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# Use of Static Method to remove Heavy Metal of the Contaminated Water, using Porous Geopolymer and Magnetically Loaded

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**Abstract:** Due to several catastrophic fires in France involving flammable organic plastics, Davidovits began his search for new materials resistant to heat, developing an alkaline activated silico-aluminous material, which was called a geopolymer. The polymeric Si-O-Al network gives the geopolymer ion exchange property, allowing the immobilization of heavy and radioactive metals within the material matrix. Due to the geopolymer's characteristic of immobilizing heavy metals in its matrix, this project aims to evaluate the geopolymer's ability to absorb heavy metals in contaminated water. For this, samples of porous geopolymers with magnetic charges in concentrations of 1, 2 and 3% were produced. And, subsequently, toxic metal solutions were made, such as Chromium, Cadmium and Lead at a concentration of 3ppm, then the sorption was carried out using the static method, where 0.5 g of the gepopolymer was dispersed in 25 ml of contaminated water and left stirring for 5 minutes, with the aid of a mechanical stirrer, and left to rest for 24 hours for the geopolymer to settle and the supernatant to be collected (this procedure was performed for geopolymers with and without magnetic charges). Afterwards, the treated water was analyzed by the atomic absorption technique, in order to investigate the geopolymer's sorption capacity. All tests were performed in triplicate and the mean, standard deviation and 95% confidence limit were evaluated to determine the reliability of the results.

**Keywords:** Geopolymer, magnetic charge, heavy metals, cádmium, cromium, lead, sorption.

**Adherence to the BJEDIS' scope:** The use of the statistical method used here, was to evaluate the mean values and 95% confidence limits of the data obtained by atomic absorption analysis, which showed the efficiency of heavy metal removal using the geopolymer composites.

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## 1. INTRODUCTION

Heavy metals are highly dangerous contaminants for the environment and human health, and these are presented in solid or liquid form and are present in industrial activities, such as electroplating, textiles and ore extraction industries (1). When in contact with the environment, they cause degradation of the soil, water, and animal mortality. When in contact with humans, they are bioaccumulated and lead to irreversible chronic diseases and even death (2).

In the face of technological and industrial advances, there was an increase in consumption and brought about an increase in production, this activity is of great importance for the growth of the country's economy but must be accompanied by plans to mitigate environmental impacts and solid environmental recovery, which promote the benefit of both the population and the environment (3). But in recent years this has not happened, some large companies have brought great harm to the environment due to the lack of maintenance of their production systems and environmental emergency measures. Then accidents like Brumadinho were seen in 2019, where a dam broke, and left kilometers of degraded areas and the Paraopeba River contaminated with lead and mercury (4). In China, a report published by the China Daily newspaper in 2011, showed cases of inappropriate discharges of heavy metals into rivers, with metals, mercury, lead and cadmium being found (5). A study published by Muhammad and colleagues in 2019, showed that the waters of the Zhob and Loralai rivers exceeded the limit of heavy metals allowed by the World Health Organization, leaving the water unfit for consumption, due to the presence of 71% iron, 76% nickel, 71% cobalt, 57% chromium and 45% cadmium in 1 liter of water (6).

In view of this scenario, environmental remediation techniques are of paramount importance. Currently, the static method is the most used in treatment systems, where river water is collected and taken to the Water Treatment Station (ETA) in this material, such as activated carbon, graphene nanocomposites and starch resins, which are capable of to remove heavy metals, they are agitated in a tank and left to rest for the decanting process to take place. After this period, the treated water is collected (7, 8).

However, the use of these materials is not effective for all types of metal ions and, as a result, they open the door to the study of new materials that can remove heavy metals. Thus, a new class of materials known as geopolymers, has gained prominence in recent decades. Discovered by the French chemist Joseph Davidovits, in his search for flame resistant polymers, this material has been widely studied for several applications and one of them is the ability to adsorb metals with 2+ and 3+ charges (9).

Geopolymers are inorganic polymers made up of a three-dimensional structure of aluminosilicates. They have the capacity to adsorb heavy metals through the alumina ions present in their structure. This material can be shaped in different ways, and its synthesis adjusted to the desired application (10).

The magnetic nanoparticles are produced from the reaction of Fe2 + and Fe3 + in alkaline medium, which are widely used in the sorption of heavy metals. However, its sorption capacity is around 96% for the metals Lead (Pb) and 94% for Cadmium (Cd). Therefore, modifications are made to these nanoparticles so that it is possible to increase the efficiency of removal of these heavy metals, such as, for example, the use of humic acid, the use of hyper-branched polyglycerol and also polytetamethylene terephthalate (11, 12).

In this sense, this work aims to produce geopolymers loaded with magnetic nanoparticles in concentrations 1%, 2% and 3% and to evaluate the adsorption capacity of heavy metals, Chromium, Cadmium and Lead of contaminated water by the method static.

All sorption tests were performed in triplicates and statistical analyzes such as mean and 95% confidence limits were performed. By coupling analytical tests to statistical calculations, it was possible to infer that the adsorption capacity of the geopolymers was 99% and 98% for the metals used here.

## 2. MATERIALS AND METHOD

### 2.1. Production of geopolymers with and without magnetic charges

The production of porous geopolymers with and magnetic charges, took place in two stages:

The first stage consisted in the production of magnetic nanoparticles modified with silica. For this, solutions of iron salts (Ferric Chloride and Ferrous Sulphate) were used in the concentration of 0.46M and alkaline solution (sodium hydroxide) and silica at 4.33 M (the insertion of silica in the nanoparticles was carried out with the objective of promoting geopolymer matrix / magnetic nanoparticles interaction). Thus, the magnetic nanoparticles oxidized and

became maghemite. After the preparation of these solutions, the co-precipitation of these nanoparticles was carried out, which consisted of the reaction between the solution of iron salts and alkaline solution plus silica. The reaction proceeded by means of mechanical stirring at 300 rpm for 2 minutes. At the end of the reaction, the magnetic particles were decanted with the aid of a ferrite magnet (5x5 cm), the supernatant was removed, and the nanoparticles washed 3 times. After washing the particles were dried at 50 ° C in an oven.

The second stage was based on the production of geopolymers without charge and with porous magnetic charges. For the unloaded geopolymer, an alkaline solution containing sodium silicate ($Na_2SiO_4$) and sodium hydroxide (NaOH) with molar ratio $SiO_2$ / $Na_2O$ = 1.6 was prepared under mechanical stirring at 300 rpm. Then, the metakaolin in the molar ratio $Na_2O$ / $Al_2O_3$ = 1 was added to the alkaline solution and left to stir for 10 minutes, after 0.5% w / w of the $H_2O_2$ porosity agent was added and stirring for 2 minutes. After the reaction, the porous geopolymer obtained was taken to the oven and heated to 80 ° C for 2 days for the curing process to take place (3 syntheses were carried out for the geopolymer without magnetic charge) The production of the magnetic geopolymers was carried out in the same way as the unloaded geopolymer. However, before the insertion of the porosity agent, 1%, 2% and 3% w / w of magnetic charges were inserted (3 syntheses were performed for each percentage of magnetic charge).

### 2.2. Prepare of Heavy Metals solution

For the sorption test, 3 heavy metal solutions were prepared at 3 ppm, using MERC standards of 1000 ppm, so 750 µL of the MERC $Cd^{2+}$, $Pb^{2+}$ and $Cr^{3+}$ standard were collected and swelled using a 250mL volumetric flask with 249.25 mL of 1M hydrochloric acid solution.

### 2.3. Sorption Test

The sorption test was performed using the static method, which consisted of using a 50 mL beaker, in which 25 mL of the heavy metal solution were added. For each test, 0.5 g of geopolymer were used with 0%, 1%, 2% and 3%, totaling 4 tests at a time. It was left stirring at 300 rpm for 5 minutes, after the solutions were at rest and the geopolymer was decanted and the supernatant was collected to be analyzed by the atomic absorption equipment. This procedure was performed 3 times, for each metal and geopolymer produced.

### 2.4. Characterization

The samples were characterized before the sorption test by the following techniques.

#### 2.4.1. X-Ray Diffraction

X-ray diffraction tests (XRD) were performed on a Rigaku X-ray diffractometer, model Miniflex. The method used was the FT, in an angular step of 0.05º, in the range of 2θ between 10 ° to 80 °, with acquisition time in each point of 1.0s.

#### 2.4.2. Fourier Transform Infrared Spectroscopy (FTIR)

The spectra of the samples were obtained in FTIR - Nicolet iN10 equipment, using the attenuated total reflection accessory (ATR) equipped with zinc selenide crystal. The parameters used were resolution of 4 cm-1, with background reflection (running without a sample) collected before each sample, in the range of 4000 to 400 cm-1 and the samples analyzed in powder form.

#### 2.4.3. Scanning Electron Microscopy

This technique was used to evaluate the influence of the magnetic charge on the porosity of the geopolymer. Here the amplitude of 2.5k, HV: 15kV was used.

#### 2.4.4. Atomic absorption

This technique was performed using a Varian spectrometer (AAS 240FS, Santa Clara, United States), equipped with deuterium background correction and with a detection limit of Cd - 0.00549 ppm, Cr - 0.0374ppm and Pb - 0.081 ppm.

## 3. RESULTS AND DISCUSSION

From the characterizations performed, it was possible to obtain the following results:

The x-ray analysis showed the formation of the porous geopolymer without magnetic charges, shown in Figure 1 (d), where it was possible to identify the crystalline peaks referring to the main components of the geopolymer formation, these being Sodalite at 17 ° angles, 29 °, 37 ° and 41 ° and Quartz at an angle of 31 °. Then, it was possible to identify the peaks related to composites (magnetically charged geopolymers), presented by Figure 1, letter (a) geopolymer with 3% maghemite, (b) geopolymer with 2% maghemite, (c) geopolymer with 1% of maghemite, which showed the presence of Sodalite in the angles of 17 °, 29 °, 37 ° and 41 ° and Quartz in the angle 31 ° proving the geopolymerization and the angle in 35 ° by the presence of the maghemite. In addition, it was possible to verify that the presence of the magnetic particles modified with silica in the geopolymers decreased the intensity of the peaks, and this indicates that there was an amorphization of the structure, because the greater the amount of silica in the matrix, the more amorphous the geopolymer formed. This factor allowed the formation of a new structure to Faujasite with molecular formula $(Na)_2 (Si, Al)_{12}O_{24}$ $15H_2O$ and angles 6 °, 14 ° and 25 ° (13–15).

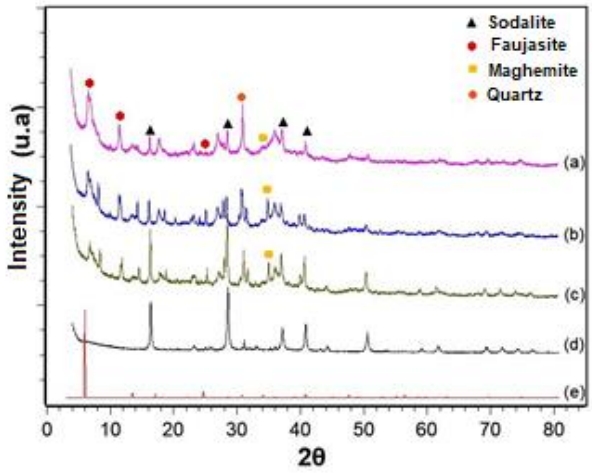


**Figure 1.** X-ray diffraction (a) geopolymer with 3% maghemite; (b) geopolymer with 2% maghemite; (c) geopolymer with 1% maghemite; (d) unloaded geopolymer and (e) faujasita.

Infrared Spectroscopy with Fourier Transform was performed with the objective of verifying the chemical composition of the geopolymers with and without magnetic charges, by identifying the characteristic bands of the material. The results obtained showed bands at 455 $cm^{-1}$ and 559 $cm^{-1}$, referring to the stretching of Fe-O bonds due to the presence of maghemite in the matrix. The band at 657 $cm^{-1}$ showed the vibration of the aluminosilicate groups (Al-O-Si), at 732 cm-1 and 876 $cm^{-1}$ the bands show the vibrations of the AlO4 groups. The bands at 980 $cm^{-1}$ and 1,435 $cm^{-1}$ indicate the stretching of Si-O bonds, at 1650 $cm^{-1}$ and 3,432 $cm^{-1}$, the bands referring to hydroxyls were identified. At 1,407 $cm^{-1}$ it was possible to identify the C-O bond band, that band in particular, appears due to the reaction that occurs between NaOH / $Na_2SiO_4$ with atmospheric $CO_2$ (16–19).

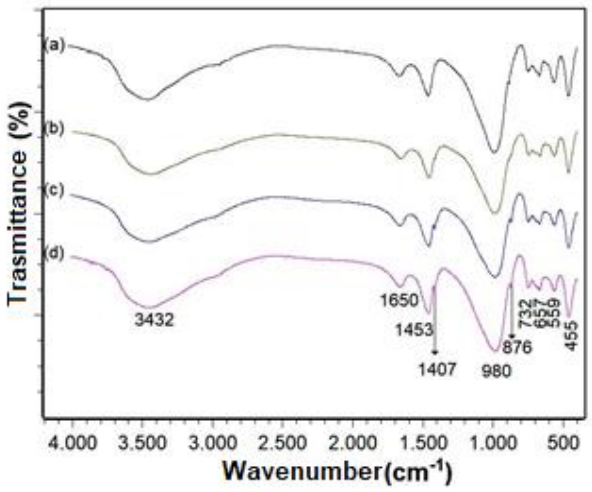

**Figure 2.** Infrared Spectroscopy with Fourier Transform (a) unloaded geopolymer; (b) geopolymer with 1% maghemite; (c) geopolymer with 2% maghemite and (d) geopolymer with 3% maghemite.

The Scanning Electron Microscopy was performed, and by this technique it was possible to verify if the porosity agent was effective in the formation of pores in the geopolymeric matrix and the influence of magnetic charges on the material surface. Thus, the images obtained showed that the porosity agent was effective in the unloaded geopolymeric matrix (Figure 3 (a)) where it is possible to see the pores formed on the surface of the material. However, the sample containing 1% (Figure 3 (b)) of magnetic particles with 200 micrometers in size, showed a surface with less porosity compared to the unloaded one. Geopolymers with 2% and 3% magnetic charge (Figure 3 (c and d)) showed a decrease or almost no pore. This effect indicates that the magnetic particles when in reaction with the geopolymers decrease the porosity, as they occupy the pores of the matrix (20).

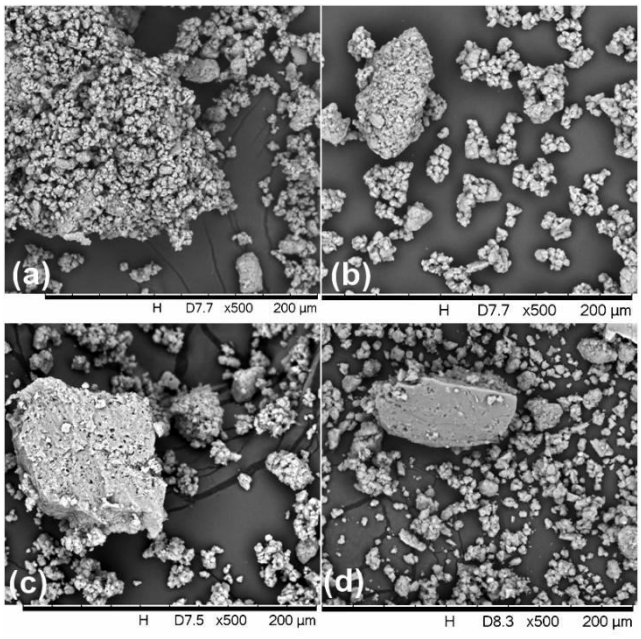


**Figure 3.** Scanning Electron Microscopy (a) unloaded geopolymer; (b) geopolymer with 1% maghemite; (c) geopolymer with 2% maghemite and (d) geopolymer with 3% maghemite.

The analysis by Atomic Absorption was performed to verify the sorption capacity of geopolymers with and without magnetic charges (21). The results obtained showed that all the composites were efficient in removing heavy metals and the confidence limits showed that they all sipped in the same way (Table 1). These results prove that, the insertion of the magnetic particles in the matrix, did not interfere in the sorption capacity of the materials.

**Table 1.** Sorption capacity of geopolymers with and without magnetic charges.

| Geopolymer | 0% | 1% | 2% | 3% |
|---|---|---|---|---|
| Heavy metals | Sorption capability (%) | | | |
| $Cd^{2+}$ | 98±1 | 99±0 | 99±0 | 98±1 |
| $Cr^{3+}$ | 98±0 | 99±0 | 99±0 | 98±0,4 |
| $Pb^{2+}$ | 98±0,36 | 99±0 | 99±0 | 98±0 |

## 4. CONCLUSION

From the results obtained it was possible to conclude that the objectives were achieved. The characterization techniques showed the formation of geopolymers and the presence of magnetic particles in the matrices, proved that the composites were formed. The increase in the amount of silica in the reaction contributed to the formation of a new mineral: Faujasite. The porosity agent was effective in the formation of pores in the geopolymeric matrix

without and with charges, however, the increase of the magnetic particles in the matrix, decreased the porosity, by being inserted in the pores. The results obtained by atomic absorption showed that geopolymers have a high capacity for removing heavy metals, which provides their use for the desired application. It is known that the use of new technologies for water treatment has been sought today, this need opens the way for research as presented here, where it was possible to produce low-cost and highly efficient materials.

**Sample CRediT author statement**

**Fabíola da Silveira Maranhão:** Conceptualization, Methodology, Data analysis, and Writing-Original draft preparation. **Fernando G. de Souza Junior:** Conceptualization, Supervision, Reviewing and Editing. **Bryan Henrique de Oliveira Athayde:** Reviewing, **Ana Ísa Pérez:** Reviewing, **Felipe Ferreira de Carvalho:** Reviewing, **Adan Lino:** Data analyses and Reviewing, **Sérgio Thode Filho:** Conceptualization, Supervision, Reviewing and Editing, **Diganta B. Das:** Reviewing, Editing and Validation.

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