

## Zinc ions adsorption under dynamic conditions with the use of Georgian minerals

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### Abstract

The article deals with the studies of chemically active natural minerals of Georgia: travertine and limestone under dynamic conditions, which have been explored for the first time as adsorbents in the process of aqueous solutions' purification from zinc ions.

Tests have been conducted in filtration columns at different hydraulic loads until the ratio of zinc concentration in sewage waters  $C_k$  to initial zinc concentration  $C_o$  ( $C_k/C_o$ ) reached the value of 0,95.

The dependence of zinc adsorption degree on aqueous solution delivery rate, time duration of adsorbent operation and dependence of zinc ions adsorption rate constant on contact time have been studied. Zinc adsorption percentage, with initial solution delivery at the rate of 0,3 l/h, was equal to 82% and 70% for limestone and travertine, respectively.

The best outcome during column tests has been reached in case of limestone, for which the zinc adsorption percentage comprised 80% with contact time duration equal to 5 hours.

**Keywords:** Dynamic conditions; Column devices; Adsorption; Limestone; travertine

### 1. Introduction

Sewage waters contamination with heavy metals poses a significant threat for the environment and human health.

These metals are of natural occurrence in the earth crust, however the human activity, such as extraction of mineral resources, as well as rapid urbanization, industrialization and large number of industrial processes have led to increase of heavy metal concentrations in the environment [1, 2].

The growth of industrial activity has created unprecedented problems for the mankind, as far as industrial enterprises discharge waste waters into water channels and cause significant contamination.

Presence of heavy metal ions (HMI) in the nature, especially in water may cause serious problems and lead to dangerous consequences for animal, plant and human health [3, 4].

These metals may have an effect through respiration, as well as through skin, due to contaminated food and water consumption. After hitting the organism, they may impair normal cell functions and disturb the basic biological processes. Among heavy metals, zinc manifests extremely acute toxicity [5-8].

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Based on the mentioned above, the development of methods for HMIs removal from aqueous solutions is an important aspect of environmental protection and public health. These methods are used for elimination of the mentioned metals or reduction of their concentrations in different ecological matrices, such as water, soil and air [8].

Several methods, which can be divided into physical, chemical and biological ones, are used for heavy metal removal.

Adsorption removal of heavy metals from sewage waters is a widely used method due to its activity and ecological compatibility [9-10].

Adsorption process includes heavy metal ions adjoining to solid material surface, which is known as an adsorbent. Usually, the adsorbents under study include activated carbon, zeolites, various types of clays etc.

These materials have large surface area and peculiar chemical properties, which make them effective when capturing heavy metal ions from water or sewage waters. Natural minerals are preferable as adsorbents due to their chemical structure, adsorption properties and global (world-wide) distribution [11-12].

In the previous work [12], we have studied for the first time chemically active natural minerals of Georgia: travertine and limestone, as adsorbents in the process of aqueous solution treatment from zinc ions. Experiments were carried out under static conditions, the dependence of adsorption degree and adsorptive capacity on adsorbent dosage, contact time, adsorbate concentration and solution pH were studied. Optimum conditions for zinc ion adsorption on the mentioned adsorbents were selected. Under specified conditions maximum efficiency of adsorption degree and adsorptive capacity was equal to 89% and 29 mg/g for travertine and 82% and 28 mg/g for limestone.

The given work represents the results of study of aqueous solution treatment process from zinc ions under dynamic conditions in the presence of Georgian minerals travertine and limestone.

The mentioned studies have set a goal to characterize minerals travertine and limestone and to explore zinc adsorption on filtration columns of these minerals under dynamic conditions. We have conducted column tests of the mentioned minerals under dynamic conditions for confirmation of results obtained by us under static conditions.

Travertine or else calcareous tuff (sinter) is a fine-grained crystalline fragile rock, which is a transient material between limestone and marble and is even called "unripened marble". It is spread in the mountainous regions of Georgia and is mainly used in construction as a lining (finishing) material.

Limestone or else marbleized limestone is a natural rock as well, which is used for claddings of building, it is featured by high durability to external conditions and mainly extracted in the Kakheti region [13-14].

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## 2. Material and methods

Two species of the natural minerals – travertine and limestone, which were used as adsorbents in the process of aqueous solutions treatment from zinc ions were transported from mountainous areas of Georgia. These minerals were used without any preliminary treatment, they were just grinded and sieved with selection of 2-1 mm fractions.

As a source of zinc ions source there was used a solution prepared as follows: granulated zinc metal (CFA – clean for analysis) was dissolved in nitrogen acid, filled with deionized water up to 1 liter and a solution with 1000 mg/l concentration was prepared. All the rest solutions were prepared via dilution of this standard solution.

Analysis of major and minor components was performed at the Complex Laboratory of Geological Research of Al. Janelidze Institute of Geology of Iv. Javakhishvili Tbilisi State University. Sample chips were finely powdered using RETSCH RS200 vibrating mill. Major and trace element were determined by X-Ray fluorescence spectrometry (XRF) using SPECTROSCOUT X-Ray spectrometer with Cu-Rh X-Ray tube.

In the work there is given the chemical composition of the mentioned minerals, which may slightly differ from each other depending on deposit and admixtures. Travertine composition is as follows: CaO – 55.37%, SiO<sub>2</sub> – 0.08%, the rest components: Fe<sub>2</sub>O<sub>3</sub> – 0.04%, Al<sub>2</sub>O<sub>3</sub> – 0.07%, TiO<sub>2</sub> – 0.007%, while in case of limestone: CaO – 50,61%, SiO<sub>2</sub> – 0,5%, Al<sub>2</sub>O<sub>3</sub> – 0.13%, Fe<sub>2</sub>O<sub>3</sub> – 0,55%, MgO – 2.85%.

## 2.1. Experimental part

Column tests of zinc sorption process have been conducted with the use of glass columns 13 mm in diameter and 400 mm in length, which have been filled with sorbents 250 mm in height. Grain sizes are 2-1 mm. Columns have been supplied by aqueous (standard) zinc solution with concentration of 100 mg/l. Samples for determination of zinc concentration in treated aqueous solutions (run-offs from the column) have been selected after filtration at regular time intervals (15 minutes) in the quantity of 50 ml.

- The feeding of zinc aqueous solution through columns was lasted until the ratio of zinc concentration in runoffs  $C_k$  to concentration of the initial solution  $C_0$  reached 0.95.
- All filtrate samples collected after sorption process have been delivered for analysis on determination of zinc content.
- Zinc adsorption percentage has been calculated according to formulas given in the previous work [12].
- Below we have determined the constants of zinc ion sorption rate, which was calculated by the formula:

$$K = \frac{2.303}{\tau} \log \frac{C_0}{C_k}$$

Where

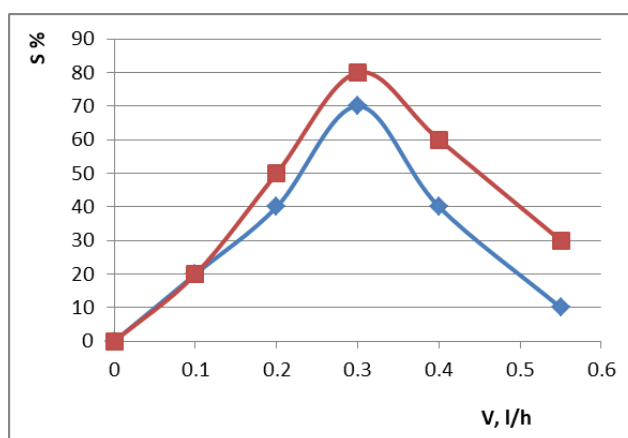
$\tau$  – time of contact between sorbent and sorbate;

$C_0$ - zinc concentration in the initial solution;

$C_k$ - zinc concentration after reaction

## 3. Results and discussion

The work investigates the efficiency of zinc ions removal from aqueous solutions under dynamic conditions in the presence of minerals (travertine and limestone) and effect of hydraulic load on the process.



**Figure 1** Dependence of the degree of  $Zn^{2+}$  adsorption on the solution feed rate.  $C_0=100\text{mg/l}$ ,  $t=25C^0$ ,  $m_{ads}=40\text{g}$ .  
blue (◆)- travertine, red (■) - limestone

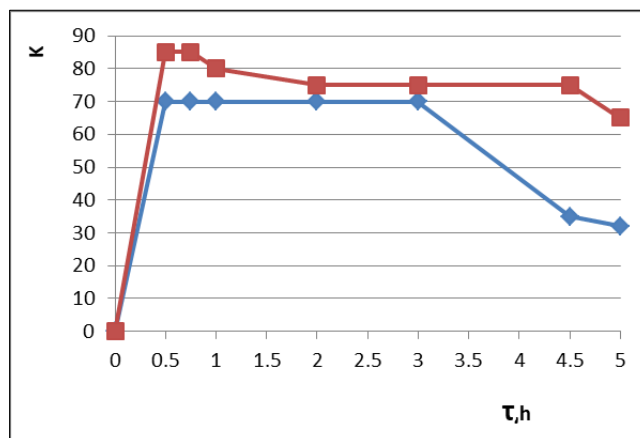
The dependence of  $Zn^{2+}$  adsorption degree on aqueous solution feeding rate is given in Fig.1. For selection of optimum solution feeding rate the experiments have been conducted at different velocity values from 0,1 l/h to 0,8 l/h.

It is seen from the Figure that adsorption degree for both adsorbents gradually rises with the increase in feeding rate of solution under study and reaches the maximum at the value of 0,3 l/h, and then slowly decreases.

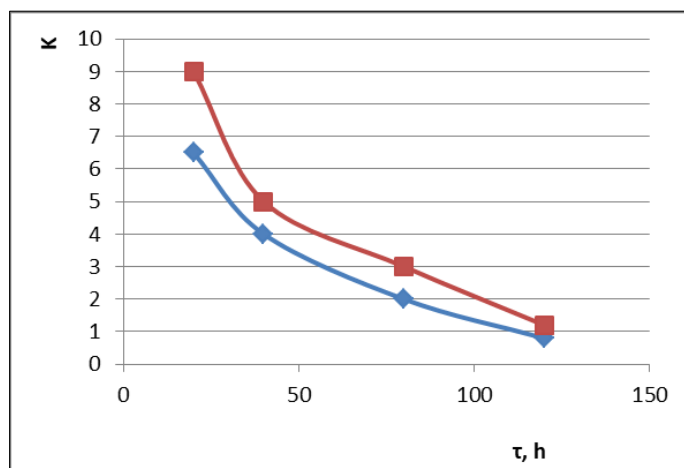
Limestone turned out to be the best adsorbent, since zinc adsorption degree on it was equal to 82% under optimum conditions, and 70% in case of travertine.

The dependence of zinc adsorption percentage on contact time has been studied as well (Fig. 2). As is seen from the Figure, at the constant value of  $Zn^{2+}$  adsorption percentage (78%), the test was lasted for 5 hours in case for limestone.

Afterwards, the adsorption percentage slowly drops with increase in contact time. In case of travertine the results were slightly reduced. Adsorption percentage was equal to 70%, and duration of adsorbent's permanent work was 3 hours.



**Figure 2** Dependence of the percentage of  $Zn^{2+}$  adsorption on the contact time.  $C_0=100\text{mg/l}$ ,  $t=25C^0$ ,  $m_{ads}=40\text{g}$ ,  $V=0.3\text{ l/h}$ . blue (♦)- travertine, red (■) - limestone



**Figure 3** Dependence of the  $Zn^{2+}$  sorption rate constant on time.  $C_0=100\text{mg/l}$ ,  $t=25C^0$ ,  $m_{ads}=40\text{g}$ ,  $V=0.3\text{ l/h}$ . blue (♦)- travertine, red (■) - limestone

Fig. 3 shows the dependence of the constant of zinc ion sorption rate on contact time. It is seen from the Figure that sorption rates gradually decrease with increase in adsorbents' working time

#### 4. Conclusion

Tests carried out on adsorbents under dynamic conditions with the use of travertine and limestone allowed us to make conclusion on the opportunity of application of these materials in water purification technology.

The best result in column tests has been shown by a limestone, for which the adsorption percentage was equal to 82%, with contact time 5 hours.

#### Compliance with ethical standards

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*Disclosure of conflict of interest*

All authors of the Article, have no conflict of interest.

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