resulting suspension was stirred continuously for another 24 hours. The suspension was filtered and the resulting precipitate was rinsed several times with mixture of water and methanol in ratio

80:20, in order to remove remaining impurities and monomers. The conversion of the synthesized emeraldine salt to emeraldine base is required in order to achieve effective removal of the metal ions. There are more free electron pairs in the emeraldine base, where metal ions can be bound (Fig.1). This was achieved when washing the resulting precipitate with a 0.1 M NaOH solution to pH 10.0 - 11.0. The washed precipitate (composite) was dried at 60 °C to constant weight for 48 hours. Well dried composite is ground to a homogeneous powder.

#### *Preparation of standard solutions of copper ions*

Initial model solution with concentration 1 g L<sup>-1</sup> of Cu<sup>2+</sup> was prepared, using 3.93 g  $CuSO_4 \cdot 5H_2O$ , diluted with freshly distilled water to 1 L. 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<sup>-1</sup> were prepared.

#### *Experimental*

In order to determine the influence of the contact time and the composite dosage on the copper ions removal from an aqueous medium by the composite, individual samples with initial copper ions concentration of 50 mg L<sup>-1</sup> have been prepared. Various amounts of clinoptilolite/emeraldine base composite powder (0.1, 0.5, 1.0, 1.5 g) were introduced into volumetric flasks. In order to achieve pH = 5, proper for the copper ions removal, acetate buffer was added to each sample [10, 19]. The samples were shaken at 24 °C in a plate shaker for 1, 3, 5, 7, 10, 15, 60 and 360 min, respectively. Samples with a volume of 20 ml were taken and filtered through blue ribbon filter paper to remove suspended particles of the composite. The filtrates were analysed by ISP - OES ("Prodigy" High dispersion ICP-OES, Tellelyne Leeman Labs) in order to determine the copper ions concentration.

Samples with different concentration of copper ions (1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 30.0, 50.0 mg L<sup>-1</sup>) were prepared in order to determine the influence of the initial Cu<sup>2+</sup> concentration. The volume of each sample was 50 ml. A certain amount of the

composites (0.1 g) was added to each sample. An acetate buffer was added to adjust pH to 5.0. The samples are placed in iodine flasks and were shaken for 30 min. Then samples with a volume of 20 ml were taken and after filtration through a blue ribbon filter paper were analyzed for Cu<sup>2+</sup> ions concentration.

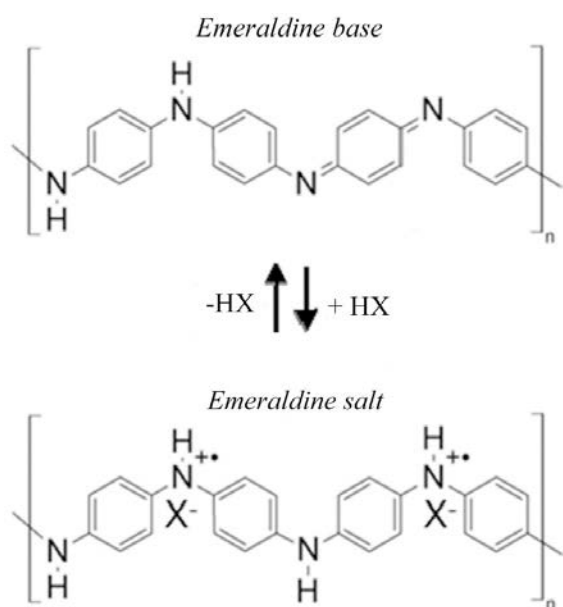


Fig. 1. Chemical structure of emeraldine base and emeraldine salt.

The removal efficiency was determined according to the formula:

$$\text{Removal efficiency} = 100 - \left( \frac{C_t}{C_0} \right) \times 100$$

where C<sub>0</sub> is the initial concentration and C<sub>t</sub> is the concentration at time t in mg L<sup>-1</sup>.

### Results and Discussion

*Influence of the contact time and the composite dosage on the copper ions removal*

The results show that the binding of the metal ions with the composite occurs immediately after mixing the composite with the aqueous medium (Fig. 2). Comparing the removal efficiency, which was achieved using *Composite I* and *Composite II*, correspondingly, it is obvious that the *Composite II* is more effective (Table 1). This is probably due to the fact that for the synthesis of *Composite II* a larger amount

of clinoptilolite was used. The larger surface area of the adsorbent, and accordingly the greater number of the active sites are contributing to more effective removal of copper ions from the aqueous medium.

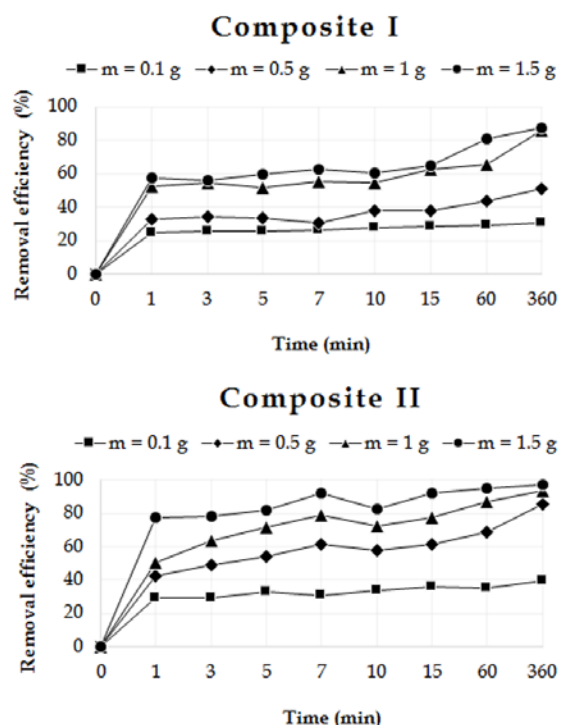


Fig. 2. Influence of the contact time on the copper ions removal at different *Composite I* (a) and *Composite II* dosage (b).

Table 1. Summary of removal efficiency achieved using *Composite I* and *Composite II*.

Time, min	Dose, g			
	0.1	0.5	1.0	1.5
<i>Composite I</i>				
1	24.5	33.1	52.1	57.5
60	26.4	43.5	65.4	80.9
360	29.2	51.1	85.9	87.3
<i>Composite II</i>				
1	29.1	42.1	50.4	77.3
60	34.7	68.5	87.0	95.3
360	39.3	85.8	93.8	96.8

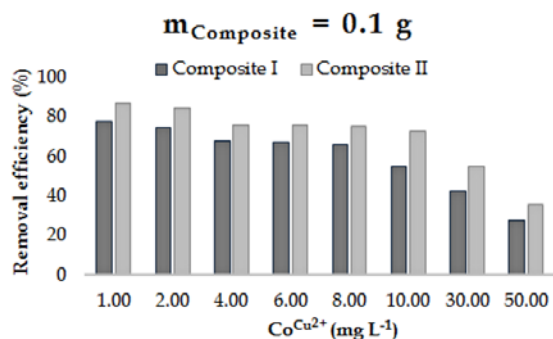
*Influence of the copper ions initial concentration on their removal*

In the experiments with 0.1 g *Composite I*, the increase of the initial copper ions concentration leads to decreased removal efficiency (Fig.3). For example, after 30 minutes treatment of aqueous solutions with

initial copper ions concentration of 1.0, 10.0 and 50.0 mg L<sup>-1</sup>, the removal efficiency was 78.0%, 54.7% and 27.7%, respectively. The higher removal efficiency of copper ions at lower concentrations can be explained with the presence of sufficient free nitrogen atoms with higher electron density in the polymer chain which are involved in the complexing with copper ions.

With increasing of the metal ions concentration, the possibility of their insertion into the structure of the composite decreases, as the amount of clinoptilolite is low and there is no sufficient free surface area, where to attach the copper ions.

When using 0.1 g *Composite II* by increasing of the Cu<sup>2+</sup> concentration the effect of their removal was decreased as follows: for 1.0, 10.0 and 50.0 mg L<sup>-1</sup> copper ions concentration the removal efficiency was 87.0%, 73.1% and 35.6%, respectively. The results show the same tendency as that with *Composite I*. However, it was noted that the usage of *Composite II* leads to greater removal efficiency in comparison with *Composite I*.



**Fig. 3.** Influence of the copper ions initial concentration on their removal with *Composite I* and *Composite II*.

### Conclusions

The possibility of clinoptilolite/emeraldine base composites to remove copper ions from model aqueous medium was studied. For this purpose preparation of composites consisted of emeraldine base and different quantities of clinoptilolite was successfully performed by *in situ* polymerization of aniline. It was established that the clinoptilolite/emeraldine base

composites have significant potential to remove copper ions from aqueous solutions. The synthesized composites can quickly and effectively to remove the contaminants with a high rate of efficiency. Highest removal efficiency of 96.8% was obtained using 1.5 g *Composite II*.

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