Geopolymer derived from bentonite: Structural characterization and evaluation as a potential sorbent of ammonium in waters

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Abstract. In this work, a Colombian sodium bentonite geopolymer, montmorillonite type, activated with commercial sodium silicate, was synthesized for its later use as sorbent material of ammonium cations in leached waters from soils treated with PINAL, an ammonia-based herbicide of glufosinate used to eradicate the use of illicit crops. The raw material and geopolymer obtained are characterized by the Fourier transform infrared spectroscopy, X-ray diffraction and scanning electron microscopy technique, to determine the structural difference between the bonds created during the geopolymerization process, as well as to know the transformation of the crystalline phases of the material. Through this analysis and study of dispersion spectroscopy, it was possible to establish the effect of the eliminated ammonium cation on the structure of the geopolymeric material and propose a sorption mechanism, in addition, an improvement in the removal capacity of these ions from the geopolymeric material was observed.

1. Introduction
Montmorillonite is a clay of the bentonite type that has the ability to adsorb several times its size, taking a jelly-like appearance due to the hydration it acquires upon contact with aqueous solutions [1], which gives it a capacity to ion sorption, enhanced by performing an alkaline activation that will form an inorganic polymer or geopolymer [2-4]. Geopolymers are materials widely used in different applications, one of the industries that uses them the most is the cement plant, due to the replacement that can be done in Portland cement [5]; in turn they have been implemented as adsorbent materials due to the tetrahedral structure and octahedral that allows these compounds to have a high sorption capacity [6]. Recent research has evaluated the use of geopolymers in the adsorption of organic dyes such as methylene blue and cations such as Cu\textsuperscript{2+}, Pb\textsuperscript{2+}, Cr\textsuperscript{3+}, Cd\textsuperscript{2+}, NH\textsubscript{4}\textsuperscript{+} among others [7]. On the other hand, ammonium contamination due to the contact of herbicides with water sources, is a problem of high environmental impact in aquatic ecosystems, because it increases eutrophication causing instability in the environment [8]. In addition, it has been determined that for concentrations greater than 1 mg/L - 1.5 mg/L this ion is harmful to living beings [9] Due to this, it is necessary to find ways to remove the greatest amount of ammonium and mitigate the environmental impact that it brings, being zeolites one of the most used materials [10] due to its great ion exchange capacity, even so, because of the demanding conditions such as high temperatures and pressure for its synthesis, the method of removal to be used
on a large scale becomes expensive. Because of this using geopolymeric materials for this purpose, it becomes a good alternative, since its synthesis part of aluminosilicate compounds which occupy about 55% of the earth's crust [11] and does not require high energy for processing which makes them low-cost materials [12].

2. Materials and methods

2.1. Synthesis of geopolymeric material
The Colombian sodium bentonite geopolymer was synthesized by alkaline activation of this clay with commercial sodium silicate and aluminum oxide, until a homogeneous mixture was obtained. Mixture was placed in the oven at 100°C for 36 hours, then allowed to preserve for 24 hours, it was ground and sieved until it reached a particle size equal to 120 μm [13].

2.2. Characterization
The microstructure of bentonite and the geopolymer before and after sorption, was evaluated by Fourier transform infrared (FTIR) spectroscopy scanning between 400 cm\(^{-1}\) and 4000 cm\(^{-1}\) using a Bruker Tensor 2. By means of X-ray diffraction (XRD) the crystalline phases present of both, raw and geopolymeric materials were determined in a Bruker D8 ADVANCE model with DaVinci geometry, using a polymethylmethacrylate (PMMA) sample holder, a copper radiation (Cu Kα) λ =1.5406 Å and a LynxEye linear detector. Data was 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. Morphology was obtained by scanning electron microscopy (SEM) using a FEI QUANTA FEG 650 microscope equipment by placing the samples in the equipment support using the following conditions: HV: 20.5 kV; amplitude 14.88; TYPE APOLLO X SDD detector, resolution 127.2.

3. Results and discussion

3.1. Geopolymer synthesis
When performing the synthesis of the geopolymer of bentonite, it was successful through the process of leaving it for 31 hours at 100° and subsequently being in a curing process 24 hours at room temperature. It was observed that not all the bentonite underwent geopolymerization process since it was evidenced the presence of two phases in the polymer solution. Geopolymer obtained was a dark gray compound which, when ground, it turned to beige, this powder was used for the respective characterization and subsequent tests.

3.2. Fourier transform infrared spectroscopy characterization of bentonite and geopolymer
Figure 1(a) shows the infrared spectra of the raw material and Figure 1(b) shows the spectra of the geopolymer it was observed that for the precursor clay the bands at 3400 cm\(^{-1}\) and 3623 cm\(^{-1}\) corresponding to hydroxyl groups, these are within the crystalline network and are responsible for making an exchange when they are in contact with the cations that adsorb. For the geopolymeric material these two peaks are not evidenced due to the temperature used in the synthesis process. Geopolymer has the following bands: 450 cm\(^{-1}\) vibrational interactions Si-O-Si, 1000 cm\(^{-1}\) vibrational plane Si-O, 1462 cm\(^{-1}\) CO\(_3^2-\) carbonate groups, 1661 cm\(^{-1}\) H\(_2\)O crystallized. For the geopolymer after the absorption of ammonium (Figure 1(c)), the following signals were obtained: 450 cm\(^{-1}\) vibrational interactions Si-O-Si, 1000 cm\(^{-1}\) vibrational plane Si-O , 1462 cm\(^{-1}\) CO\(_3^2-\) carbonate groups, these are generated during the geopolymerization reaction, in the synthesis the formation of air bubbles in the material is observed, which try to move towards the surface to leave it, however some of these carbonates remain within the polymer formed 1462 cm\(^{-1}\) CO\(_3^2-\) as seen in the infrared, a peak is observed 1661 cm\(^{-1}\) H\(_2\)O crystallized. It should be noted the appearance of the band at 3350 cm\(^{-1}\) corresponding to the vibration of the NH\(^+\) group within the geopolymeric material that could have been caused by the ionic exchange of the
ammonium ion by the sodium ions present in the geopolymeric material which allows confirming that the geopolymer adsorbed the ammonium cations.

![Figure 1](Image)

**Figure 1.** Infrared spectrum of (a) bentonite, (b) geopolymer, and (c) impregnated geopolymer.

### 3.3. X-ray diffraction characterization of bentonite and geopolymer

Figure 2 shows the diffractograms of the raw material (Figure 2(a)) and the synthesized geopolymer (Figure 2(b)) and the post-impregnation geopolymer (Figure 2(c)). It can be seen that when performing the alkaline activation of bentonite with sodium silicate, it was observed that, in general, most of the phases remain constant, albite (A), quartz (Q), gypsum (Y), kaolinite (C), muscovite (M) and montmorillonite (Mo). An increase in the intensity of the quartz phase to values of 2θ equal to 68° is also recognized, which can be attributed to the presence of the SiO$_2$ crystalline phases of the sand in the geopolymer.

![Figure 2](Image)

**Figure 2.** Diffractograms of (a) bentonite, (b) geopolymer, and (c) impregnated geopolymer.

In the bentonite there are also phases with values of 2θ equal to 9°, 20°, 26°, 36°, 52° and 62° that belong to the muscovite (M), in addition value of 2θ equal to 57° and 44° belonging to microline (Mi) and kaolinite respectively that are not found in the geopolymer, and the appearance of the phases of the albite (A) at 20 values of 30°, 34°, 46°, 55°, which are only in the geopolymer, indicating that when the geopolymerization was carried out there was a change in the crystalline phases of the material, but not
in its composition chemistry, changing the phase from muscovite, kaolinite and microline to albite. This can happen because there is an increase in silica and aluminum in the presence of an alkaline activator, which makes it possible to transform the phases present in the precursor clay, by hydrolysis into the silicon and aluminum atoms that after this, are combined tetrahedrally, forming sialates and sialate octahedra, which in turn causes an increase in peak intensity. The X-ray diffraction pattern of the post-sorption geopolymer (Figure 2(c)) shows that it lacks the gypsum phase (Y) and changes are also observed for the albite phase (A) at values of 2θ equal to 30°, 46°, 54°, indicating that when it is impregnated with the ammonium ion, a change occurs in the crystalline phase, so a reorganization of the crystalline phases is observed when the material is impregnated with the cation.

3.4. Analysis by scanning electron microscope
In Figure 3(a) and Figure 3(b) the micrographs with a magnification of 20000X obtained by SEM can be observed, which allow the morphology of the precursor material (bentonite) to be compared with that of the geopolymeric material obtained. Bentonite exhibits a larger particle size, amorphous crystals and a greater disorder are observed, there are also elongated crystals and to a lesser extent crystal with defined geometry. In the case of geopolymer, there is a type of agglomerates and a greater amorphousness, so, presumably, it allows a greater availability of interstitial spaces in the middle of the structures and a greater number of tetrahedral and octahedral voids, which leads to a better interaction given for the elimination of ions, in this case the ammonium ion. Finally, in Figure 3(c), it is observed that when impregnating the material with the ammonium cation, it loses the amorphousness that it possessed, which is also observed by XRD. This is due to the change in phases that occurs when impregnation occurs, passing from the phases, suggesting that the hydroxyl groups present were fixed by the ammonium ion, demonstrating that the geopolymer not only adsorbs the cation that fills the interstitial spaces, if not also performs an ion exchange that is evident in the phase change of the geopolymer before and after impregnation.

Energy dispersive X-ray spectroscopy (EDS), was carried out for each of the materials in order to obtain data about their chemical composition, for the bentonite these concentration percentages are found in Table 1, once the alkaline activation with silicate is performed of sodium to obtain the geopolymer it is observed that there is an increase in sodium cations 1.68% to 7.99% as observed in Table 2. In the case of oxygen there is a small increase from 52.94% to 54.01%, while for aluminum it found a decrease initially being the concentration of 7.59% and the final of 3.09%, the same happened with the iron that went from 1.72% to 0.88%, respectively, these data show the ionic character of the geopolymer which it allows to "encapsulate" a greater amount of ammonium ions and their corresponding against ion, significantly improving the capacity of sorption with respect to the precursor clay. Table 3 corresponds to the analysis of the impregnated geopolymer, a significant decrease in the sodium element was observed, which increased from 9.27% in the geopolymer to 1.05% in the impregnated geopolymer, which can be attributed to an ionic exchange between the sodium ions of the geopolymer and the ammonium ions of the solution.

Figure 3. SEM micrograph of (a) bentonite, (b) geopolymer, and (c) geopolymer after sorption.
4. Conclusion

The geopolymer synthesized from bentonite, presents a greater amorphousness, favoring the formation of different types of voids, improving the sorption capacity, which in turn presents a greater removal of ammonium ions. When characterizing by IR, XRD and SEM, bentonite and geopolymer show structural differences between the two, evidencing geopolymerization. On the other hand, through the characterization by FTIR, XRD and SEM, it shows the structural and morphological change that the material experiences, obtaining by means of FTIR the peak of the ammonium ion, the structural change when a phase change is observed in the XRD of the geopolymer before and after sorption, and the differences between the two, evidencing geopolymerization. On the other hand, through the characterization by FTIR, XRD and SEM, it shows the structural and morphological change that the material experiences, obtaining by means of FTIR the peak of the ammonium ion, the structural change when a phase change is observed in the XRD of the geopolymer before and after sorption, and the morphological change seen in the SEM and the composition that is evident in the EDS collection.

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