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Adsorptive removal of zinc icons from aqueous solutions in the presence of Georgia minerals

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Abstract

The article represents the new chemically active natural minerals of Georgia – travertine and limestone. In this work, for the first time there have been studied adsorptive properties of the mentioned minerals in the process of aqueous solution purification from zinc ions. Materials under study are represented by unprocessed forms of travertine and limestone. Factors having an impact on sorption capacity of these minerals are analyzed based on the experiments.

The dependence of degree of adsorption and adsorptive capacity on adsorbent dosage, time contact, adsorbate concentration and solution pH has been studied. Optimum conditions for aqueous solution purification from zinc ions have been selected. Under the mentioned conditions, the maximum efficiency of degree of adsorption and adsorptive capacity has been 89,8% and 29 mg/g for travertine and 82% and 28 mg/g for limestone.

Keywords: Travertine; Limestone; Adsorption; Zinc Ions; Degree of Adsorption; Adsorption Capacity.

1. Introduction

Environment pollution with heavy metals is a global ecological problem. Heavy metal ions are referred to the category of extremely dangerous and toxic substances of water supply system, which are characterized by non-biodegradable properties, that increases their toxic action.

Water pollution with heavy toxic metals is a result of development of industry. Among main sources of metal-containing waste water are the enterprises engaged in chemical and electrochemical metal treatment, ferrous and non-ferrous metallurgy, mining enterprises, shaft and ore mining industries etc. [1-3].

The presence of heavy metal ions in water is a reason of number of health problems suffering plants, animals and humans. They may constitute a danger even when their concentration doesn't exceed allowable limits. Availability of these metals in water has a carcinogenic action on lung, liver, kidney etc. [4-6].

Among heavy metals Zn^{2+} manifests significant acute and chronic toxicity, causes serious health problems, including symptoms of neuralgia, abdominal pains, dizziness, diarrhea, loss of appetite, mental depression, sluggishness [7, 8]. Allowable concentration of Zn^{2+} in water was established as no more than 3 mg/l, and according to Chinese recommendations – no more than 1 mg/l.

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Based on the below-mentioned, study and development of simple technological methods for waste water purification from heavy metal ions is deemed highly relevant.

There is a great number of purification methods, which include: sedimentation, flotation, galvanic coating, ion exchange, extraction, membrane separation, adsorption etc. [9-11]. Adsorption method is one of the most important ways of waste water treatment. There are lots of works related to heavy metal ions adsorption by natural and synthetic materials, aluminosilicates, activated carbons of different grades etc. [12, 13]. Natural minerals are preferable as adsorbents due to their chemical structure, adsorption properties, global spread, cheapness and ecological compatibility.

Travertine and limestone, new chemically active natural minerals of Georgian origin for the first time are represented as adsorbents in the presented article.

The given work set a goal of investigation of mentioned minerals as adsorbent in the process of aqueous solution purification from zinc ions and study of their adsorption properties, varying the experimental conditions.

Travertine is a calcareous tuff, which represents poly-crystalline fine-grained rock. It is generated from calcium carbonate minerals deposited at the bottom of water bodies. According to classification, travertine takes intermediate position between marble and lime substances and it can be characterized as an “immature marble”. This natural stone is well known ever since Ancient Rome. It was used as a construction material. Nowadays it is used in the construction as a decorative stone for claddings of buildings. The large travertine deposits are located in many countries: Italy, Germany, Turkey, USA, Georgia etc. In Georgia, travertine can be found in Truso Valley, in Lekhura and Liakhvi river valleys, in Racha, Imereti and Svaneti.

There is a wide choice of natural cladding stones in Georgia. Marmorized limestone is one of them. Plates of natural limestone are used in the construction for claddings of buildings and churches, since is stands out with its high resistance to external conditions. Bodbe marmorized limestone deposit is located in Kakheti region, Kvemo Bodbe village. It is produced on the basis of mining license, which is issued by the National Agency of the Ministry of Economy and Sustainable Development of Georgia [14, 15].

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_2 – 0.08%, the rest components: Fe_2O_3 –0.04%, Al_2O_3 –0.07%, TiO_2 –0.007%, while in case of limestone: CaO – 50,61%, SiO_2 – 0,5%, Al_2O_3 – 0.13%, Fe_2O_3 – 0,55%, MgO – 2.85%.

2.1. Experimental part

Zn^{2+} adsorption process on the selected materials have been investigated under static conditions. Experiments have been conducted for establishment of optimal values of adsorbent dosage, contact time, dosage of test solution and pH value. The rest experimental parameters (solution volume – 100 ml, experiment temperature – 20°C) have been taken into account in the course of testing.

In Fig. 1 there is shown an impact of adsorbent dosage on degree of Zn^{2+} adsorption. Adsorbent quantity has been varied from 1 to 7 g, at pH – 4,9. Tests have been conducted in containers with a capacity of 250 ml, to which 100 ml of test solution have been poured and different quantity of adsorbent has been added. Flask has been shaken up for 60 minutes, then filtered and a filtrate has been analyzed. Then an optimal amount of adsorbent has been established, which contains 4 g.

For determination of optimal contact time an adsorbent in the quantity of 4g has been placed into container, 100 ml of standard Zn^{2+} solution has been poured and experiments have been conducted. Samples have been collected after 15, 30, 60, 90 and 180 minutes. Optimal time contact has been established, which comprises 60 minutes. The optimal value of test solution concentration has been established the same way, and it was equal to 100 mg/l. (Fig. 3).

Experimental study of pH factor impact on Zn^{+2} adsorption on the surface of adsorbents have been conducted in the range of pH 2-9, which has been established via addition of 0.1 M of hydrochloric acid or potassium hydroxide. The test solution with given pH, 100 ml quantity and 100 mg/l concentration has been poured into containers, where 4 gr of adsorbent have been placed. Container has been shaken up for 60 minutes, filtered and a filtrate has been analyzed for Zn+2 content. . Analyses have been taken using atomic-adsorption (AAC Perkin-Elmer-200) and chemical methods. Experiments have been conducted three times and the mean values with standard deviations have been used.

The amount of zinc adsorbed per unit weight of adsorbent surface (adsorption capacity) A mg/g, and Zn (II) adsorption degree R have been calculated according to formulas:

$$A = \frac{C_o - C}{m} \cdot V \text{ mg/g}$$

$$R = \frac{C_o - C}{C_o} \cdot 100\%$$

Where C_o - initial solution concentration, mg/dm^3;
C - aposteriori (after the test) concentration;
m - sorbent weight, g;
V - volume of purified solution, dm^3.

3. Results and discussion

In the given work the zinc ion adsorption from aqueous solutions in the presence of Georgian minerals, travertine and limestone has been studied. Impact of adsorbent dosage, contact time, quantity of adsorbate and pH value on adsorption capacity of mentioned minerals has been studied.

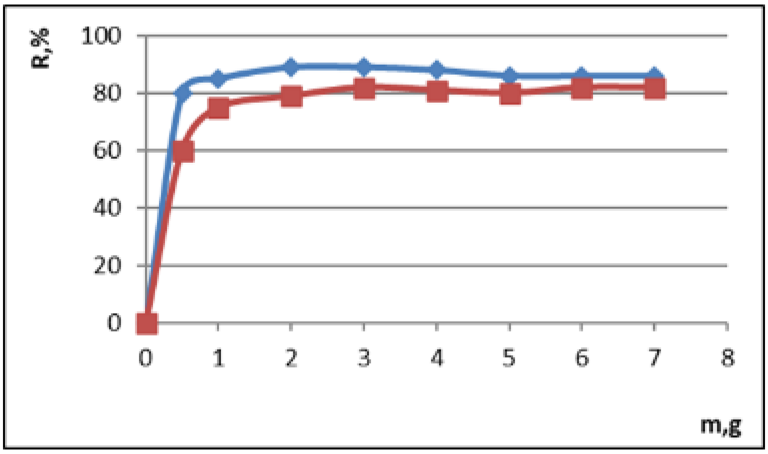

Figure 1 Adsorbent dosage (m, g) impact on Zn(II) adsorption degree (R,%). pH = 4,9, τ = 1h, t = 20°C, $C_{Zn^{2+}}$= 100mg/l. blue (⧫)– travertine, red (■) – limestone.

Effect of adsorbent dosage on Zn^{+2} ions adsorption is shown in Fig. 1. The figure shows that with increase of adsorbent dosage the degree of Zn^{+2} adsorption on both adsorbents rapidly grows first from 80% to 89% in case of travertine and from 60% to 80% in case of limestone. Adsorption process becomes almost constant, when adsorbent amount is 2-6 gr.

Improvement of zinc ions adsorption efficiency with increase of adsorbent dose takes place at the expense of increase of sorbent contact area with solution, that leads to wider opportunities of sorption processes, following which an equilibrium state occurs [16].

The study also confirms the correlation between growth of Zn^{+2} adsorption degree at the expense of increased dosage of adsorbent and simultaneous reduction of adsorption capacity. For instance, if a maximal adsorption capacity equals to 83 mg/g and 89 mg/g when adsorbent amount is 1-2 g, expansion in quantity of adsorbent up to 6 g causes reduction of adsorption capacity down to 14,5 mg/g and 13 mg/g, for travertine and limestone, respectively.

In order to assess the adsorption process, an impact of contact time on the process of Zn^{+2} removal from the solution has been investigated. As it seen from Fig. 2, with increase of contact time the quick growth of Zn^{+2} adsorption occurs first in case of both adsorbents, 82% and 80% during 15-30 minutes, and afterwards the adsorption rate decreases, and degree of adsorption goes to almost constant values, 89 and 82% for travertine and limestone, respectively.

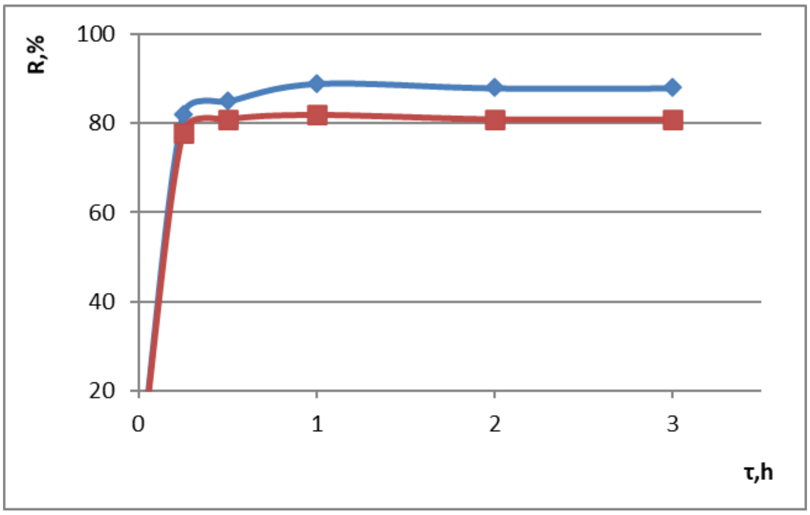

Figure 2 Contact time impact on Zn (II) adsorption degree. pH = 4,9, m = 1g, t = 20°C, $C_{Zn^{2+}}$ = 100mg/l. blue (♦)– travertine, red (■) – limestone.

It can be explained by adsorbent surface saturation. Initial zinc adsorption rate was higher, since all places in adsorbent were vacant, and substance concentration was high. With extension of adsorption time, zinc ions occupied vacant places and after a time almost all active centers were occupied by zinc ions that lead to adsorption rate decrease [17].

Impact of initial concentration on zinc ions adsorption capacity has been studied by means of change in test solution concentration from 25 to 500 mg/l at pH – 4.9, temperature 20°C, contact time 60 minutes and adsorbent dosage 4g. As is seen from Fig. 3, with increase of concentration, a number of zinc ions interreacting with active centers of adsorbents is getting higher, that leads after a time to adsorbent surface saturation and, respectively, reduction of adsorption percentage. At that, the degree of zinc ions adsorption in case of travertine drops down from 88% to 5%, while in case of limestone – from 92% to 52% [18].

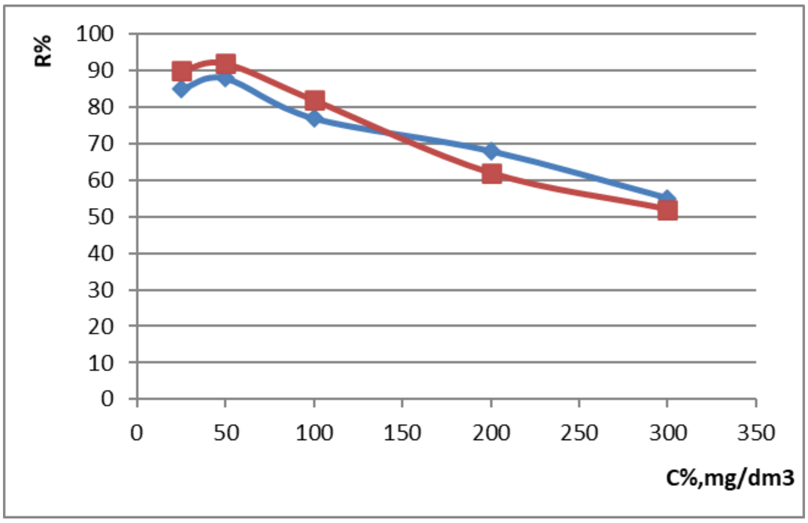

Figure 3 The effect of the solution concentration on Zn (II) adsorption degree. pH = 4,9, m = 4g, t =20°C, τ =1h. blue (⧫)– travertine, red (■) – limestone.

Solution pH value plays a crucial role in metal ions adsorption, since pH has an impact not only on metal compounds' formation, but also on adsorbent's surface charge. Effect of initial solution pH on zinc ions adsorption from aqueous solution in the presence of travertine and limestone has been investigated within a range of pH 4-9 at temperature 20°C for 60 minutes, at zinc concentration 100 mg/l and adsorbent dosage 4 g. As is seen from Fig. 4, reflecting the dependence of degree of zinc ions adsorption on initial value of solution pH, metal ions adsorption substantially rises with increase of pH and reaches maximum, when pH – 7-9.

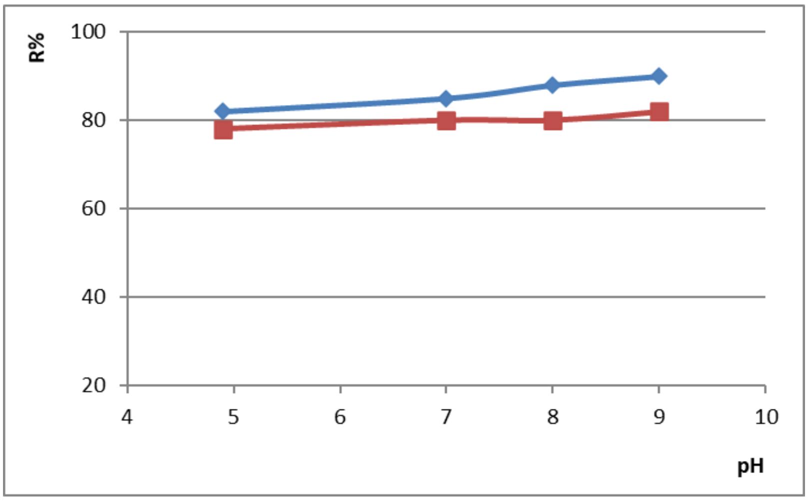

Figure 4 Impact of medium pH of solution under study on Zn (II) adsorption degree. m = 4g, τ =1h, t = 20°C, $C_{Zn^{2+}}$ = 100mg/l. blue (⧫)– travertine, red (■) – limestone.

In case of low values of pH – 2-6, ions are present in the solution in form of zinc cations, while hydrogen ions completely dominate on adsorbent surface, promote Zn^{+2} ions repulsion and reduction of their adsorption. Increase of pH value from 7 to 10 causes formation of hydrolytic forms ($Zn(OH)^{+2}$). Therefore, increase of pH from neutral to alkaline values provide optimum conditions for zinc ions attraction, since adsorbent surface is heavily saturated with negatively charged hydroxyl groups, so zinc ions electronic attraction and increase of metal adsorption on the sorbent occur [19].

4. Conclusion

Adsorption capacities of Georgian minerals, travertine and limestone in the process of aqueous solutions treatment from zinc ions have been investigated for the first time in this work. Experiments showed that adsorption depends heavily on values of solution pH, adsorbent dosage, contact time and adsorbate concentration.

Optimal value of pH proved to be within the range of 5 - 8, first the adsorption rate was high and reached equilibrium in 15-30 minutes. Optimal conditions for zinc adsorption have been selected, in case of which the maximum degree of adsorption (in percentage terms) – 89% and 83% has been attained, when contact time was equal to 60 minutes, quantity of adsorbent – 3 - 4 g, adsorbate concentration 100 mg/l for travertine and limestone, while adsorption capacity under these conditions comprised 29 mg/l and 28 mg/l, respectively.

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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