Use of synthetic polymers of pumice for the removal of chromium in the tannery industry

J Grillo¹, A M Montañó¹, and C P González²
¹ Universidad Industrial de Santander, Bucaramanga, Colombia
² Universidad Pontificia Bolivariana, Bucaramanga, Colombia

E-mail: claudia.gonzalez@upb.edu.co

Abstract. Synthetic inorganic polymers are materials called geopolymers that have structural characteristics used for the removal of contaminants in wastewater. Thanks to its easy synthesis and low production costs, they have become one of the most studied materials in removal processes. In the tannery industry, huge amounts of water are used, which are mixed with chromium salts and whose final disposal is made directly on the water slopes, becoming a serious environmental problem for the world. In this work, geopolymer synthesized with pumice was used to determine the efficiency in the removal of chromium in the wastewater of a tannery in the city of Bucaramanga, Colombia. Initially, aqueous solutions were prepared to study the influence of the contact time, the pH of the initial solution and the dose of adsorbent, on the removal capacity of the metal. The maximum adsorption was presented at nine hours and at a pH value of 4, by comparing the adsorption percentages it was found that the geopolymer has better removal capacity than the precursor material, in turn a study of the sorption kinetics using the Langmuir and Freundlich isotherm model were made. Obtained geopolymer and raw material were characterized by Fourier-transform infrared spectroscopy, X-ray diffraction and scanning electron microscope, before and after the adsorption process.

1. Introduction

The tanning of skins in Colombia, is one of the industrial activities that more concern because of its high water consumption since it is one of the most polluting industries, this is because approximately 85% of the hides in the now they are tanned with chrome [1]. Chromium (Cr) is a metal that in the oxidation state Cr (III) is considerably less dangerous than Cr (VI) [2], which is rapidly absorbed in the body after ingestion or inhalation, forming complexes that are considered carcinogenic [3]. In 2010, the “Instituto de Hidrología, Meteorología y Estudios Ambientales (IDEAM), Colombia”, found that in the Bogotá river, chromium values were above 37.3 mg/kg, these values were attributed to the fact that tanning activities are carried out in the municipalities of Chocontá and Villapinzón [4]. This record exceeds the limits allowed in Colombian regulations, since according to resolution No. 0631 of 2015 issued by the “Ministerio del Medio Ambiente y Desarrollo Sostenible, Colombia” the maximum permissible parameters in discharges to surface water bodies and the public sewerage systems for the manufacture of leather and tanned items, are 1.5 mg/L for chromium [5], becoming a reason to find solutions that help in mitigating the damage that this industry is causing to the environment and consequence to life.

In response to this problem, idea arises of implementing geopolymers for the removal of heavy metals such as chromium [6]. Geopolymers are polymers synthesized from the alkaline activation of aluminosilicates, whose structure is formed by a polymeric network of sialates [7]. These materials
have different properties that depend on the choice of the raw material and the synthesis conditions, which is why they can be used in sorption processes. The purpose of this research work is to establish the optimal parameters that allow obtaining the highest percentage of chromium removal in water using pumice geopolymer, and in this way initiate a process of change in the management of tannery discharges that allow decrease the concentration of metal that is deposited in the country's water sources.

2. Materials and methods
Geopolymer synthesis was carried out using as a raw material pumice stone from the Geopomez company, located in the municipality of Sabaneta, Antioquia, Colombia [8]. The polymeric material obtained was ground to obtain particles of a size of 125 µm and finally it was characterized. For the determination of the optimal parameters of removal, a solution of chromium chloride of 3 mg/L was prepared. Geopolymer was characterized after removal by scanning electron microscopy (SEM) in a MIRA3 Tescan microscope with EDX Bruker detector. Crystalline phases were studied by X-ray diffraction (XRD) in a Bruker model D8 ADVANCE powder diffractometer and in the analysis of the obtained diffractograms the PDF-4 database was used.

2.1. Sorption test
Sorption tests were performed by varying several parameters: time, geopolymer dose and pH. Initially 25 mL of 3 mg/L chromium chloride solution was added to 0.05 g of geopolymer, for a time between 3 and 24 hours with constant stirring of 200 rpm. After determining the optimal time to achieve the maximum removal percentage, the other parameters were varied, keeping the initial volume of chromium chloride solution constant. Samples were then filtered and the residual chromium was measured by atomic absorption (AA) in a Thermo Electron S4 SOLAAR. Finally, using the optimum parameters obtained above, sorption tests were performed on the samples from a tannery. The efficiency percentage was calculated using the following Equation (1).

\[
%E = \frac{[Co - Ce]}{Co} \times 100, \quad (1)
\]

where Co is the initial concentration (mg/L) and Ce is the remaining concentration of chromium (mg/L) [9]. The amount of milligrams of chromium absorbed per gram of the geopolymer was determined by the Equation (2).

\[
(q) = \frac{[Co - Ce]}{m} \times \frac{V}{m}, \quad (2)
\]

where V corresponds to the volume of sorbate (L) and m to the mass of the sorbent (g) [10].

3. Results and discussion

3.1. Effect of contact time
Figure 1 shows the results obtained by the variation of the contact time between the geopolymer and the chromium solution. There the percentage of effectiveness of chromium removed in eight different times is shown.

A variation of the contact time was made from 3 to 24 hours at intervals of 3 hours keeping the geopolymer dose at 0.05 g and the concentration of chromium chloride of 3 mg/L, Figure 1 shows the percentage values obtained. It is observed that the best percentage of removal efficiency with the geopolymer is achieved at 9 hours with 72.04%. This result indicates that it is at that time that the geopolymer apparently reaches a saturation point, since immediately, there is a considerable decrease in the percentage of chromium removed. In addition, a removal test was performed in parallel with the pumice, using the same variables and it was obtained that the maximum removal percentage is 53% at
21 hours, showing that the geopolymer has better structural characteristics than its precursor, which makes it a better adsorbent, not only for its high percentages, but also for the low time it takes to reach its maximum capacity.

![Figure 1](image1.png)

**Figure 1.** Percentage of chromium removed evaluated at different contact time.

3.2. Effect of geopolymer dose
For the evaluation of the geopolymer dose, amounts of 0.03 g, 0.05 g, 0.1 g, 0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1.0 g were used, with constant agitation of 200 rpm during 9 hours. Removal percentages obtained are shown in Figure 2, with 0.2 g, a percentage of 69% is obtained. It is noted that the change in the amount of geopolymer used in the adsorption, presents a constant variation between the data, where the maximum difference between the highest and the lowest percentage of effectiveness is 17.33%. This difference indicates that an increase or decrease in the dose is significant for the chromium ion sorption process. That is, the dose of geopolymer that can be used to carry out chromium removal can be variable and does not interfere with the percentage obtained, and the difference with which chromium cations are removed does not necessarily respond to an increase or decrease in the amount of sorbent, if not perhaps the way the material is disposed at the time the process occurs.

![Figure 2](image2.png)

**Figure 2.** Geopolymer dose evaluation.

3.3. Effect on the variation of the pH in the initial solution
For the study of optimal pH, solutions of pH 2, 3, 4, 5 and 6 were prepared, keeping the parameters the geopolymer dose at 0.2 g, contact time of 9 hours and the concentration of chromium chloride of 3 mg/L. Figure 3 shows that the highest removal percentage is 67.13% and the lowest is 60.09% at pH 4 and 5 respectively, that is, the difference between these percentages is only 7.04%, this variation is not enough to consider the initial pH as a determining variable in the removal process.

In order to better understanding of such behavior, it must be notice that when the geopolymer comes into contact with the solution, the pH ascends dramatically to 9-10, therefore, the removal effectiveness is not affected by the initial solution pH.
3.4. Determination of sorption isotherms

This study was conducted in assays on a single sample to which 0.8 g of sorbate was added to 200 mL of solution. Every 90 minutes and for 9 hours aliquots of 25 mL of the solution was filtered and pH adjusted to measure concentration of the metal present by atomic absorption.

Geopolymer was added to metal solution with constant stirring of 200 rpm. After measuring the residual concentration of the metal present in the aliquots taken, the effectiveness of sorption was calculated. The data obtained (Figure 4), were adjusted to the Langmuir and Freundlich isotherm models [11]. The Equation (3) shows the Langmuir model.

\[ \frac{1}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} \]

where \( K_L \) is constant in relation to the heat of adsorption and \( q_m \) (mg/g) is the maximum adsorption capacity of monolayer. Otherwise, the Equation (4) shows Freundlich model:

\[ q_e = K_F C_e^{1/n} \]

where \( q_e \) is the mass of adsorbate per unit mass of adsorbent in equilibrium, \( C_e \) is the equilibrium concentration of the adsorbate in solution, \( K_F \) is the constant for a given adsorbed and adsorbent at a specified temperature.

The parameters obtained for the adjusted models of the Langmuir isotherm (Figure 5) and Freundlich isotherm (Figure 6) are reported in Table 1. Values for the correlation \( R^2 \) of both models are close, however the value calculated for the Freundlich model is closer to 1, which suggests that the chromium adsorption process using the synthesized geopolymer conforms to this model. Since Freundlich's model would be the one that describes the process of chromium adsorption in the synthesized geopolymer, it is inferred that this process occurs heterogeneously in the material [12] and
that the sorbate is attached to the sorbent by electrostatic attractions. The chromium ion is retained by electrical forces that are generated in the polymer network due to the provision of positive and negative point charges generated by aluminum and the counter ion of the geopolymerization activator solution (Na\(^+\)).

![Figure 5. Freundlich adsorption isotherm.](image)

Contact time: 9 hours, Geopolymer dose: 0.2 g and pH 2.0.

![Figure 6. Langmuir adsorption isotherm.](image)

Contact time: 9 hours, Geopolymer dose: 0.2 g and pH 2.0.

| Model       | \(R^2\) | K           | n       |
|-------------|---------|-------------|---------|
| Freundlich  | 0.9863  | 0.313       | -5.844  |
| Langmuir    | 0.9836  | 0.1128      | -       |

3.5. Characterization of the material after adsorption

After performing the removal tests, the geopolymer used by XRD was characterized. Figure 7 shows the diffractograms corresponding to the initially synthesized geopolymer (upper) and the geopolymer after adsorbing chromium (lower), there it can be seen that there are no changes in the peaks corresponding to the different crystalline phases, showing that as a product of the Adsorption of chromium ions does not occur change in the structure of the geopolymer and the process is developed by physisorption.

![Figure 7. Geopolymer diffractogram before and after removal.](image)

The dark line corresponds to the pre-adsorption geopolymer and the light line is the post-adsorption geopolymer.
4. Conclusions
The synthesized geopolymer using pumice stone as a precursor, has great effectiveness in chromium removal, achieving percentages greater than 70% under optimal conditions of 9 hours and 0.2 g geopolymer doses, it is also inferred that the geopolymer has better structural properties that its precursor aluminosilicate (pumice) which gives it a greater removal capacity. Through the study of the sorption isotherms it was found that the chromium adsorption process conforms to the Freundlich model, that explains how the cations bind to the geopolymer through attractions that make the metal remain in a process of sorption and desorption at times of contact superior to the optimal one. This result added to its easy synthesis and low cost of production makes this geopolymer a good alternative to help in the removal of chromium from the residues that are generated in the industries, and in this way contribute to the decrease of the pollution in water sources.

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