Removal of cadmium in wastewater through geopolymeric materials based on pumice.

J Grillo¹, A M Montaño¹, C P González², and G C Barón¹
¹Universidad Industrial de Santander, Bucaramanga, Colombia
²Universidad Pontificia Bolivariana, Bucaramanga, Colombia

E-mail: amontano@uis.edu.co, claudia.gonzalez@upb.edu.co

Abstract. Heavy metal pollution in the effluent water due to industrial waste product of various economic activities is not adequately regulated in Colombia, this is because the agencies do little control track discharge and easily granting environmental licenses. As a result of this little regulation currently they do not have updated figures that provide real information on the amount of waste that ends up in the resort, causing health effects of living beings. In the tanning industry, in particular, there cadmium residual concentration higher than the maximum allowed by the Ministry of the environment. This work considers the use of a geopolymeric material based on pumice stone, to capture cadmium ions present in wastewater and thus reduce its concentration in the water resource in order to reduce the population's exposure to diseases that are associated with accumulation of cadmium in the body. The synthesis of geopolymer began from the alkaline activation of pumice stone with commercial sodium silicate, the use of sand:pumice stone in a 1:1 ratio and 31 hours of reaction, these proportions were defined in a previously work by the authors. The morphological and crystallographic characterization of the sorbent geopolymeric material was performed by scanning electron microscopy and X-ray diffraction. To assess the sorption process, a study of the geopolymer's contact time with a known solution of cadmium was performed. Cadmium concentration was determined using atomic absorption spectroscopy and the geopolymer was characterized after removal.

1. Introduction
Geopolymers are materials synthesized from aluminosilicates which are mainly used as a substitute for portland cement, due to its high resistance to compression and to the fact that in its manufacturing process, low CO₂ emissions are generated [1]. During the last years, some studies have found that these materials can also be sorbents for different substances [2,3], thanks to their network of sialates, which generates porosities that allow capturing ions in solution. In addition, the heavy metals are one of the most dangerous forms of pollution in the environment, which correspond to those cations that have an atomic number greater than 23. These metals, which are not biodegradable, accumulate in the form of organic compounds or dissolve as ions, are absorbed easily in live organisms generating consequences that affect their health and may even cause death. Among the metals that cause most concern is cadmium, which is highly toxic, and has been considered carcinogenic since 1993 by the International Agency for Research on Cancer (IARC), which evaluated the risk of cancer derived from exposure to cadmium, and concluded that it should be considered remarkable carcinogenic to man [4,5].
In Colombia, the low availability of drinking water is worrisome and it is for this reason that the use of this resource is restricted in some areas of the country [6]. This occurs largely because industrial and mining activities generate waste that contains metals that are discharged into rivers and water sources,
this situation has generated an increase in the study of geopolymers for metal removal and elimination in wastewater, based on its efficiency and low profitability [7]. Resolution 0631 of 2015 of the Ministry of the environment and sustainable development, established that the maximum permissible limit values in specific discharges to bodies of surface water and public sewage systems for cadmium, must not exceed 0.1 mg/L [8].

In order to reduce the concentration of cadmium in water sources in the country, different chemical, physical and biological methods have been sought that are not only efficient but also of low profitability and ecological. Geopolymers are materials that have these characteristics since their synthesis is carried out in conditions that do not generate a negative environmental impact and also the pumice is used, a volcanic rock whose obtaining does not cause alterations in nature. In this way, this new method for metal removal becomes an easily accessible option for its implementation in the industry. In this work, the synthesis of geopolymers based on pumice stone was carried out; these polymers were structurally characterized and used to cadmium removal in aqueous solutions.

2. Materials and methods
For the preparation of geopolymers silica:pumice ratio of 1:1 was used. The pumice from Geopomez Company, located in the municipality of Sabaneta, Antioquia, Colombia, was used as a source of aluminosilicates. The mixture was homogenized and poured into molds to the geopolymerization process, which was carried out at 80 ± 5 °C during 31 hours. Once the geopolymerization reaction was completed, removal capacity of the new material was evaluated. Geopolymer from pumice was ground and reduced to a particle size of 125 μm, then 0.2 g of geopolymer was added to cadmium sulfate solutions (2 mg/L) for 3, 6, 9, 12, 15, 18, 21 and 24 hours with continuous stirring. Finally, cadmium in the residual solution was measured by atomic absorption in a Thermo Electron S4 Solaar.

At the same time, both the raw materials and the geopolymer material before and after removal were characterized in terms of their morphology by scanning electron microscopy in a microscope Mira3 Tescan with detector Bruker. Crystalline phases were studied by x-ray diffraction in a Bruker powder diffractometer model D8 advance, with DaVinci geometry, using a polymethyl methacrylate sample holder, copper radiation (Cu Kα λ = 1.5406 Å) and a LynxEye linear detector. Data recorded with a step of 0.02035° (2θ) between 3.5° - 70.0° (2θ), operating with a voltage of 40 kV and a current of 40 mA.

3. Results and discussion

3.1. Analysis by X-ray diffraction
Mineralogical phases of the samples are analyzed by X-ray diffraction using de database PDF-4+ [9]. In Figure 1 it can be seen in the range 2theta between 25° and 30°, the appearance of two peaks corresponding to the albite (A) and quartz (Q), natural minerals formed mainly by silica and aluminum, also found the presence of iron oxide (I) (36° 20). For the geopolymer Figure 2 crystalline phases corresponding to different macrocrystalline varieties of quartz (Q) are evidenced (21°, 37° and 39° 20), also new signals for albite (A) appear (28° and 23°). There is also the presence of sodium carbonate (CS), formed during the geopolymerization process [6,7]. The pumice presents an amorphous and quite differentiable structure with respect to the geopolymer, which makes it possible to establish that the geopolymerization process has occurred with effectiveness.
Figure 1. Pumice diffractogram.

Figure 2. Geopolymer diffractogram.

3.2. Analysis by scanning electron microscope

Micrographs show in Figure 3, the raw material (pumice), the geopolymer and the geopolymer after being in contact with a cadmium solution of 2 ppm. Pumice shows a crystalline morphology, where small elongated particles are distributed on the surface evenly. Meanwhile, in geopolymer it can see the formation of some agglomerates, perhaps a product of the reorganization in tetrahedra SiO$_4$ and AlO$_4^-$ linked alternatively with oxygen atoms. This structural modification occurred during the synthesis.
Figure 3. Micrographs of Pumice (a), geopolymer (b) and geopolymer after adsorption (c).

There are also small particles that give an amorphous appearance, attributed most likely to the process of geopolymerization, because alkaline activation does not occur uniformly.

In the micrograph for geopolymer after being in contact for 24 hours with the cadmium solution, it is observed that the agglomerates have disappeared and smaller particles have been formed that form a non-homogeneous surface, probably due to the adsorption of cadmium ions product to the porous structure offered by the geopolymer [1,7,10-12].

3.3. Evaluation of cadmium removal capacity of the geopolymer

The effect of contact time is changing from 3 to 24 hours, at three-hour intervals. Figure 4 shows the contact time between geopolymer and the solution. It is observed that the best percentage of elimination of Cd\(^{2+}\) ions was achieved over 12 hours with a 98.1% effectiveness, followed by the time of 3 hours with 95.8%, while the lowest percentages were found in 6 hours with a 70.7% and 24 hours with 73.8%. Although with these values it is not yet possible to determine the time where the equilibrium of the sorption reaction occurs if it is possible to affirm that the geopolymer has a point of saturation where a process of desorption begins and then the product of its structure begins to adsorb ions again cadmium [13]. In addition, it can also be inferred that the time required for the Cd\(^{2+}\) elimination is relatively long because it is in 12 hours where it achieves the highest percentage of removal.

At the same time, in order to evaluate geopolymerization advantages on cadmium removal, there was a test using precursor pumice for Cd\(^{2+}\) sorption finding that the highest percentage of removal with pumice after 18 hours of contact was just of 79%. This result shows that the geopolymeric material exhibits much better properties than pumice for the process of removal of Cd\(^{2+}\) ions.

Figure 4. Removal of Cd by geopolymer vs contact time.
4. Conclusions
Cadmium adsorption properties exhibited by the geopolymeric material are the product of the geopolymerization process, where the temperature, the reaction time and the concentration of the raw material define its chemical behavior. Contact time of the geopolymer with the solution is decisive to define the equilibrium point where the greatest amount of Cd$^{2+}$ is adsorbed since excessively long times lead to the desorption on the surface of the geopolymer. It is necessary to spread the study between 3 to 12 hours, where the geopolymer exhibited the largest removal percentage, in this way it will be possible to determine the kinetics of the reaction and to optimize the sorption process. It was determined that the geopolymeric material presents better results than its predecessor (pumice) in the adsorption of cadmium ions in aqueous solutions, thus supporting the use of geopolymer for removal processes.

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