



IMPREGNATION OF MAGNETITE NANOPARTICLES SUPPORTED ON PUMICE STONE FOR MERCURY REMOVAL IN WASTEWATER

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Abstract

Environmental pollution caused by mercury represents a serious threat to human health, especially in areas close to mining activities. Fortunately, there are various techniques to remove mercury from wastewater, such as the use of nanoparticles and porous rocks. In this study, the Bottom Up in situ coprecipitation method was used to impregnate magnetite nanoparticles into pumice, in order to enhance the adsorption capacity of mercury in contaminated water. This method allowed for a homogeneous distribution of nanoparticles in the pumice, turning it into a porous support matrix that improves the adsorption capacity and resistance to deactivation of nanoparticles. The results of the adsorption tests, carried out with mercury solutions at 1 ppm and different contact times, as well as pH modification, demonstrated the effectiveness of the technique. The adsorption capacity was measured, and the adsorption kinetics were analyzed to evaluate the process of mercury removal. Additionally, the adsorption capacity of pumice was evaluated under the same established times for comparison.

Keywords: Mercury Removal, nanoscience, nanoparticles, pumice, magnetite.

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1. INTRODUCTION

Mercury in its elemental state can be released into the air as a result of the burning of fossil fuels, which is why it can be inhaled, thus improving air quality, and its non-biodegradable nature causes it to accumulate in the environment. Increasing the levels of contamination and thus representing a serious threat to human health, it can be released into the environment in various ways, but studies reveal that activities related to mining are one of the main sources of contamination by this metal globally compared to other human activities, due to the excessive use of amalgamation techniques for gold extraction. (1), in this context, the WHO established tolerance limits for mercury in drinking water being 1 mg/L..(1,2) In fact, mercury is one of the most toxic metals known and can have serious effects on human health, including damage to the central nervous system and kidneys, as well as fetal development problems (1,2) As mentioned above, mining activity is one of the main sources of environmental contamination, especially with respect to the release of heavy metals including mercury, these are filtered and mixed with effluents or groundwater, which increases its propagation capacity, thus compromising water quality and significantly increasing the risks to human health (3).

The lack and inexistence of treatment plants in areas close to gold and mining deposits further aggravates the problem, presenting itself as a barrier in the field of environmental conservation and public health (4). Together with illegal mining, an activity that is not properly regulated and authorized by the state, it does not comply with the necessary indications to protect health and the environment (2). This is usually practiced by informal groups which use dangerous and polluting methods. Consequently, the International Labor Organization (ILO) focuses its efforts on developing programs and projects to address labor exploitation in illegal mining, as well as promoting sustainable and responsible practices in the mining industry. To this are added several global organizations which have expressed their concern about the impact of mercury on human health and the environment (5). Thus, in 2017, the Minamata Convention was established, a global treaty to prevent and reduce exposure to mercury, which establishes measures to reduce and eliminate its use in different sectors, including mining. In addition, the United States Environmental Protection Agency (EPA) names mercury as one of the most dangerous pollutants of air, water and food, establishing maximum contamination limits for mercury in different sectors and implementing measures to reduce mercury emissions into the environment (6). In the southwestern part of Ecuador, specifically in the

province of Oro, is the largest gold mining district in the country, which has been in operation for decades (7). In this center, day-to-day activities are carried out as well as artisanal activities (AGM) and small-scale (SGM). Various techniques are used for gold extraction and mining waste management, including mercury amalgamation and gravity separation (8). Most of the gold is extracted from raw ores collected from numerous local mining concessions, as well as imported materials from other regions of Ecuador and northern Peru (9).

Currently worldwide there are preventive techniques, and post-treatment which are hampered by their high prices, the use of harmful solvents and their long application time, this is how recent studies outline nanostructures as a potential solution to address this problem, presenting itself as a promising and low-cost alternative (10,11) being nanomaterials with magnetic properties one of the alternatives for water purification, since it allows its separation from the liquid phase simply by applying a magnetic field (12). How the scientific community has directed its efforts to undertake actions and address this problem, making use of nanotechnology to develop various techniques that allow the elimination of mercury in wastewater in an optimal and adequate way. In this sense, the use of iron oxide nanoparticles as an adsorbent material for heavy metal ions, including mercury (10,12), has been reported; these are characterized by having a high adsorption capacity, which is attributed to their specific surface. It is important to highlight that there are various techniques for their synthesis in different sizes, which gives them a significant advantage in the removal of heavy metals (10). Likewise, the pumice, being a volcanic rock of a porous nature and low density, presents adsorption properties due to its permeable structure (6,13).

In previous research, pumice impregnated with iron nanoparticles has been shown to be capable of adsorbing mercury with encouraging results (13,14). In the same way, adsorption tests have been carried out using only pumice with good results. In this context, the high volcanic activity that characterizes the Andes Mountains, due to its geographical location in the Pacific Ring of Fire, provides for the presence of large pumice reserves in the area, which is presented as a promising solution for surrounding mining towns, significantly reducing the negative environmental and health impact associated with the use of mercury, in the same way, by using pumice instead of other reagents, treatment costs can be reduced, which decreases the need to buy expensive chemical products, reducing thus the negative economic impact associated with this problem. That is why, in the present investigation, the combination of magnetite nanoparticles with pumice is proposed to improve the adsorption capacity of mercury in

wastewater. Magnetite has the ability to capture mercury ions (7,12,13), while pumice pores can physically retain mercury, suggesting great potential for use as an adsorbent in contaminant removal (7,9). This is how Nps was impregnated with magnetite in pumice to improve the stability and reactivity of the nanoparticles. In situ impregnation allowed a homogeneous distribution of the nanoparticles in the pumice stone, this provides a porous support matrix that improves the adsorption capacity and resistance to deactivation of the nanoparticles. To evaluate the effectiveness of the technique, adsorption tests will be carried out using mercury solutions at 1 ppm similar to the literature by Marimon (15), at different contact times and modifying the pH of the Solution, the adsorption capacity will be measured by Likewise, the adsorption kinetics will be analyzed to evaluate the mercury removal process. In addition, the capacity of the pumice was evaluated at the same times and pH modification in order to compare them.

2. MATERIALS AND METHODS

2.1 Experimental Design

Pumice samples were collected from the high Andean ecosystem located in the vicinity of the Chimborazo Volcano, located at the coordinates 1°29'53.9"S 78°52'30.4"W, due to the presence of this material in said volcanic area. The study was carried out in the instrumental chemistry and research laboratory of the Higher Polytechnic School of Chimborazo. In this study, the efficiency of mercury adsorption was compared between pumice impregnated with magnetite nanoparticles and unimpregnated pumice. The impregnation of the magnetite nanoparticles was carried out using the in situ coprecipitation method. First, the pumice was prepared for its subsequent impregnation, and then it was characterized by infrared spectrophotometry and scanning electron microscopy. Finally, both the impregnated and the non-impregnated pumice were subjected to mercury adsorption tests, varying the contact time and the pH of the solution.

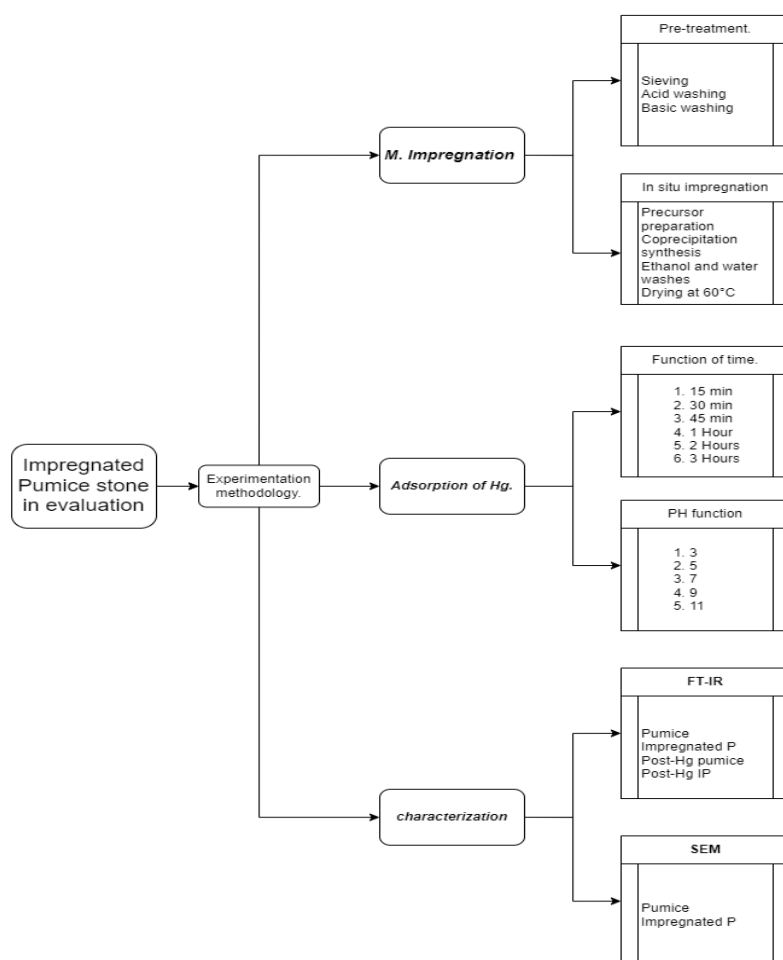


Figure 1 Experimental design of magnetite impregnation in pumice

2.2. Pumice pretreatment

For the treatment of pumice, the literature of (16) has been used as a reference, who has worked with ash volcanic. Due to the volcanic nature of the pumice, a similar process has been followed with some modifications. It is essential to consider the characteristics and conditions in which the stone is found, since they can present various contaminants, such as dirt and certain impurities. Firstly, the pumice is cleaned using aqueous washes with deionized water which is left to rest for at least 5 hours in the sonicator, later, it proceeds to crush the pumice stone to obtain smaller particles that were sieved, using a Mesh35 sieve. to obtain a sample with a thickness of 500 micrometers, they are again washed with deionized water, as well as with ethanol to eliminate organic matter present, to then be calcined at 700 ° C. with the purpose of eliminating carbonic and sulphureous materials. Calcination was carried out in a Thermolyne muffle model f48010-33.

2.3. Nps impregnation of magnetite in pumice

The methodology of (17) was adopted for the synthesis, combining it with the pumice impregnation methodology described by (13) In this way, a solution of ferrous chloride and ferric chloride was prepared with a ratio of 1:2 respectively, which is graduated to 100 ml. Only 50 ml of this solution are used to carry out the precipitation of the nanoparticles. With the help of the burette, 1M sodium hydroxide is dropped into the iron chloride solution until an intense black color is generated and the pH of the solution is around 10. It is important to mention that this reaction must be carried out under constant stirring, as well as in an inert atmosphere, so it is essential the introduction of gaseous Nitrogen throughout the duration of the impregnation process. Once a pH of 10 is reached, the sample is subjected to washings with water and ethanol to eliminate any type of contaminant. After these washes, the sample is dried at a temperature of 50 degrees Celsius for a period of 24 hours and is stored for subsequent treatments.

2.4. Characterization

2.4.1. Scanning Electron Microscopy SEM

To characterize the impregnated pumice, samples of the material were taken before and after impregnation. Due to the non-conductive nature of the pumice materials, they were coated with a thin layer of gold power to allow the electrons to not clump together. In this way, detailed images of the structure and morphology of both the original pumice and the impregnated pumice. The

Equation 1 described by (18) is used:

comparison between the two allowed us to determine the effects of the impregnation on the structure and surface of the pumice, as well as to evaluate the impact that the impregnation on the physical and chemical properties of the material (14).

2.4.2. Infrared spectrophotometry

Infrared spectroscopy was used to analyze impregnated and unimpregnated pumice. A Jasco brand FTIR 4100 infrared spectrophotometer with a wavenumber measurement range of 7800 to 350 cm⁻¹ and a maximum resolution of 0.7 cm⁻¹ was used. The data obtained were interpreted to identify the inherent functional groups of the magnetite present in the impregnated sample, which were not observed in the non-impregnated sample. In this way, it was possible to determine the presence of magnetite in the impregnated sample through its spectrum.

2.5. Adsorption methodology

For the comparison of the samples in the elimination of mercury, standards of this metal were prepared at a concentration of 1 part per million (ppm) as described in the Marimon experiment (15). To measure the efficiency of mercury adsorption, a THERMO brand ICE 3300 atomic absorption spectrophotometer was used, which analyzed the absorption in a standard wavelength range of 185 nm to 760 nm.

2.5.1. Depending on contact times

0.2 g of impregnated pumice was placed in 20 ml of the 1ppm mercury standard, as was also done for the unimpregnated pumice. Six samples were made for each of the times to ensure that the volume did not vary, the solution was extracted after contact at established times of 15, 30, 45 minutes, 1 hour, 2 hours and 3 hours. Subsequently, the sample was filtered with the help of 20-micrometer microfilters and stored in a cold environment for later evaluation by atomic absorption.

2.5.2. Depending on PH

An additional parameter was evaluated in the mercury adsorption process, which was the pH of the solution. The same one that was modified by adding 0.1M sodium hydroxide, letting the solution drip until the established pH of 3, 5, 7, 9 and 11 was reached. In these tests, the concentration of Hg (II) and the amount of adsorbent were kept constant., and the contact time was 1 hour for the experimental process.

2.6. Adsorption percentage

$$\text{Adsorption (\%)} = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

Where:

C_i = Concentration of the solution 1ppm

C_f = Final concentration

2.7. Mercury adsorption capacity

To obtain the adsorption capacity, the difference in initial and final concentrations is calculated (19)

$$C_a = \frac{(C_i - C_f)V}{M} \quad (2)$$

Where:

C_a = Adsorption capacity C_i = Initial concentration 1ppm

C_f = Final concentration of Hg (II) in the solution (mg/l)

V = Volume of solution (l)

M = Mass of solid adsorbent used (g)

3. RESULTS AND DISCUSSION

3.1 SEM morphology before and after impregnation

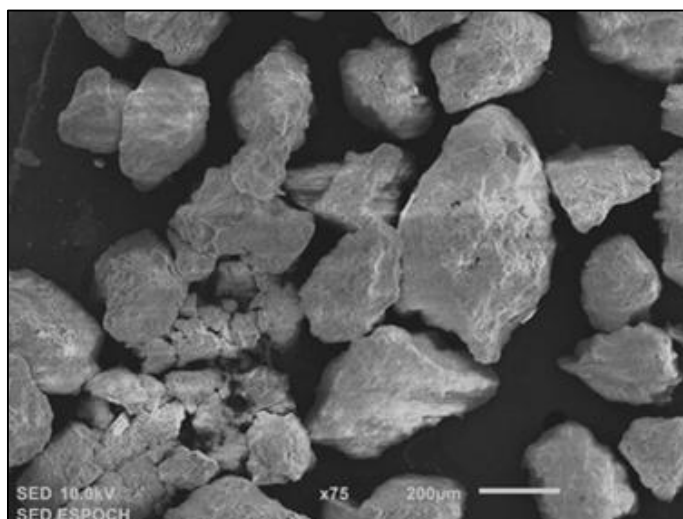


Figure 2 Unimpregnated pumice

In (Figure 2) you can see the porous nature of the pumice which is the result of its origin and formation Volcanic, which is attributed to the expansive effect and rapid cooling in its development. This porosity translates into a large surface area, which makes pumice an ideal support for impregnating the magnetite nanoparticles, since by developing the coprecipitation synthesis method (Bottom-up) on top of the pumice allows the deep penetration of these in the surface of the support, maximizing the interaction between the stone surface and adsorbed particles, generating greater efficiency in the retention and removal of contaminants in aqueous media, in this way also the impregnation, in addition to allowing a much better adherence more effective

and homogeneous, than nanoparticles.

Previous research has shown that pumice contains highly selective aluminosilicate molecules, similar to the composition of other types of zeolites, it is composed of an irregularly shaped crystalline network and internal cavities interconnected with the external surface (13,20). The pumice stone has proven to be a support highly effective for impregnating nanoparticles, especially iron nanoparticles, thanks to its pore volume of 85% (13). In fact, iron nanoparticles impregnated in pumice stone have been used with success in fluidization beds as low-energy biological reactors.

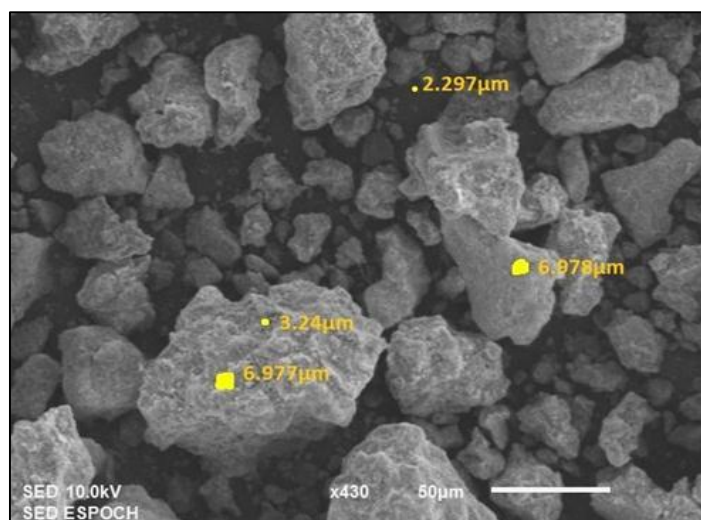


Figure 3 Impregnated pumice

In (Figure 3), small clumps of nanoparticles can be seen, suggesting that pumice is an excellent option to improve the dispersibility of nanoparticles. In addition, the performance of pumice stone with other materials such as zeolite, kaolinite, bentonite and chitosan beads, which have shown similar results in dispersion and adhesion of nanoparticles, which are also effective as supports (20,21). As mentioned above the chemistry of pumice is a relevant factor to consider in its applicability, since its aluminosilicate composition makes it highly selective. In addition, its low cost and easy acquisition make it a promising material in the field of mining, especially in areas near volcanoes where there is a problem with the presence of mercury in mining activity. It is important to note that volcanic eruptions also emanate mercury, but in low quantities. Therefore, the presence of pumice with high concentrations of mercury, which demonstrates its natural adsorbent capacity. Therefore, the pumice stone is presented as a promising alternative in the elimination of contaminants in mining activity.

3.2. IR spectroscopy

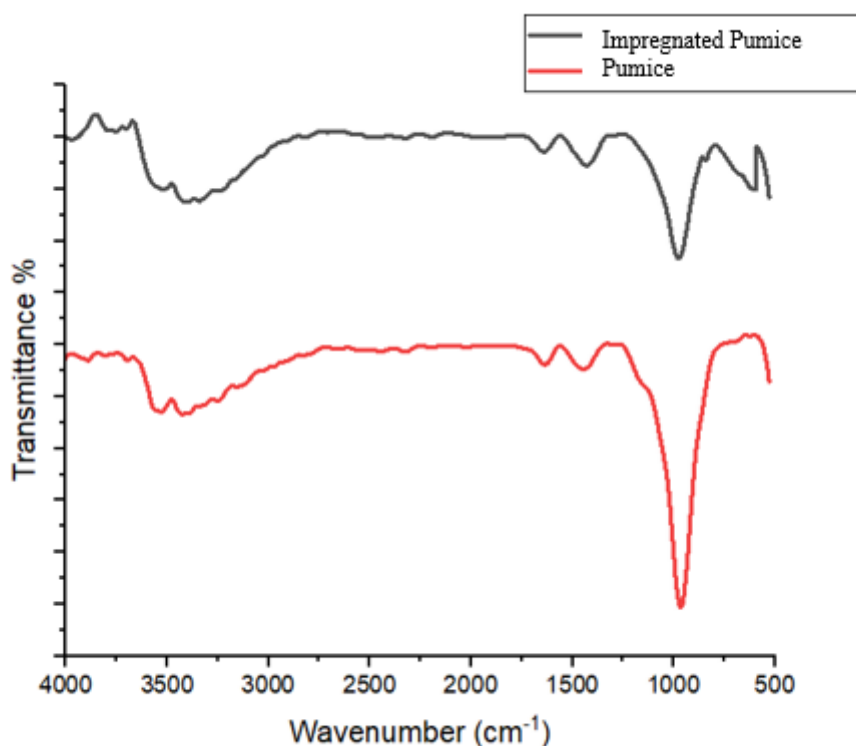


Figure 4 Infrared spectrum impregnated and unimpregnated pumice

FTIR (Fourier Transform Infrared Spectroscopy) analysis was used to identify the different functional groups present in the sample. A band was observed in the range of 3200-3600 cm⁻¹ which is attributed to the stretching vibrations of the OH group, as well as bands in the range of 2850-2960 cm⁻¹ that correspond to the stretching vibrations of the CH links these 2 ranges are inherent in the composition of the pumice (22,23). The presence of isolated aluminol and silanol groups on the surface was evidenced at the peak at 3780 cm⁻¹ 246 (Al-OH-Si-OH) (23).

In addition, the difference between the two can be evidenced since the 560 cm⁻¹ peak is related to the bond (Fe-O) which is characteristic of magnetite,

while the resonance vibrations 1650 and 3100 cm⁻¹ indicate the presence of hydroxyl groups (O-H) in magnetite (24).

3.3. Comparison of mercury removal efficiency of pumice and impregnated pumice

3.3.1. Final concentration and percentage of mercury removal.

The amount of mercury remaining in the samples after the experimentation as a function of time is indicated in (table I) and (figure 5). The results of the percentage of mercury removal as a function of time, determined according to the methodology mentioned in section 2.5, are shown in (table II) and (figure 6).

Table: I Analysis of the influence of time on the final concentration of Hg (II)

Time (min)	Initial Concentration Hg (II)	Final Concentration Hg (II)	
		Pumice Impregnate	Pumice
0	1000 ppb	1000	1000
15	1000 ppb	17,93	249,22
30	1000 ppb	5,23	340,62
45	1000 ppb	4,76	342,34
60	1000 ppb	3,20	403,87
120	1000 ppb	0	360,52
180	1000 ppb	0	376,80

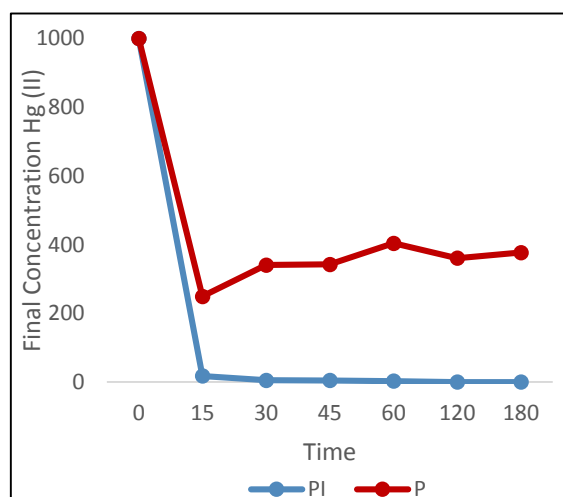


Figure 5 Analysis regarding the final concentration

Table: II Analysis of the influence of time on the adsorption of Hg (II)

Time (min)	% Adsorption	
	Pi	P
15	98,20	75,07
30	99,47	65,93
45	99,52	65,76

60	99,67	59,61
120	100	63,94
180	100	62,31

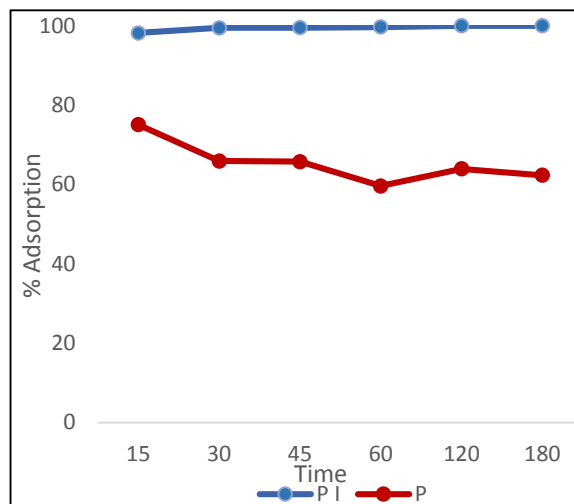


Figure 6 % Adsorption vs Time

The results obtained in the pumice impregnated with magnetite nanoparticles show that the final concentration of mercury Hg (II) tends to decrease as the contact and agitation time elapses until stabilizing. By experimenting for a time of 120 minutes, the final concentration of mercury is non-existent, that is, the removal percentage is of 100% and from this time the trend of the curve is maintained, as can be seen in figure 5. These results go hand in hand with other research works on the impregnation of magnetite in different materials, which present the tendency to decrease the concentration of mercury in the polluting solution over time, an example important to cite is the research carried out by Vassilis J. Inglezakis, in which he evaluated the adsorption of mercury using zeolite and zeolite impregnated with silver nanoparticles, it should be noted that, like pumice, zeolite has aluminosilicates in its composition(25).

The pumice evaluated in the mercury adsorption shows a mercury removal in a range of 249.2249 ppb at 403.8776 ppb, adsorption percentages between 59.61% and 75.077% respectively. at different contact times there is no clear trend in figure 5, so this result can be attributed to several reasons, one of which is of them, the particle size, which by not being controlled can affect the removal, if they are larger particles, the surface area decreases and therefore the adsorption of Hg (II) ions will be less (26). scientific works of mercury removal with magnetite nanoparticles have shown similar trends to impregnated pumice, that is say, the adsorption percentage increases until it stabilizes (27)(28). The results of the final concentration of Hg (II) in the solution, as a function of pH, are shown in table III and figure 6 and 7. The removal percentage as a function of pH is shown in Table IV.

Table III Final Hg (II) concentration

pH	Initial Hg (II) concentration	Final Hg (II) concentration	
		Impregnated	Pumice
		Pumice	
3	1000 ppb	3,20	249,23
5	1000 ppb	2,01	330,61
7	1000 ppb	1,42	379,43
9	1000 pbb	1,65	403,47
12	1000 pbb	2,31	670,72

Table IV Adsorption percentage as a pH function

pH	% Adsorption	
	Pi	P
3	99,67	75,07
5	99,79	66,93
7	99,85	62,05
9	99,83	59,65
12	99,76	32,92

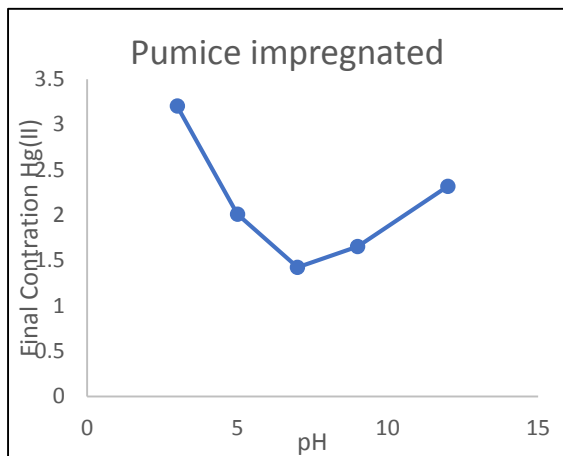


Figure 7 Final Hg concentration PI

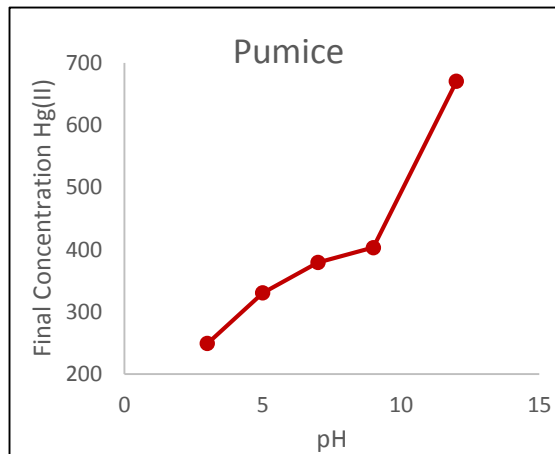


Figure 8 Final Hg concentration P

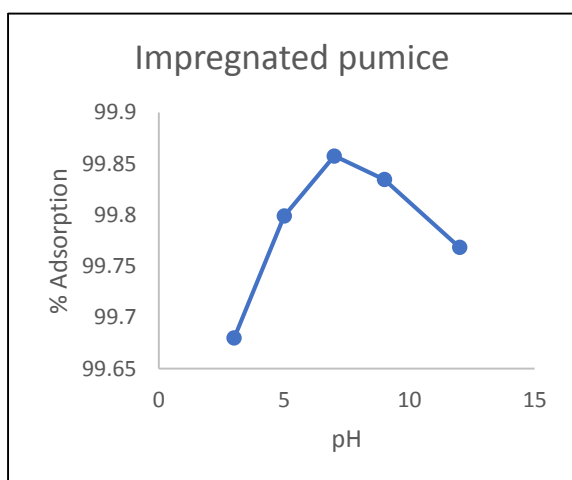


Figure 9 % Adsorption vs pH (PI)

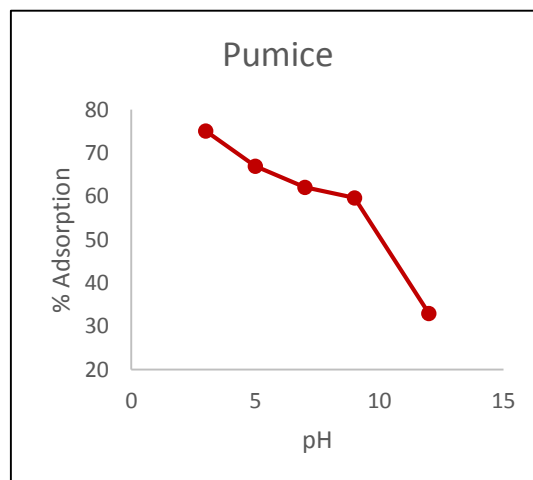


Figure 10 % Adsorption vs pH (P)

It was determined that the pH does influence the removal of mercury. For the impregnated pumice, it is observed that the largest mercury removal is achieved at pH 7, with a final Hg (II) concentration value of 1.4234 ppb corresponding at 99.857% removal rate, which indeed shows promising results for this material magnetic, the results are in accordance with the doctoral thesis "Engineering of magnetic nanoparticles for the removal of heavy metals in water" (27).

The pumice tends to decrease the removal of mercury as the pH increases, a hypothesis for this result is due to the fact that the pumice in its composition is a porous aluminosilicate, depending on the acidity it favors said pores or active sites that improve the interaction with Hg (II) ions (29).

3.3.3. Hg (II) adsorption capacity

The adsorption capacity as a function of time is shown below:

Table: V Analysis of the influence of time on the final concentration of Hg (II)

Time	Adsorption Capacity	
	PI	P
15	0,098	0,075
30	0,099	0,065
45	0,099	0,065
60	0,099	0,059
120	0,100	0,063
180	0,100	0,062

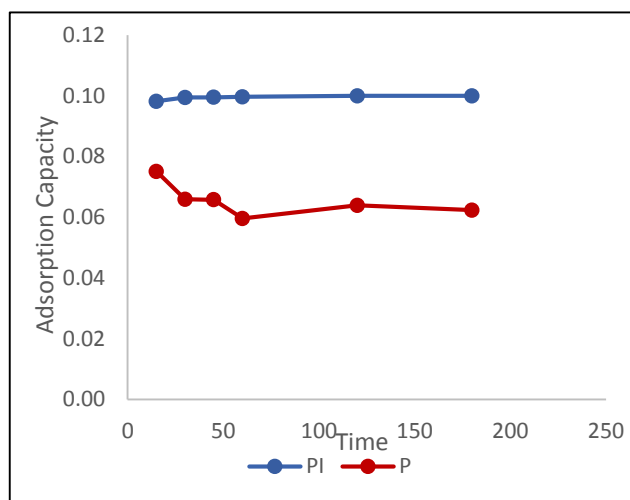


Figure 11 Adsorption capacity vs Time

Data for the adsorption capacity of the impregnated pumice and the pumice were determined experimentally. The results show that the adsorption capacity for the impregnated pumice increases with the time of contact and agitation with the contaminated solution until the curve begins to stabilize after 120 min. The adsorption capacity of the pumice has variations over time that do not

follow an exact trend, however, its adsorption capacity is at an approximate value of 0.6 mg/g. The impregnated pumice proves to be much more efficient than the natural pumice, reaching an adsorption capacity of 0.1, corresponding to 100% mercury removal in 2 hours. The results of adsorption capacity as a function of pH can be seen below:

Table VI % Adsorption vs pH

pH	% Adsorption	
	Pi	P
3	99,67	75,07
5	99,79	66,93
7	99,85	62,05
9	99,83	59,65
12	99,76	32,92

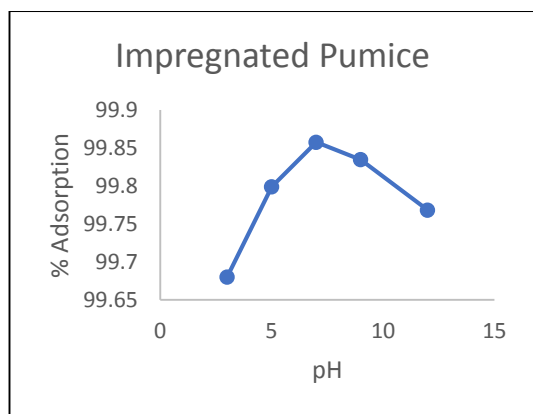


Figure 12 % Adsorption vs pH (PI)

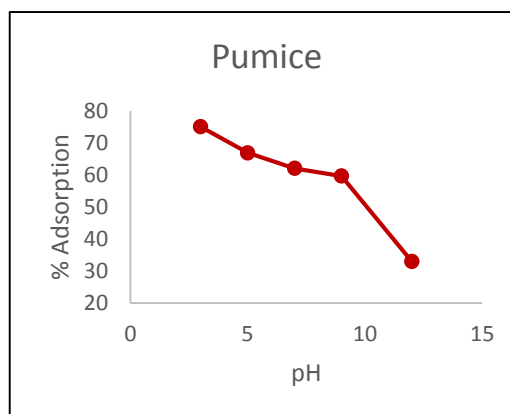


Figure 13 % Adsorption vs pH (P)

The impregnated pumice proves to have the best adsorption capacity when working with a pH 7 solution, with an adsorption capacity of 99.857%. If the solution is more acidic, the capacity will decrease, also when the solution is basified, however, at basic pH a better removal capacity of the impregnated pumice is observed, these results go hand in hand with those obtained in the experimentation of (13).

4. CONCLUSIONS

It was determined that the impregnation of nanoparticles in situ in pumice stone is feasible, since it significantly improves the adsorption capacity of mercury in wastewater, reaching a maximum adsorption of 99.85%. This solution is attractive and sustainable for the elimination of contaminants in different industrial processes, since pumice stone is a low-cost material and its impregnation with nanoparticles does not require large investments. In addition, pumice is a natural and biodegradable material, which reduces the negative environmental impact associated with the use of conventional chemical reagents. Experimentally, the amount of mercury removed from aqueous solutions was significantly improved, since magnetite traps a high percentage of ions. of mercury, and the Pumice is presented as a support due to its high number of aluminosilicates present, in addition to the fact that due to its porous nature it allows a greater dispersion of them on the surface of the rock, which translates into a high contact surface with the rock. aqueous solution.

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