

ZINC-CONTAINING CLINOPTILOLITE: JUST A SLUDGE OR A SMART MATERIAL?

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ABSTRACT

The Serbian natural zeolite can be used effectively in the removal of Zn(II) ions from aqueous solutions. At 298 K the sorption capacity varies from 32 to 64 % for the initial Zn(II) solution concentration of 100 and 600 mg Zn dm⁻³, respectively. The capacity increases with temperature and it varies from 46 to 92 % at 338 K. The zinc-loaded zeolitic tuff can remove phosphate ions from aqueous solution and it exhibits an excellent antibacterial activity towards *Acinetobacter junii*. By dehydration at about 500°C it transforms to a ZnO-containing product featuring fine nano-sized wurtzite ZnO particles widespread over the clinoptilolite surface.

Keywords: clinoptilolite, zinc removal, nano-particles, antibacterial activity, zeolite

INTRODUCTION

Adsorption using natural adsorbents is generally considered to be the most suitable method for wastewater treatment. Clinoptilolite, as the most abundant natural zeolite, can be regarded as a cost minimizing choice of the adsorbent for the developing countries.

Recently a detailed spectroscopic and structural investigations of the zinc loaded natural zeolitic tuff from the south Serbia region (Zlatokop mine) have been reported [1]. It was found that the zeolitic tuff contains three major mineral phases, the clinoptilolite being in the highest percentage (more than 70 wt. %). Treatment of the zeolite with aqueous Zn(II) solutions yielded zinc-loaded samples with the zinc ions being present exclusively in the clinoptilolite lattice [1]. Therefore the zeolitic tuff could be suitable as sorbent in removing the Zn²⁺ ions from wastewaters.

Since zinc is among the metals which exhibit antibacterial properties we have investigated the zinc-loaded zeolitic tuff as an antibacterial material, having in mind a possible utilization of the sludge. Millions of tons of residual sludge come out of the wastewater treatment plants annually. Management of the sludge is a major part of the waste treatment since up to 60 % of the total cost of operating and maintaining wastewater treatment plants is related to sludge management. For this reason, various methods have been proposed [2] with the aim of minimizing possible health risks of sludge disposal.

EXPERIMENTAL

The zeolite material (CLI) obtained from a large sedimentary Zlatokop deposit was used in the experiments. The particle size of the samples was in the range 0.063-0.1 mm. The sample was pretreated with 2.0 mol dm⁻³ solution of NaCl in order to improve the tuff's exchange capacity [1,3]. The Zn(II) sorption isotherms were determined at 298, 308, 318, 328 and 338 K using the batch method. 1.000 g of the Na-CLI was placed in 100.00 cm³ of the ZnCl₂ solution of chosen concentration. The Zn(II) concentrations were 100, 200, 300, 400

and 600 mg Zn dm⁻³. The suspension was shaken at about 100 rpm for 24 h in a thermostated water bath. The solid, Zn-loaded Na-CLI (Zn-CLI), was then recovered by filtration.

The sample of Zn-CLI (containing 8.8 mg Zn g⁻¹) was thermally treated under air at about 500°C at a heating rate of 10 °C min⁻¹. The obtained orange-colored product (ZnO-CLI) was analysed by the transmission electron microscopy (TEM). The procedure details were reported previously [4]. Identification of the crystal phase formed during the thermal treatment of Zn-CLI was done using the selected area electron diffraction (SAED) over multiple nano-crystals.

A pure culture of *Acinetobacter junii* DSM 1532 has been used for testing the antibacterial activity of Zn-containing samples (Zn-CLI and ZnO-CLI). This bacterium was used here in the bioassay and is not specifically related to the estimation of wastewater toxicity. This Gram-negative bacterium is normally present in wastewater and in the activated sludge biomass. The most widely studied physiological characteristic of this bacterium is its ability to accumulate the soluble phosphate present in wastewater in the form of intracellular non-soluble polyphosphate granules [5].

The *A. junii* was pregrown on the nutrient agar (Biolife, Italy) for 16 h at 30.0±0.1°C. Next, the biomass was suspended in sterile 0.05 mol dm⁻³ NaCl and inoculated into 100 cm³ of autoclaved synthetic wastewater (composition in mg dm⁻³ of distilled water: Na-propionate 300; peptone 100; MgSO₄·7H₂O 10; CaCl₂·2H₂O 6; KCl 30; yeast extract 20; KH₂PO₄ 88; pH=7.0±0.2). 1.00 g of Zn-CLI (or ZnO-CLI) was added into the flask, while a control flask was left without addition of the material. The flasks were incubated for 24 h at 30.0±0.5°C in a water bath (Memmert WNB22) with stirring (70 rpm).

The number of cells was reported as immobilized CFUs per one gram of the dry carrier. Statistica Software 8.0 (StatSoft, Tulsa, USA) was used for statistical analysis. The numbers of bacterial CFU were logarithmically transformed beforehand to normalize distribution and to equalize variances of the measured parameters. The comparisons between the samples were done using the one-way analysis of variance (ANOVA), and subsequently the post-hoc Duncan test was performed for the calculations concerning pair-wise comparisons. Statistical decisions were made at a significance level of p<0.05.

Leaching test was done with 1.00 g of Zn-CLI suspended into 100.00 cm³ of synthetic wastewater (pH adjusted to 7) and left for 24 h in a thermostated water bath at 30°C. After filtration the Zn content in the filtrate was analyzed by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

The sorption capacity of the CLI for Zn(II) increases both with temperature and with the initial Zn(II) solution concentration. The CLI is quite effective in removing the Zn(II) ions from aqueous solutions at ambient temperature: the sorption capacity at 298 K varies from 13.0 mg Zn g⁻¹ (for C₀= 100 mg Zn dm⁻³) to 25.6 mg Zn g⁻¹ (for C₀= 600 mg Zn dm⁻³), which corresponds to 32–64% removal efficiency. There is for about 50 % increase in sorption capacity at 338 K: from 18.5 mg Zn g⁻¹ (for C₀= 100 mg Zn dm⁻³) to 37.0 mg Zn g⁻¹ (for C₀= 600 mg Zn dm⁻³), corresponding to 46–92 % cation exchange.

TEM analysis shows that the thermal treatment of Zn-CLI at about 500°C leads to the formation of nano zinc oxide particles which are widespread over the clinoptilolite surface (Fig. 1a). The average size of the spherical aggregates is about 5 nm as shown in Fig. 1b. Since the size of nano particles is larger than the openings of the clinoptilolite lattice (about 0.4 nm), crystallization of ZnO must occur at the surface of the particles. The SAED pattern recorded over multiple ZnO particles (Fig. 1c) corresponds to the polycrystalline wurtzite

ZnO. Comparison between d-values measured from the SEAD pattern and from the wurtzite ZnO reference is given in Table 1.

Table 1. Comparison between measured d-values of ZnO nanoparticles from SEAD pattern and ZnO reference.

Distance, nm	d ₁	d ₂	d ₃
Measured distance, nm	0.243	0.167	0.132
Distance in ZnO (JCPDS 00-003-0888)	0.246	0.161	0.130
Crystallographic plane	{101}	{110}	{004}

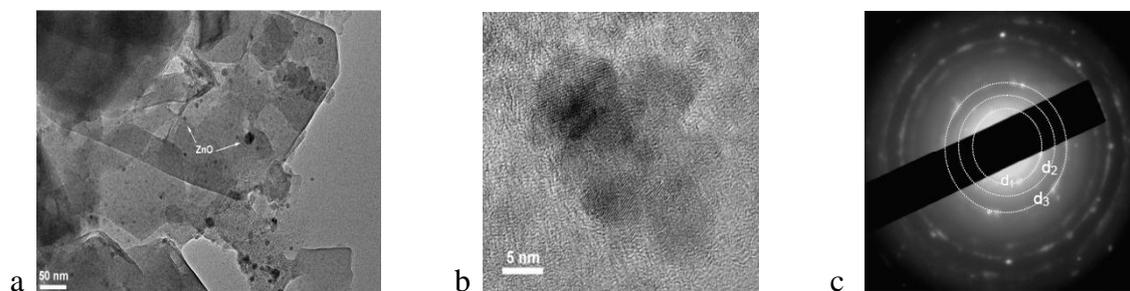


Figure 1. TEM image of the thermally treated Zn-CLI. (a) Hexagonal plates of the clinoptilolite crystals sprinkled with ZnO (dark spots); b) enlarged view showing nano-sized ZnO (dark area); (c) the SEAD pattern recorded over an area of ZnO particles; diffraction rings can be attributed to the wurtzite ZnO.

The results of the antibacterial activity study of the Zn-CLI and ZnO-CLI against *A. junii* are given in Table 2. The activity of Zn-CLI is better than the antibacterial activity of the clinoptilolite which contains nano ZnO particles. After 24 h of contact with Zn-CLI, a portion of the *A. junii* was immobilized onto the material, while the rest of the bacteria remained as planktonic cells in solution. The number of *A. junii* immobilized onto particles of Zn-CLI ($0.39 \cdot 10^6$ CFU g⁻¹) and ZnO-CLI ($61 \cdot 10^6$ CFU g⁻¹) is far lower than the numbers of *A. junii* immobilized onto other zeolitic tuffs: $9.5 \cdot 10^9$ CFU g⁻¹ immobilized on Mg-exchanged clinoptilolite [6] and $2.3 \cdot 10^9$ CFU g⁻¹ on the natural clinoptilolite [7]. The final number of total cells in the reactor with Zn-CLI and the increase of bacterial numbers (expressed as ratio of the final and starting numbers of bacteria) were significantly lower than in the control reactor. This suggests that Zn-CLI exhibits a strong antibacterial activity to *A. junii*, with a significant (99 %) inhibition of bacteria.

In separate experiments the P removal by Zn-CLI and ZnO-CLI was tested by incubating a 1.0 g of material in 100 cm³ of solution without the addition of *A. junii*. After 24 h of incubation the reduction of the starting P concentration was 80 % and 50 % in the reactors with Zn-CLI and ZnO-CLI, respectively. From the difference obtained in experiments using Zn-CLI (or ZnO-CLI) with and without addition of bacteria, it follows that *A. junii* in the reactor with Zn-CLI (ZnO-CLI) removed less than 0.06 % of the starting P, thus showing a negligible contribution of bacteria to the P removal. The conclusion is that Zn-CLI and ZnO-CLI by themselves effectively remove phosphate ions from solution.

Table 2. Performance of reactors containing *A. junii* (control), *A. junii* and Zn-CLI (or ZnO-CLI) [c_0 CFU (10^{10} dm^{-3})] = 5.33 ± 0.52 ; [$c_0(\text{P})$, mg dm^{-3}] = 21.05 ± 0.70 . Significantly different values: ^A- compared to control; ^B- compared to ZnO-CLI.

Parameter	Control	ZnO-CLI	Zn-CLI
Final pH	7.28 ± 0.02	$7.19 \pm 0.02^{\text{A}}$	$5.99 \pm 0.02^{\text{A,B}}$
Immobilized cells (10^6 CFU g^{-1})	-	61.40 ± 2.71	$0.39 \pm 0.02^{\text{B}}$
Planktonic cells (10^8 CFU L^{-1})	2560.00 ± 636.00	$3.43 \pm 0.06^{\text{A}}$	$0.016 \pm 0.004^{\text{A,B}}$
Total cells (10^8 CFU L^{-1})	2560.00 ± 636.00	$3.44 \pm 0.06^{\text{A}}$	$0.016 \pm 0.004^{\text{A,B}}$
CFU final/CFU start	4.85 ± 0.89	$0.01 \pm 0.00^{\text{A}}$	$0.00 \pm 0.00^{\text{A}}$
Inhibition (%)	-	99.862 ± 0.032	$99.999 \pm 0.000^{\text{B}}$
P removed (%)	38.23 ± 0.53	$50.12 \pm 0.49^{\text{A}}$	$80.89 \pm 0.42^{\text{A,B}}$

CONCLUSION

The results of the present study suggest that the sludge remains after zinc removal from an aqueous solution could find a possible application for a simultaneous phosphate removal and disinfection of wastewater in a final step of wastewater treatment. It exhibits an excellent antibacterial activity towards *A. junii* and effectively removes also phosphate ions from solution. In that context it is of importance that only a very small amount of Zn(II) can be leached out. The leaching test shows that the resulting Zn(II) concentration in solution is only 0.67 ppm under the experimental conditions.

A simple thermal treatment of the sludge leads to the formation of wurtzite nano-sized polycrystalline zinc oxide particles which are widespread over clinoptilolite surface. This material also exhibits disinfecting activity but is less effective in the P removal than Zn-CLI. However, the ZnO nano-clusters incorporated in the zeolitic lattice have been known to exhibit catalytic activity for several reactions [8]. This renders ZnO-CLI a potential candidate for novel applications.

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