# SULPHATES REMOVAL FROM AQUEOUS MEDIUM USING SURFACE MODIFIED CLINOPTILOLITE

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**ABSTRACT.** Wastewater from mining industry is seriously polluted due to its acidic nature and heavy metals content. In aquatic environment the metal sulphides are oxidised into sulphates, that is a reason for their high concentrations in the outgoing water streams. Experiments for removal of sulphate anions from aqueous medium using natural and modified natural clinoptilolite, respectively, have been carried out. The influence of physico-chemical parameters such as initial sulphate concentration, clinoptilolite mass, contact time, and stirring speed, were investigated. When clinoptilolite modified with barium chloride (particle size of 0.1 - 0.8 mm) was used, the removal efficiency increased up to about 50 %, while the removal efficiency with natural not treated clinoptilolite was about 10 %.

**Keywords:** acid mine drainage, sulphates, clinoptilolite, surface modification

## ОТСТРАНЯВАНЕ НА СУЛФАТИ ОТ ВОДНА СРЕДА ЧРЕЗ ПОВЪРХНОСТНО МОДИФИЦИРАН КЛИНОПТИЛОЛИТ

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**РЕЗЮМЕ.** Отпадъчните води от минната индустрия са сериозно замърсени, поради киселия си характер и съдържащите се в тях тежки метали. Във водна среда металните сулфиди се окисляват до сулфати, което е причина за техните високи концентрации в изходящите водни потоци. Проведени са експерименти за отстраняване на сулфатни аниони от водна среда с използването на природен и модифициран клиноптилолит, съответно. Изследвано е влиянието на физико-химични параметри като началната концентрация на сулфатите, масата на клиноптилолита, времето на контакт, както и скоростта на разбъркване. С използването на модифициран с бариев хлорид природен клиноптилолит (размер на частиците 0.1 - 0.8 mm), е постигнат ефект на отстраняване на сулфатните аниони до 50 %, докато ефектът на отстраняване с немодифициран клиноптилолит е около 10 %.

**Ключови думи:** кисели руднични води, сулфати, клиноптилолит, повърхностна модификация.

## Introduction

Wastewater from mining industry is seriously polluted due to its acidic nature and heavy metals content. Because of the oxidation the metal sulphides are converted into sulphates in aquatic environment. As a result their concentrations in the outgoing water streams are very high. There are various methods for metal and sulphates removal. It is possible to achieve their significant removal using some specific microorganisms. During the sulphate reduction the metal ions concentrations are also decreasing [Kiran et al., 2017; Kiran et al., 2017; Bratkova et al. 2013]. There are electrochemical processes for mining wastewater treatment too. Wang et al., using a novel microbial electrolysis cells with intermittent electrical supply, achieve significant decrease of chemical oxygen demand (COD) and sulphates concentration. They found that the electrolysis cells working at intermittent electrical field for longer period of time are more effective in sulphates removal compared to the conventional microbial electrolysis cells. Microbial fuel cells are also used for sulphates reduction [Angelov et al, 2013; Lee et al., 2014; Weng and Lee, 2015]. These ions can be removed from wastewater using fluidized bed crystallization process [De Luna et al., 2017], but the most widely used method for sulphates ions removal from the mine wastewater is the chemical precipitation [Tolonen et al., 2016; Dou et al., 2017]. Using this method the sulphates are precipitated and the formed mineral called ettringite can be used as an adsorbent for subsequent removal of the arsenates contained in this type of wastewaters. Ion exchange, reverse osmosis and electrodialysis are also used for sulphates removal. The high cost of these methods is a limitation for their widespread usage. Adsorption is cost-effective and efficient method for wastewater treatment too. It is well known that its efficiency depends on the type and properties of the sorbent. Widely used sorbents are the zeolites. There are various zeolite types [Wang and Peng, 2010]. The natural zeolites are widely spread and low coast materials. Due to their structure the zeolites belong to the cationic exchangers [Margeta et al. 2014]. They effectively remove the positive charged ions from the wastewater, due to their negatively charged surface, but in slight extent they can trap anions too. After chemical modification with inorganic salts or organic surfactants, the number of positively charged exchange sites on their surface increases [Barczyk et al., 2014; Oliveira and Rubio 2007; Barczyk et al., 2014; Ghiaci et al., 2004; Allen et al., 2009; Samatya et al., 2007; Sun et al., 2011]. So, the anions contained in the wastewater, can be removed. The aim of this study was to examine the possibility for sulphate ions removal from an aqueous solution by modified clinoptilolite.

## Materials and methods

### Chemicals and solvents

Pure for analysis $BaCl_2.2H_2O$, NaCl, $H_2SO_4$, $CuSO_4.5H_2O$ and deionized water were used in the experiments. The zeolite used in the experiments is clinoptilolite ($(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12H_2O$), obtained from the eastern part of the Rhodope mountain in Bulgaria. Two fractions of the material were used (0.1 - 0.8 mm; 0.8 - 2.5 mm).

### Clinoptilolite modification

To obtain 10 g of modified clinoptilolite, 10 g of natural clinoptilolite (particle size of 0.1 - 0.8 mm; 0.8 - 2.5 mm) was mixed with 100 mL of 1M NaCl and the resulting suspension was shaken on a plate shaker for 24 hours at room temperature to prepare the surface of the material for further modification. Then the suspension was filtered and the clinoptilolite was washed with 1 L deionized water. The washed material was dried at 105 °C for 24 hours. The modification of the pre-treated clinoptilolite was carried out by contacting the activated clinoptilolite with 100 mL of 1M $BaCl_2.2H_2O$. The suspension was shaken again on a plate shaker for 24 hours at room temperature. After this period of time the suspension was filtered and the modified clinoptilolite was washed with 1 L deionized water and dried at 105 °C for 24 hours.

### Preparation of standard solutions of sulphate ions

Initial model solution with concentration 1 g/L of $SO_4^{2-}$ was prepared, by diluting $H_2SO_4$ with deionized water. Then standard solutions with concentrations of 50.0, 100.0, 150.0, 250.0, 300.0, 350.0 mg/L were prepared.

### Removal technique

In order to establish the influence of the initial sulphate ions concentration on their removal, 50 mL of model solutions with different initial sulphate ion concentration ($C_o$ = 50 - 350 mg/L) were prepared. A certain amount of clinoptilolite (m = 1 g) with grain size of 0.1 - 0.8 mm or 0.8 - 2.5 mm, was added to each of the samples, respectively. The samples were agitated at temperature of 17±1 ºC for 96 hours. At the end of this period of time, 20 mL portions of each samples were taken, filtered through blue ribbon filter paper to remove clinoptilolite particles and analyzed.

In order to establish the influence of the contact time on the sulphate ions removal as well as the influence of the clinoptilolite dosage, 2000 mL solution with initial sulphate ions concentration of 100 mg/L was prepared. To the aqueous solution was added a weighed amount of clinoptilolite (m = 3 - 5 g). The suspension was agitated for 1 hour (Heidolph RZR 2100 electronic) at 200 rpm. Samples were taken after 1, 3, 5, 8, 10, 15, 20, 30, 40, 50, 60 min and filtered through blue ribbon filter paper to remove suspended adsorbent particles. Then they were analyzed.

### Instrument and measurements

The sulphate concentration was determined using the precipitates standard procedure (APHA, 1992).

### Removal efficiency

The efficiency of $SO_4^{2-}$ removal by clinoptilolite was calculated according to the formula:

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

where $C_o$ is the initial $SO_4^{2-}$ concentration and the $C_t$ is the concentration at time “t” in mg/L.

## Results and discussion

### Effect of the initial $SO_4^{2-}$ concentration on the removal efficiency

In order to estimate the influence of the initial sulphate ions concentration on the removal efficiency, 1 g of the natural and modified clinoptilolite was used, and the initial $SO_4^{2-}$ ions concentration was varied from 50 to 350 mg/L. The results are presented in Figure 1. As shown on the figure, almost twofold decreasing of sulphates concentration was obtained at 50 mg/L initial concentration using 1 g natural clinoptilolite with particle size of 0.1 - 0.8 mm. The results show that with the increasing of the initial sulphate ions concentration, the effect of their removal by 1 g of natural clinoptilolite is decreasing. This is particularly evident at initial sulphate ion concentrations of 50 to 150 mg/L. At higher initial concentrations (from 250 to 350 mg/L) the removal efficiency was not significantly changed. For example, the removal efficiencies obtained at 150 and 350 mg/L were 7.7 and 7.3 %, respectively. About 10 % average sulphate anion removal efficiency using natural clinoptilolite with a particle size of 0.1 - 0.8 mm was obtained. The adsorption capacity of this material increased from 0.47 to 1.21 mg/g with the initial $SO_4^{2-}$ concentration increasing from 50 to 300 mg/L. After that a plateau was reached. After modification of natural clinoptilolite with barium chloride, its removal efficiency significantly increases. Removal efficiency of 69.7 % was achieved using modified clinoptilolite (fraction 0.1 - 0.8 mm) for treatment of aqueous solution with initial sulphate concentration of 50 mg/L. This efficiency is 3.6 times higher than that achieved at the same conditions with nonmodified natural clinoptilolite. After that the removal efficiency was decreasing when the initial concentration was increasing up to 250 mg/L. After this concentration a significant change was not observed. Probably this insignificant change of the removal efficiency after initial concentration of 150 mg/L and of 250 mg/L using natural and modified clinoptilolite, respectively, is a result of specific sites saturation. For example, the removal efficiency obtained at 250, 300 and 350 mg/L were 35.4 %, 34.1 % and 31.8 %, respectively. The adsorption capacity of this material increased from 1.8 to 6.1 mg/g with the increase of the initial $SO_4^{2-}$ concentration from 50 to 350 mg/L. The results show that the adsorption capacity of the modified clinoptilolite is significantly higher than that of the natural clinoptilolite. The same tendency was observed using larger grain size of the clinoptilolite, but the removal efficiency achieved was lower than that achieved with the finer fraction. Treating the aqueous solution with 50 mg/L initial sulphates concentration using natural and modified clinoptilolite (0.8 - 2.5 mm), respectively, the removal efficiencies obtained were 1.6 and 1.1 times lower than that achieved using natural clinoptilolite with the finer fraction. The adsorption capacities were also lower than that achieved with the finer fraction.

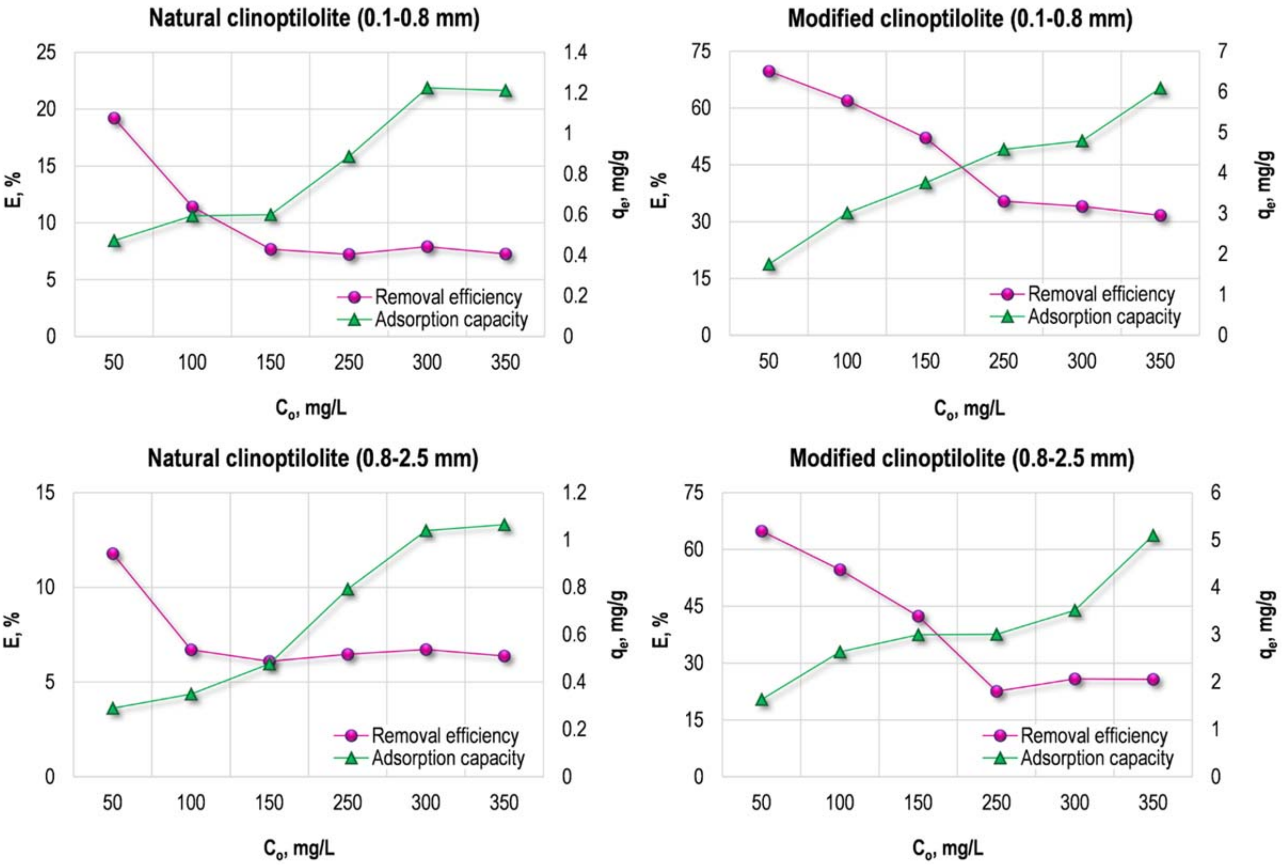

Fig. 1. Removal efficiency and adsorption capacity of the natural and modified clinoptilolite

Its maximal values obtained for model solutions with 350 mg/L initial sulphates concentration, were 1.1 mg/g and 5.1 mg/g, respectively, using natural and modified clinoptilolite, respectively.

### Effect of contact time and clinoptilolite dosage on the removal efficiency

The removal of sulphate ions from the solution with 100 mg/L initial concentration with time is shown in Fig. 2. It is observed that the sulphate uptake occurs immediately after the addition of the clinoptilolite to the aqueous solution, followed by a nearly constant values. 66.2 % removal efficiency by 3 g modified clinoptilolite with particle size of 0.1 - 0.8 mm was obtained in the first minute. After that the $SO_4^{2-}$ removal remains without significant change up to the 60th minute. After the 10th minute the removal curve is reaching a plateau, suggesting that equilibrium has been reached. This may be attributed to the lower availability of the specific sites on the modified clinoptilolite surface with time progressing. The removal efficiencies that were achieved at 30th and 60th minutes are 73.9 % and 77.6 %, respectively.

In general, an increase in the amount of clinoptilolite is followed by the increased removal efficiency of sulphate. In the experiments with the same initial sulphate ions concentration (100 mg/L) but greater clinoptilolite dosage (4 and 5 g), the removal efficiency, achieved at the first minute, were as follows: 70.5 % and 81.2 %, respectively. At the 60th minute the removal efficiencies were increased up to 79.7 % and 88.4 %, respectively, using 4 and 5 g of clinoptilolite. The increase of the dosage leads to an increase in the number of the available vacant specific sites, resulted in an increase of $SO_4^{2-}$ removal efficiency by modified clinoptilolite.

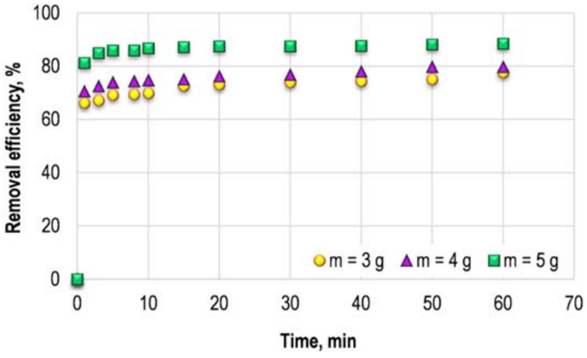

Fig. 2. Effect of the contact time and modified clinoptilolite dosage on the removal efficiency

### Effect of the stirring speed on the removal efficiency

Experiments at 200 and 400 rpm were carried out in order to enhance the contact of $SO_4^{2-}$ with the modified clinoptilolite (0.1 - 0.8 mm) (Table 1).

Table 1.
*Removal efficiency at different stirring speed*

| t, min | Removal efficiency, % | | | | | |
|---|---|---|---|---|---|---|
| | 3 g | | 4 g | | 5 g | |
| | 200 rpm | 400 rpm | 200 rpm | 400 rpm | 200 rpm | 400 rpm |
| 60 | 77.6 | 84.1 | 79.7 | 86.03 | 88.4 | 88.7 |

The results show that the faster stirring of the system leads to better removal of the sulphates. Thus, for 60 minutes stirring at 400 rpm using 3, 4 and 5 g of the modified clinoptilolite the removal efficiency increases about 1.1 times in comparison to that at 200 rpm stirring.

## Conclusions

*In situ* modification of the natural clinoptilolite was successfully performed. The sulphate removal proceeds quickly and at the first minute 66.2 % removal efficiency was achieved when the initial sulphate ions concentration was 50 mg/L and 3 g clinoptilolite. The removal efficiency of sulphate ions increases with the clinoptilolite dosage, the contact time and the speed stirring increase. The modified clinoptilolite removal efficiency was higher than that with the natural clinoptilolite.

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