

Adsorption removal of copper ions from water medium with the use of travertine and limestone

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Abstract

Copper removal from aqueous solutions with the use of natural minerals of Georgia – travertine and limestone, which have been used for the first time as adsorbents in the mentioned process, has been studied. Travertine and limestone are not expensive, mechanically strong, ecologically clean and widely spread minerals.

Based on the experiments, the factors having impact on sorption capacity of these minerals have been analyzed.

Dependence of adsorption degree and adsorptive capacity on adsorbent dosage, time contact, adsorbate concentration, grain fraction size and pH of solution medium has been studied.

Optimum conditions for aqueous solution treatment from copper ions have been selected. Maximum efficiency of Cu^{2+} removal was equal to 95% and 92%, while adsorptive capacity – 46.8 mg/g and 45.2 mg/g for travertine and limestone, respectively.

Keywords: Travertine; Limestone; Copper; Adsorption

1. Introduction

Heavy metals discharge to the environment is one of the basic ecological challenges worldwide. Heavy metals cause problems related to water and soil quality, plants, animals and human life.

They are not biodegradable. Therefore, their accumulation in sewage waters may lead to dangerous consequences.

Environmental pollution with toxic metals is a result of many types of human activity, such as metallurgy, extraction (mining), coal-mining and chemical industries, fertilizers manufacturing etc. [1, 2].

The mentioned enterprises discharge industrial effluents to the water channels, cause significant contamination of water and have a negative influence on the environment [3,4].

Copper is considered as less toxic among these metals and has important biological functions. In lower concentration range (<1.5 mg/dm 3), copper promotes correct functioning of enzymes, participates in hemoglobin and melanin formation. But even its small excess may cause acute poisoning.

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Its presence in higher concentrations in organism leads to Wilson disease, kidney, liver, myocardium diseases etc. [5-7].

Maximum permissible concentration of Cu^{2+} in drinkable water is 1.5 mg/dm³ as recommended by the authors of [5].

Methods of heavy metals removal are important aspects of environment protection and healthcare, they are used for heavy metals' elimination or reduction of their concentration in water, soil and air.

Different methods of physical-chemical treatment, including chemical deposition, coagulation, ion exchange, filtration, adsorption etc. are used for heavy metal removal from contaminated waters [8].

Adsorption is a process when an adsorbate (contamination) adheres to the adsorbent surface by physical (electromagnetic attraction) or chemical (ion exchange, precipitation) [9].

Due to its efficiency and economic feasibility adsorption is a widely used method of heavy metals removal from waste waters. Normally used adsorbents include activated coal, zeolites, different clays and minerals, graphene oxide, mesoporous silica, adsorbents from residuals of agricultural by-products etc. [10-12].

In the previous works [13-14] for the first time we have studied chemically active natural minerals of Georgia – travertine and limestone as adsorbents in the process of aqueous solutions treatment from zinc ions both under static and dynamic conditions.

This work sets a goal of study of adsorption capacity of Georgian minerals – travertine and limestone in the process of aqueous solutions treatment from copper ions and exploration of the effect of adsorbent dosage, time contact, adsorbate concentration, solution pH and grain fraction size on copper ions adsorption degree and adsorptive capacity.

Detailed characteristics and particular deposits of the mentioned minerals are given in the work [13].

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 copper 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.

For preparation of standard solution, the electrolytic copper (99.999%) was weighed, dissolved in nitric acid and filled two times with distilled water up to 1 liter. 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

Copper ions adsorption on minerals – travertine and limestone has been studied with the purpose of determination of optimum values of adsorbent dosage, contact time, concentration of the solution under study, value of pH and grain size under static conditions.

Experiments have been conducted in containers with the volume of 250 ml, containing 100 ml of the copper ions solution under study. For determination of optimum quantity of adsorbents in the process of Cu^{2+} ions removal, the different quantity of adsorbents, namely 0.5; 1; 2; 3; 4; 5 and 6 g has been loaded into containers, which has been poured by investigated copper solution with the volume of 100 ml and shaken. As is seen from Fig. 1, a steady-state condition has been reached in case of adsorbent dosage from 1 to 4 g, that is why an optimum dose equal to 1 g has been selected for all subsequent experiments.

The dependence of copper ions adsorption percentage on time of shaking has been measured within the limits of 15; 30; 60; 90; 120; 150 min. In order to establish an optimum contact time, the samples containing adsorbent (in amount of 1 g) and investigated 100 ml copper solution have been shaken. Samples have been collected after the above-mentioned time intervals, then filtered and analyzed.

As is seen from Fig. 2, the equilibrium has been reached after 60 min, so the experiments were held for the mentioned contact time. Optimum concentration value of the solution under study has been established the same way.

100 ml copper solution under study has been poured into containers with optimum amount of adsorbent – 1g. Initial metal concentration has been varied within limits of 25; 50; 100; 150; 200 mg/l, have been shaken for 60 minutes. Samples have been filtered and analyzed. Optimum concentration value of the solution under study was equal to 100 mg/l (Fig. 3).

Effect of pH factor on adsorbents' surface has been experimentally studied within a range of pH 2-7, which has been established through addition of 0.1 M hydrochloric acid or caustic potash to the solution. Investigated solution with a given pH in amount of 100 ml and concentration 100 mg/l has been poured into containers with 1 gr of adsorbent and shaken for 60 minutes.

After shaking, an obtained solution has been filtered and a filtrate has been analyzed in terms of copper content by means of atomic-adsorption spectrometer (AAS Perkin-Elmer-200).

There have been carried-out experiments concerning the effect of adsorbent fraction (grain) size on copper sorption. Trials have been conducted with grain sizes within a range of 0.5-2.5 mm. Optimum value of adsorbent grain size has been selected and it was equal to 2-1 mm (Fig. 4).

The amount of copper adsorbed per unit weight of adsorbent surface (adsorption capacity) A mg/g, and Cu (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/dm³;
- C - posterior (after the test) concentration;
- m - sorbent weight, g;
- V - volume of purified solution, dm³

3. Results and discussion

Adsorbent dosage is one of the most important parameters of adsorption process. Fig. 1 shows an impact of adsorbent (travertine and limestone) dosage on copper ions adsorption.

It is clearly seen from the Figure, that increase of adsorbent dosage leads to fast growth of Cu^{2+} adsorption degree for both adsorbents, which further becomes almost constant in case of amount 1-4 g and adsorption degree equals to 95% and 92% for travertine and limestone, respectively.

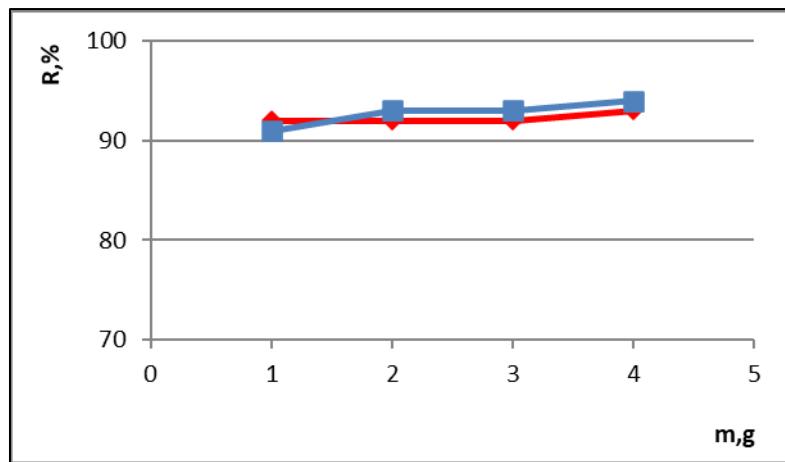


Figure 1 Adsorbent dosage (m, g) impact on Cu^{2+} adsorption degree (R, %). $\text{pH} = 5.5$, $\tau = 1\text{h}$, $t = 20^\circ\text{C}$, $\text{C}_{\text{Cu}^{2+}} = 100\text{mg/l}$. blue (■) – travertine, red (◆) – limestone

Increase of adsorbent dose has led to enhancement of Cu^{2+} ions removal efficiency at the expense of increase in number of available active sites on adsorbent surface, which become available for Cu^{2+} adsorption [16].

Dependence of Cu^{2+} adsorption degree on contact time is demonstrated in Fig. 2. This dependence point at the fact that a rapid increase of Cu^{2+} adsorption occurs with increase of contact time, at that the major part of metal ions is adsorbed within first 15 minutes and adsorption degree reaches 94% and 88% for travertine and limestone, respectively. Afterwards, adsorption rate decreases until reaching the equilibrium state, when adsorption degree is 95% and 90%, while adsorptive capacity – 46.8 mg/g and 45.0 mg/g for travertine and limestone, respectively. This circumstance can be explained by instantaneous saturation of adsorbents' surface and reaching the equilibrium state within 60 minutes [17].

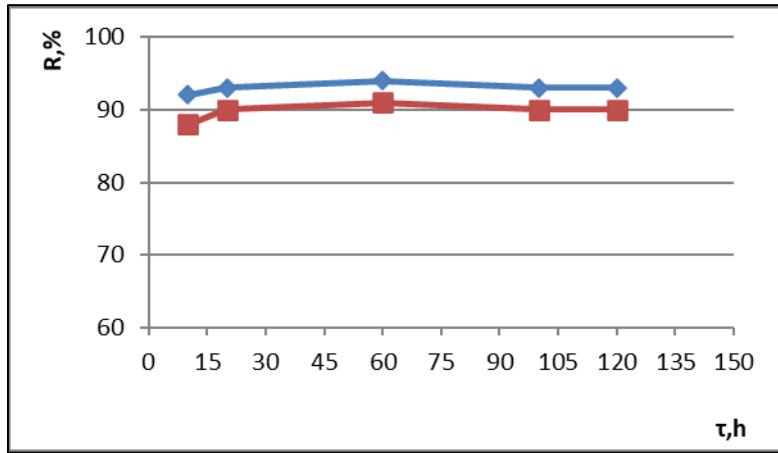


Figure 2 Contact time impact on Cu^{2+} adsorption degree. $\text{pH} = 5.5$, $m = 1\text{g}$, $t = 20^\circ\text{C}$, $\text{C}_{\text{Cu}^{2+}} = 100\text{mg/l}$. blue (◊) – travertine, red (■) – limestone

Effect of initial concentration on copper ions adsorptive capacity has been studied through change in investigate solution's concentration within 25÷200 mg/l. It is seen from Fig.3 that the adsorption percentage rapidly increases first with increase in initial concentration of copper ions and reaches 94% and 92% for travertine and limestone, and shortly after leads to adsorbent's surface saturation, so adsorption degree remains constant within a range of 50÷100 mg/l, and then decreases and drops down from 95% and 92% to 80% and 73% for travertine and limestone, respectively [18].

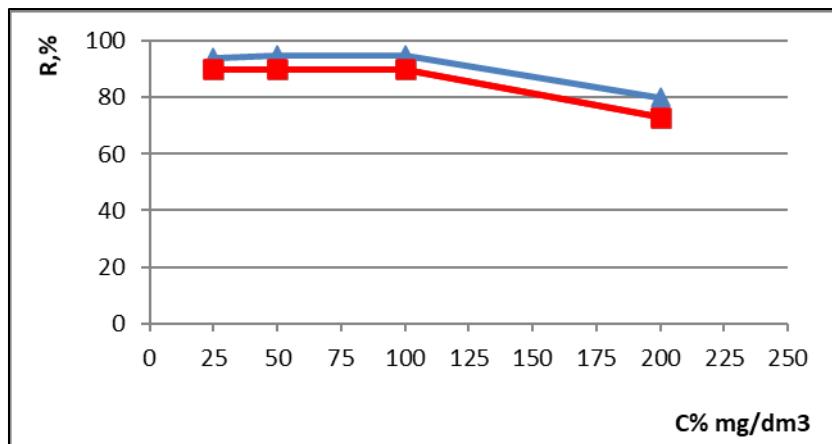


Figure 3 The effect of the solution concentration on Cu^{2+} adsorption degree. $\text{pH} = 5.5$, $m = 1\text{g}$, $t = 20^\circ\text{C}$, $\tau = 1\text{h}$. blue (◊) – travertine, red (■) – limestone

Study of dependence of copper ions adsorption percentage on initial value of solution pH showed that at low pH values, copper adsorption degree is low, as well. It slowly increases within a range of $\text{pH} = 2\text{--}5$ and reaches a maximum at $\text{pH} = 5.5$, during which the adsorption degree equals to 96% and 94% for travertine and limestone, respectively, and adsorptive capacity – 47.2 mg/g and 45.2 mg/g.

When pH value surpasses 7, Cu^{2+} precipitates as a hydroxide, which decreases the adsorption rate and, as a consequence, copper removal percentage.

Fig. 4 shows the dependence of Cu^{2+} adsorption percentage on adsorbent particle size. It is seen from the diagram that adsorption capacity of adsorbents under study almost doesn't change within 0.5÷2.5 mm range of grain size.

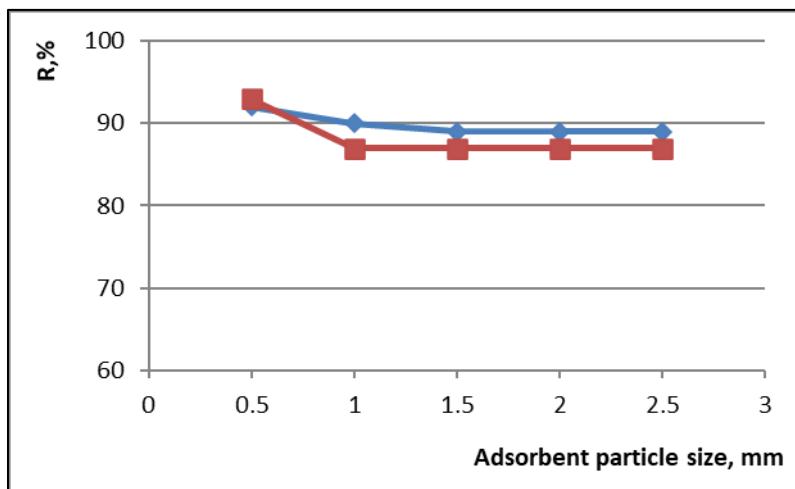


Figure 4 Dependence of the percentage of Cu^{2+} adsorption on the size of adsorbent particles. blue (◊) – travertine, red (■) – limestone

4. Conclusion

Opportunities of application of the natural minerals of Georgia – travertine and limestone in the process of adsorptive removal of Cu^{2+} from aqueous solution have been investigated in the work. It has been found out that adsorption process depends on adsorbent dosage, contact time, adsorbate concentration and pH value. Optimal conditions for the process, namely: amount of adsorbent 1 g, contact time 60 min, solution concentration 100 mg/l, and pH – 5.5 have been selected.

Under the above conditions, copper adsorption degree for travertine and limestone was equal 95% and 92%, while adsorptive capacity – 46.8 mg/g and 45.2 mg/g, respectively.

It has been shown that travertine and limestone as adsorbents are quite effective in the process of copper ions removal from aqueous solutions.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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