

**ТЕХНОЛОГИИ ЗА ОПАЗВАНЕ НА ОКОЛНАТА СРЕДА /
ENVIRONMENTAL TECHNOLOGY / ТЕХНОЛОГИИ ОХРАНЫ
ОКРУЖАЮЩЕЙ СРЕДЫ**

**REMOVAL OF CITRIC ACID FROM WASTEWATER BY NATURAL ZEOLITE
ОТСТРАНЯВАНЕ НА ЛИМОНЕНА КИСЕЛИНА ОТ ОТПАДЪЧНА ВОДА С
ЕСТЕСТВЕН ЗЕОЛИТ**



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Natural zeolite-clinoptilolite was studied with respect to its ability to immobilize citric acid from wastewater. The evaluation was made using the integral parameter COD_{Mn} . Data are presented on the process kinetics and on the impact of the zeolite particles size, acidity of the polluted water and the zeolite modification on the process efficiency.

Keywords: *natural zeolite-clinoptilolite, citric acid, wastewater*

Изследвана е способността на български зеолит-клиноптилолит да имобилизира лимонена киселина от отпадъчна вода. Оценката е направена чрез използване на интегралния параметър XPK_{Mn} . Представени са данни за кинетиката на процеса и за влиянието на размера на частиците на зеолита, киселинността на замърсената вода и модифицирането на зеолита върху ефективността на процеса.

Ключови думи: *естествен зеолит-клиноптилолит, лимонена киселина, отпадъчна вода*

Introduction. Mineral flotation technologies require addition of different reagents to the flotation pulp, in order to achieve minerals' activation and depression and thus - selective concentration. Many of added reagents are organic compounds, some of them – carboxylic acids.

Generally, citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) is applied as gangue depressant for ores containing oxide minerals [1] and as a depressant for fluor spar in barite flotation (www.mining.clariant.com).

A mixture of thioglycolic acid and citric acid as a depressant was proposed in reverse flotation of calcite and dolomite from sulfide minerals [2]. Citric acid (CA) was found to be an effective apatite depressant in calcite flotation after the bulk apatite and calcite flotation in the total process for the concentration of a phosphate ore bearing a silicate-carbonate gangue [3]. Citric acid is used to depress dolomite in the flotation of apatite and collophan [4]. It was also used as a gangue depressant for successful separation by

froth flotation of bastnaesite (which is a source of rare earth metals) from the bastnaesite oxide minerals [5].

CA was found to eliminate the detrimental effects of calcium ions, present in the flotation pulp as a result of the pH adjustment with lime and to restore the selectivity of chalcopryrite-galena separation using dextrin as depressor and a xanthate as collector [6].

Citric acid leaching was successfully used to extract zinc from low grade zinc oxide mining tailings where zinc was mainly as smithsonite [7].

Organic acids (acetic acid, citric acid, and formic acid) are used for selective leaching of carbonates in beneficiation for upgrading phosphate ores [8].

Recent studies revealed that organic acids, such as citric and oxalic acids are promising as chemical extracting reagents for removal of heavy metals from contaminated sludge. Results of a lab-scale study found that citric acid seemed to be highly effective in extracting from anaerobically digested sludge, at pH 2.33, Cr (at

100%) and Ni (at 98%) - in 5 days, Cu (at 88%) - in 1 day, Zn (at 100%) – in 2 h and Pb (at 95%) - in 11 days contact times respectively. At pH 3, citric acid seemed to be highly effective in extracting Pb (at 100%) at 1 day [9].

Citric acid is also widely used organic acid in many other industrial fields especially food and pharmaceuticals [10].

Residual amounts of organic compounds impede water reuse in the technological cycle.

When wastewater, polluted with organic acids, is discharged to water bodies, its impact is negative, mainly due to the consumption of the dissolved oxygen. As an organic compound, CA contributes to increasing the chemical oxygen demand (COD), which is an integral parameter for water pollution with organics. Citric acid, when in excess amount in the water bodies, causes problems to flora and fauna and affects the aesthetic value of drinking water. Consequently: a) Removal of organic acids, including CA, from wastewaters streams is needed in order to protect the water bodies' life and/or to reuse water in technological mineral processing cycles; b) Citric acid can be used in studies as a representative organic compound, since it is applied by different industries.

Different methods have been reported for citric acid removing from water, including chemical precipitation, reverse osmosis, membrane filtration and adsorption. The adsorbents reported included kaolinite and illite [11], activated carbon [10], activated charcoal [12], activated Pistacia Lentiscus leaves [13].

The use of natural zeolites in wastewater purification is spreading due to their properties and significant worldwide occurrence. A constructed wetland, using natural zeolite as a substrate achieved 89% removal of COD at 4 days hydraulic retention time [14]. Natural powdered zeolite (clinoptilolite) removed 44% of organic pollutants expressed as permanganate index (oxidation by potassium permanganate) from groundwater containing a high level of organic compounds in a pilot-scaled water treatment plant [15].

Zeolite-clinoptilolite removed 88 % of COD from the supernatant of a pig slurry in 2 hours experiment [16].

A dynamic adsorption through combined filtering media of zeolite and Granular Activated Carbon, developed for deep removing of organic

pollutants in drinking water, achieved removal ratios of turbidity, COD_{Cr} and COD_{Mn} correspondingly of 85%, 24.61% and 45.24% [17].

The goals of the present work were to: (a) investigate the ability of Bulgarian natural zeolite to remove citric acid, as a representative of organic pollution, from wastewater; (b) study the impact of specific process parameters and of zeolite modification on the removal effectiveness.

Methods and materials. A feature, which makes the citric acid suitable to be used in model solutions, is the stability of its solutions. It has been found that citric acid solution remained stable during a five month period, while exposed at light and air [18]. Since citric acid is used to model the total impact of organic pollution of water, an integral parameter for organics determination, i.e. the chemical oxygen demand, found by oxidation with permanganate solution (COD_{Mn}) [19], was used as an analytical tool. It is known that CA is among the relatively small number of organic substances, which can be fast (in 2-10 min) and entirely oxidized at 98 °C by acidic permanganate [20]. Model solutions were prepared by dissolving citric acid in distilled water. Having in mind that: a) for the citric acid $COD_{Mn} = 728 \text{ mgO}_2/\text{g}$ substance [21], b) the fact that many authors give value around 400-500 mgO_2/L as a medium one for the municipal wastewater [22], and c) the requirements of Regulation No 6 from year 2000 for the maximum permissible concentrations of the pollutants in wastewater streams released by different industries in Bulgaria [23], which allows for COD_{Mn} in discharged wastewater to be in the range of 150 – 300 mgO_2/L , model solutions were prepared with concentrations corresponding to COD_{Mn} values of 600 and 300 mgO_2/L .

Bulgarian natural zeolite from Kardzhali region was used. It had the following chemical composition, in mass %: $SiO_2 = 68.70$, $Fe_2O_3 = 2.28$, $TiO = 0.15$, $Al_2O_3 = 11.83$, $CaO = 2.66$, $MgO = 0.76$, $MnO = 0.04$, $Na_2O = 1.60$, $K_2O = 4.01$, $P_2O_3 = 0.14$, $SO_3 = 0.225$, ignition loss = 7.62, totalling – 100.02. Its cation exchange capacity was 134.3 meq/100 g. Clinoptilolite was found to be the predominate mineral. Zeolite was modified by heating (at 500 K) or by placing it in contact for 7 days (at room temperature and at solution to mass of zeolite ratio equal to 1 L:100 g) with 2M solutions of NaCl, NaOH, HCl, $CuCl_2$

and 20 ppm solutions of cationic flocculants FO4140 (with very high molecular weight and very low charge density) and FO 4550 SH (with very high molecular weight and medium charge density) [24]. Composition of modified zeolites was determined by classical silicate analysis. COD_{Mn} values were determined using the standard procedure [19]. Water pH values were measured with WTW Multi 3400i-meter.

The influence of a specific process parameter was determined by calculating COD_{Mn} removal by zeolite, at changing that parameter and keeping other parameters constant. Removal efficiency was calculated using the equation:

Removal, % = $[(C_o - C_f) / C_o] \cdot 100$ where C_o and C_f are the initial and the final COD_{Mn} value, mgO₂/L.

Each experimental result presented was obtained by averaging the data from two parallel experiments.

Results and discussion. Solution to zeolite mass ratio of 100:1 was found to be the optimum by means of experiments made under the following conditions: zeolite particle sizes between 0.09 and 0.325 mm; a contact time of 30 min, and solution to zeolite ratios (v:m) of 20:1, 50:1, 100:1, 200:1. This ratio was further used in experiments.

The kinetics of COD_{Mn} removal by natural zeolite (at v:m=100:1, pH_{initial} = 5, particles size of 0.09 – 0.325 mm, and initial value of COD_{Mn} = 600 mgO₂/L) is presented in Figure 1.

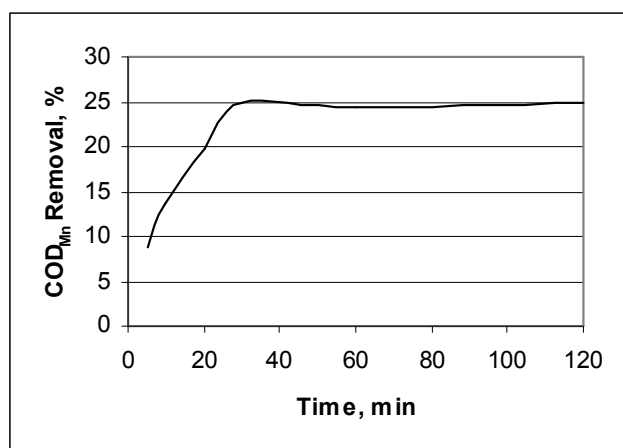


Figure 1. Kinetics of COD_{Mn} removal by natural zeolite

As it can be seen from the figure, the process

takes part actually in 30 min. Removal efficiency obtained in this study is near to the data, presented by Valentukeviciene [15]. A rapid removal of pollutants signifies the efficiency of the adsorbent for its use in wastewater treatment. Over 50% of the COD_{Mn} removal occurred in the initial 10 min. That is why a contact time of 10 minutes was chosen for the experiments aimed at revealing possible differences in COD_{Mn} removal, due to the influence of particles size and modification of zeolite.

The impact of zeolite particles size on the COD_{Mn} removal at initial value of COD_{Mn} = 600 mgO₂/L, pH_{initial} = 5, and at 10 min contact time is presented in Table 1.

Table 1. Impact of zeolite particles size on COD_{Mn} removal

Zeolite particles size	Removal
<0.09 mm	30.6 %
0.09-0.325 mm	24.9 %
0.325-0.400 mm	15.7 %

As it can be seen from Table 1, use of zeolite with finer particles leads to an increase in COD_{Mn} removal.

The influence of solution pH value on COD_{Mn} removal was investigated under the following conditions: initial value of COD_{Mn} = 600 mgO₂/L; contact time of 30 min; zeolite particles size between 0.09 and 0.325 mm; and pH values (referred to as pH_{ini.}) of 3, 5, and 7. Results obtained are presented in Figure 2.

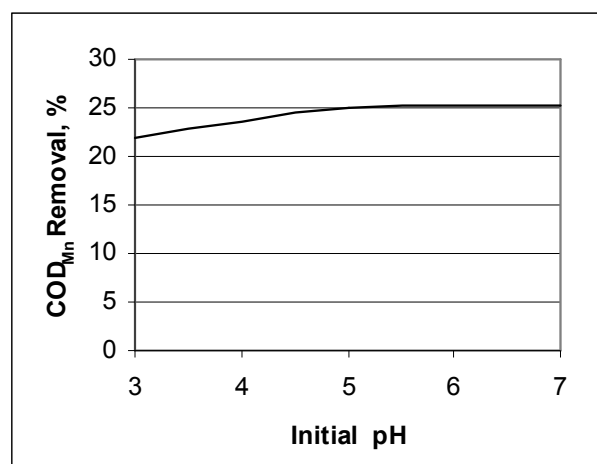


Figure 2. The impact of solution pH value on COD_{Mn} removal

Having in mind results shown in Figure 2, it

can be stated that higher COD_{Mn} removal due to the CA immobilization by zeolite is observed at pH > 5. Similar impact of pH was found by other authors [13] who observed the best removal of CA at pH equal and over 6.

The impact of the initial citric acid concentration on COD_{Mn} removal was studied at v:m=100:1, pH_{initial} = 5, and particles size of 0.09 – 0.325 mm. Results are presented in Table 2.

Table 2.
Impact of the initial citric acid concentration on COD_{Mn} removal

Conc., Time	600 mg/L	300 mg/L
10 min	13.6 %	17.7 %
30 min	24.9 %	37.3 %
60 min	24.8%	44.2 %

It is clear from Table 2, that higher percentage of CA removal can be achieved at lower initial concentrations. These observations could be explained by the fact that at lower CA concentration the ratio of interacting sites of the adsorbent surface to the total available CA molecules is higher. However, as absolute figures, higher amounts of organics are removed from the solution with higher initial concentration. A decrease in the difference of the removed absolute amounts for the two initial CA concentrations was observed at longer time, suggesting that most probably the final uptake would be the same, depending only on the zeolite capacity. Data from Table 2 also suggest that 2-3 stage treatment would be needed in order to achieve standard requirements for the COD_{Mn} [23] in wastewater discharged by mineral processing.

The influence of zeolite modification on COD_{Mn} removal was studied at v:m=100:1, pH_{initial} = 5, particles size of 0.09 – 0.325 mm, 600 mgO₂/L citric acid, and contact time of 10 min. Results are presented in Table 3.

It has been found that modification by treating with NaOH causes desilication of zeolite and a decrease of Si/Al ratio, as well as an increase in the relative quantity of Na⁺, Mg²⁺ and Ca²⁺ in zeolite. Treatment with NaCl causes an increase in Na⁺ and a decrease in Ca²⁺ concentrations in zeolite, leading to an increase of the ratios Na⁺/K⁺ and Mg²⁺/Ca²⁺. Treatment with HCl increases to some extent Si/Al ratio and also increases the relative

amount of K⁺ in zeolite, thus decreasing Na⁺/K⁺ ratio.

Results, presented in Table 3, show that zeolite modification with NaCl, CuCl₂ and flocculants impacts positively the COD_{Mn} removal. The explanation of the positive impact of modification with NaCl on the COD_{Mn} removal needs further studies, since in the case with immobilization of organics most probably the dominant removal mechanism is the hydrophobic interaction, but not the ion exchange with zeolite ions [25]. Hydrophobic zeolites were found effective in removal of organic micropollutants from wastewater [25].

Table 3.
Impact of the zeolite modification on COD_{Mn} removal

Type of modification	Removal, %
Natural zeolite	13.6
Heat treated	19.3
Modified with NaCl	24.9
Modified with HCl	13.7
Modified with NaOH	13.7
Modified with CuCl ₂	34.0
Modified with FO4140	24.8
Modified with FO 4550	22.1
SH	

The positive impact of modification with cationic flocculants could be due to their initial sorption on the zeolite surface. Thus it renders more hydrophobic and with increased affinity to organics.

The highest COD_{Mn} removal by zeolite modified with CuCl₂ could be explained in terms of formation of surface copper complexes with the citric acid. Formation of such complexes is described by other authors [26].

Conclusions. The results obtained suggest the possibility to use zeolite-clinoptilolite (an environmentally friendly material) for removing citric acid (and more generally carboxylic acids) from wastewater. Zeolite modification with cationic flocculants improves its capacity to remove organic pollutants, in particular citric acid, from polluted water. The removal capacity of clinoptilolite could be enhanced also by its use

initially to uptake ions, such as copper, which form organic complexes.

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