ADSORPTIVE REMOVAL OF COPPER (II) IONS FROM AQUEOUS SOLUTION USING PUMICE

Marine Kalantaryan[1]*, Hovsep Hoveyan[1], Suren Hovsepyan[1], George Abrahamyan[2]

[1] *National University of Architecture and Construction of Armenia, Yerevan, RA*

[2] *Shant Laboratories sa/nv, Brussels, Belgium*

Abstract: *This article presents the use of modified pumice as an environmentally friendly adsorbent for copper (II) removal from wastewater. The water pollution by toxic elements is a major concern for human health and environmental quality. New and cheaper methods of wastewater treatment are increasing the quality of the environment and reducing negative impacts on fauna, flora, and human beings. The sorption technique is considered a cost-effective method for effectively removing heavy metals. In recent years, there have been increasing studies dedicated to using low-cost adsorbents such as pumice. For the study, Kuchak pumice has been used. The modified pumice was prepared by surface modification with polysiloxane, evaluated by studying the effects of pH, contact time, dosage, and initial concentration, and was optimized in batch processing mode. The chemical changes in pumice were fully characterized using FT-IR techniques. Overall, these results suggest that surface-modified pumice is a low-cost adsorbent for the removal of copper (II).*

Keywords: *pumice, modification, polysiloxane, adsorbent, heavy metal removal.*

Marine Kalantaryan*

E-mail: kalantaryanm@mail.ru

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Introduction

The rapid development of the industry has resulted in a significant increase in heavy metal contamination, which has become a major environmental issue. The most significant challenge facing humanity today is effectively managing the problem of water pollution caused by heavy metals. The physical and chemical techniques traditionally used for cleanup are associated with high capital costs and can damage already contaminated areas. In today's highly industrialized society, several industrial operations release aqueous effluents containing heavy metals. The presence of heavy metals in aquatic systems can harm numerous living species [1]. Copper (Cu^{2+}) ions are present in many biological systems at low levels but can be toxic at high concentrations. Although copper can exist in different forms, such as Cu (0), Cu (I), and Cu (II), Cu (II) is the primary species of concern in aqueous solutions. Cu^{2+} rapidly binds to organic and inorganic compounds in aqueous solutions, which is pH dependent. It harms aquatic life and makes natural water unsuitable for human use. Ingesting high concentrations of Cu can also be toxic to humans, leading to cancer and promoting oxidation [2,3]. Toxic metals can now be removed from soil and water using various clean-up technologies developed over time. Currently, physical-chemical processes such as filtration, chemical precipitation, ion exchange, adsorption, and electrodeposition, form the foundation of the most extensively utilized remediation technologies [3]. Different types of materials have been used as adsorbents for copper adsorption, such as activated carbons and zeolites [4], alumina - silica [5], molecular sieve powder [6] and different pumices. The current study aims to establish the ideal conditions for the maximum amount of copper to be absorbed by pumice from aqueous solution and to evaluate the effects of various experimental parameters on copper adsorption.

Different treatment strategies, such as physical, chemical, and biological treatments, were discussed based on the past few years. These introduced methods are adsorption, membrane filtration, electrodialysis, and photocatalysis. However, there are some precautions that should be taken seriously as they are influenced by parameters such as the initial concentration of copper ions, pH values, economic parameters such as operation cost, and the environmental effects and compatibility of each of the various methods conducted.

Currently, many adsorbents are being produced and used for cleaning up wastewater. These adsorbents can be of either natural or artificial origin. Considering the numerous advantages of natural materials, including their availability in large quantities and non-toxicity, it is more appropriate to use adsorbents based on natural materials. Efforts have been made recently to modify the surface of these natural adsorbents to increase their efficiency, and extensive research has been conducted in this direction [1,2].

The aim of the present study is to investigate the influence of various experimental parameters on copper adsorption and determine the optimum conditions for maximum adsorption of copper by pumice from aqueous solution. The influence of temperature, sorbent mass, solution pH and sorbent chemical modification on adsorption process is discussed.

The Republic of Armenia is rich in non-metallic mineral diversity and abundance. The light rocks (tuffs, perlite, pumice stone, zeolite, scoria, etc.) generated because of volcanic activities in the mountains of Armenia are of particular value and significance.

In this article Kuchak pumice deposit is used as an adsorbent for copper removal from aqueous media. The pumice on the territory of the Republic of Armenia according to their petrographic, physical and mechanical characteristics are divided into two types: Ani and lithoidal Kuchak pumice is one of the Ani type pumice varieties. It is located at an altitude of 2050 meters above sea level. On the southern side of the pumice deposit there is a powerful layer of pumice grains with a capacity of 6 ... 7 meters and pumicite with a capacity of 4 ... 6 meters. Studies have shown that the pumice is composed of alumicillicates in which the alkali oxide content varies from 1.5 to 5%, SiO_2 from 71% to 75%, and Al_2O_3 from 12% to 14%. In the Kuchak pumice deposit samples, the content of alkaline oxides varies from 0.03 to 0.1%, SiO_2 from 70% to 73% and Al_2O_3 from 12 to 16% [7].

Materials and Methods

The analysis of the data obtained shows that the Kuchak pumice deposit is environmentally safe and is a chemically neutral silicate rock in water medium. Kuchak pumice has a porosity of 1.64 to 32.70 µm (Fig. 1). The total porosity is about 72.2 - 79.4 % [7].

The presented data show that Kuchak mine pumice is an aluminosilicate rock with well-developed porosity, mechanical strength, high buoyancy. It is chemically inert and eco-friendly.

In this study the following reagents were used: polysiloxane emulsion, copper sulphate ($CuSO_4.5H_2O$), and hydrochloric acid (HCl). All the reagents used were of highly pure grade. The deionized water was used for all reagent solutions.

Polysiloxane has an extensive record of success and is frequently used in medical applications. Elastomers, gels, lubricants, foams, and adhesives are examples of different material types. Polysiloxane is relatively stable and chemically inert. They have minimal moisture uptake and are hydrophobic. They offer excellent electrical insulation qualities. Nearly all polysiloxane is based on polymethylsiloxane (Fig. 2).

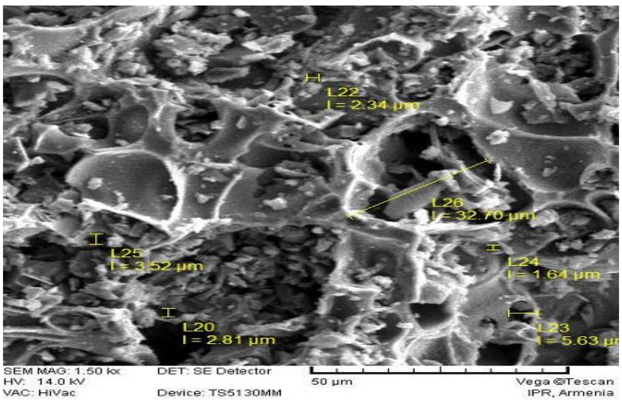

Fig. 1. *Pore sizes of Kuchak pumice deposit [8]*

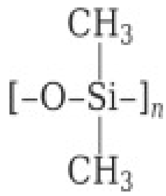

Fig. 2. *Chemical structure of polysiloxanes*

Polysiloxanes (PDMS) or silicones, are a general category of polymers consisting of a silicon-oxygen backbone with organic groups, typically methyl groups, attached to the silicon atoms [9,10,11]. Organic side groups can be used to link two or more chains together. By varying the -Si-O- chain length, side groups, and crosslinking extent, silicones with properties ranging from liquids to hard plastics can be synthesized. Silicone synthesis typically involves the hydrolysis of chlorosilanes into linear or cyclic siloxane oligomers, which are then polymerized into polysiloxanes by polycondensation or polymerization, respectively. Polysiloxanes, characterized by unique material properties combining biocompatibility and biodurability, have found widespread application in healthcare [12,13,14,15].

About 1.0 g of polysiloxane was mixed with 10 g of pumice and 30 mL of distilled water. First, the pumice was washed with water and dried in an oven at 105°C for one hour. Then the polysiloxane emulsion was mixed in 1:30 ratio with distilled water to form a stable mixture. The mixture was then stirred for 5 hours at room temperature. Then it was filtered from the solution, washed, and dried in an oven at 70 °C for 3 hours to allow the emulsion to adhere to the surface. Finally, the modified pumice was washed with water to remove excess emulsion and dried again. Different particle sizes (2.36, 3.54, and 4.87 mm) were collected and used as an adsorbent for the analysis. All pH values were measured with a pH meter (HACH LANGE HQ 14d). Cu^{2+} solutions of different concentrations (5 mg/L, 10 mg/L, 50 mg/L, and 100 mg/L) were prepared in deionized water using $CuSO_4$. Batch adsorption equilibrium studies of Cu were carried out at room temperature in beakers filled with 2.5 g of modified pumice. The contact times were one or two hours. The pH dependence experiment was carried out as a preliminary experiment to establish if the material possesses any affinity for Cu (II) ions. The pH of the solution is a known factor with significant impact on metal ion removal processes. The experiment was conducted in the pH range 2–6.

Fig. 3 shows the effect of pH on copper adsorption onto pumice. The adsorption capacity of pumice samples increased with increasing pH. The highest adsorption value is observed at a pH of four.

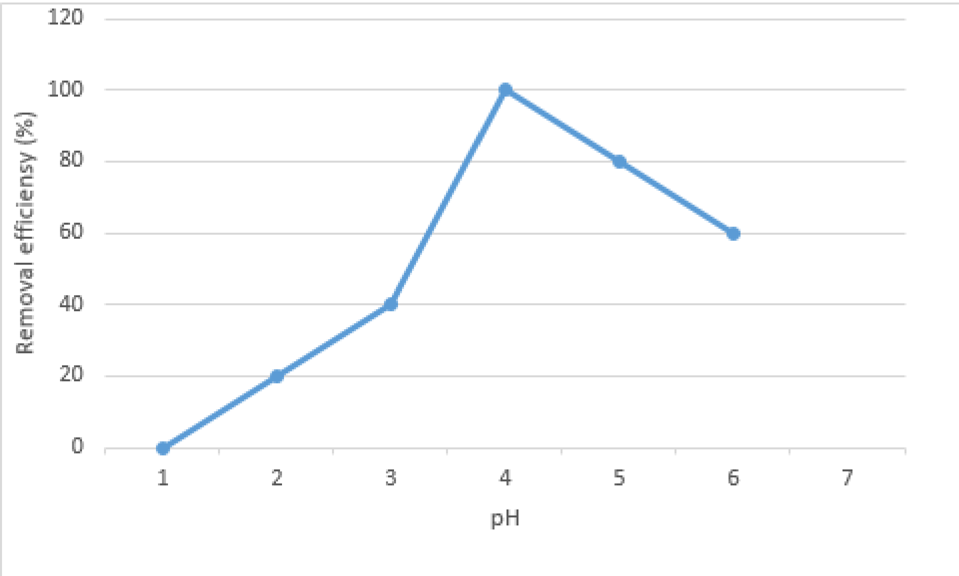

Fig. 3. *Effect of pH on the adsorption of copper by surface-modified pumice*

Results and Discussion

The effect of temperature on the adsorption of copper was studied by conducting a series of experiments at 25, 30, and 40 °C. There is a small effect of temperature on the adsorption of copper by pumice in aqueous solution. Because elevated temperature would be costly in commercial applications, experiments were run at 25 °C. The functional groups were found from the pumice and polysiloxane-modified samples using FT-IR spectrometer. The FT-IR spectrum of pumice is shown in Fig. 4. Compared to that of pumice, Si-CH_3 stretching bonds are observed for modified pumice under 1260 cm^{-1} and (Si-O-) bonds under 1100 cm^{-1}.

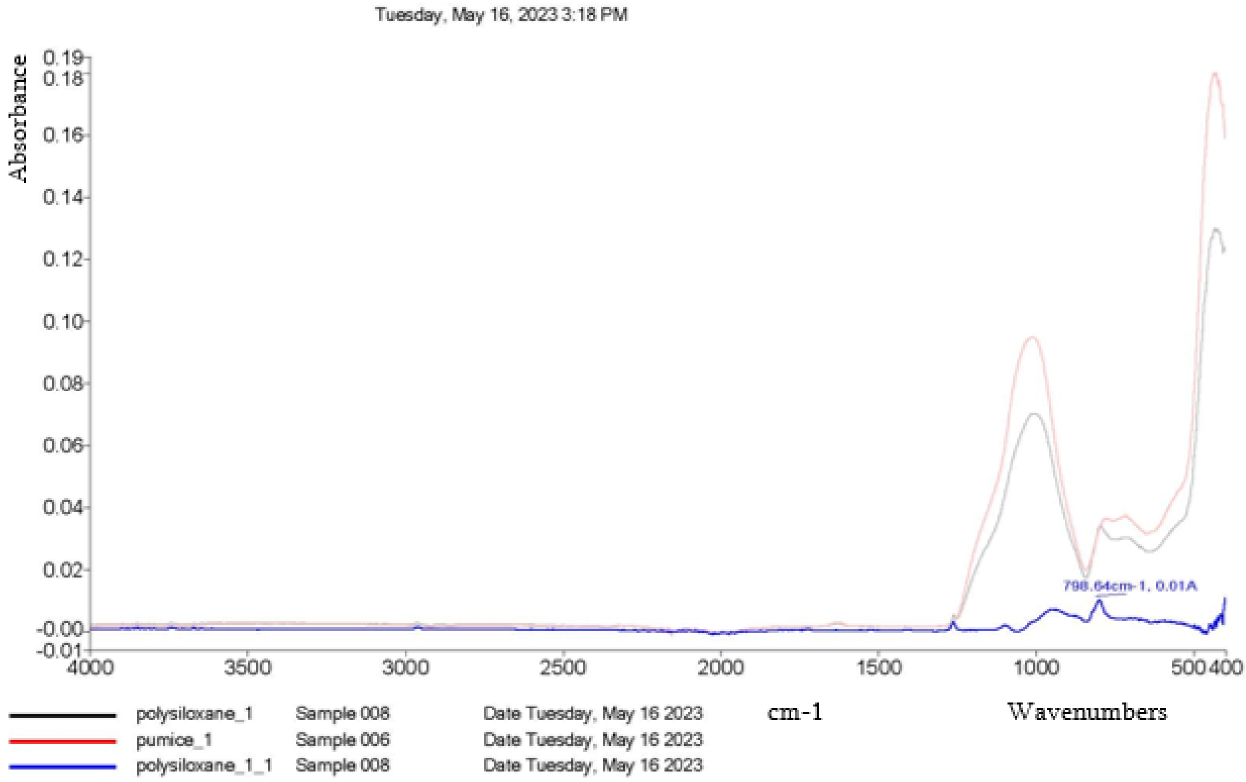

Fig. 4. *FT-IR spectrum of modified and unmodified pumices (PerklinElmer, Spectrum Two)*

The siloxane groups on the modified pumice surface can form coordinate bonds with metal ions such as copper (Cu^{2+}), allowing for effective removal from solution. The adsorption performance of polysiloxane-modified pumice will depend on various factors, including the surface area, pore size, concentration of metal ions, pH, and contact time.

Copper concentrations before and after adsorption were measured using UV-Vis Spectrophotometer (Cary-60). The wavelength of 10.0 nm^{-1} corresponds to the maximum absorbance of the copper on pumice. The spectra show after modification by polysiloxane the copper absorbance increased by 65% compared with unmodified pumice (Fig. 5).

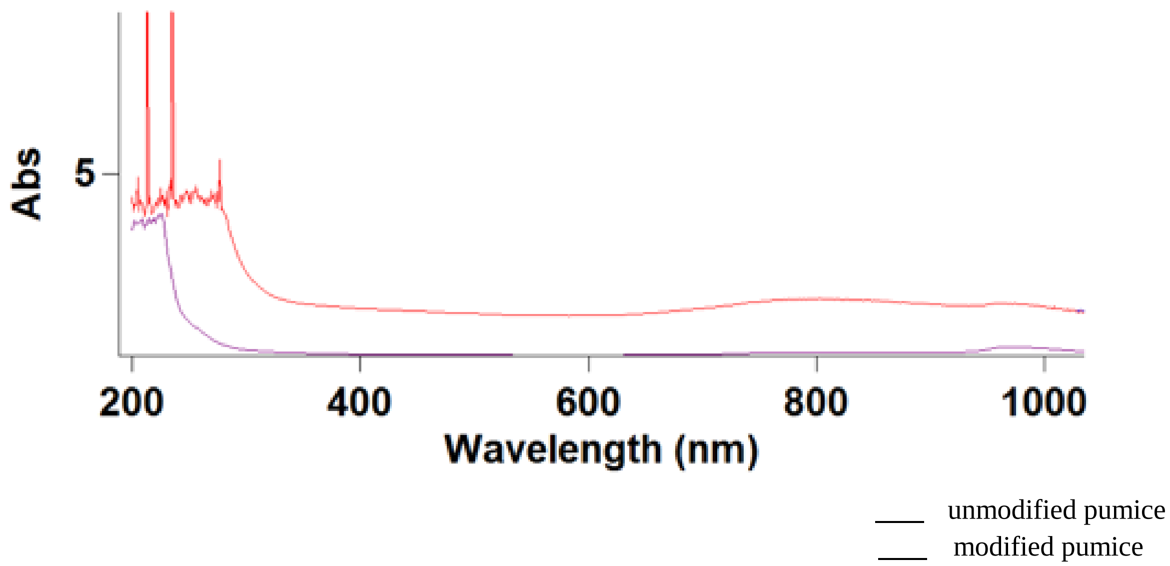

Fig. 5. *UV-Vis Spectrophotometric data (Cary-60)*

Conclusion

The efficiency of the pumice for the adsorption of copper from an aqueous solution was investigated using batch adsorption technique under different experimental conditions. Reported results showed that the adsorption varied strongly by pH. Temperature had a minor effect on the adsorption of copper by pumice. Due to its low cost and ready availability, it can be used as an efficient adsorbent material for the adsorption of copper from contaminated aqueous solutions. The modification of pumice with PDMS introduces siloxane (-Si-O-) functional groups onto the surface of the pumice particles. These siloxane groups can provide adsorption sites for metal ions due to their ability to coordinate with metal cations.

The high surface area and porous nature of pumice, combined with the adsorption properties of PDMS, can enhance the adsorption capacity for metal ions. The siloxane groups on the modified pumice surface can form coordinate bonds with metal ions such as copper (Cu^{2+}), allowing for effective removal from solution. The adsorption performance of polysiloxane modified pumice will depend on various factors, including the surface area, pore size, concentration of metal ions, pH, and contact time. Additionally, the specific synthesis and modification methods of the polysiloxane-modified pumice may influence its adsorption properties.

Overall, polysiloxane-modified pumice has the potential to be an effective adsorbent for copper ions. However, the actual adsorption capacity and efficiency would require experimental evaluation and optimization for specific conditions and metal ion concentrations. In our future research, we aim to develop methods to extract copper ions from polysiloxane-modified adsorbents.

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Marine Kalantaryan, Doctor of Philosophy (Ph.D) in Chemistry *(RA,Yerevan) -National University of Architecture and Construction of Armenia, Associate professor at the Chair of Production of Construction Materials, Items and Structures, Head of the Research Laboratory "Construction Chemistry", kalantaryanm@mail.ru*

Hovsep Hoveyan, Doctor of Philosophy (PhD) in Engineering *(RA,Yerevan) -National University of Architecture and Construction of Armenia, Chief of the Staff, Assistant at the Chair of Technology and Organization of Construction Production, hoveyan@nuaca.am*

Suren Hovsepyan, Doctor of Philosophy (PhD) in Engineering *(RA,Yerevan) -National University of Architecture and Construction of Armenia, Assistant at the Faculty of Management and Technology, surenhovsepyan@gmail.com*

George Abrahamyan, Doctor of Philosophy (PhD) in Biology *(Belgium, Brussels), CEO & President of Shant Laboratories sa/nv, ag@shantlabs.com*