Geopolymeric filter based on metakaolin and rice husk ash for removal of chromium ions

Cinthya Alvarado, MSc[1], María Susana Cavero, Eng[2], Hernán Alvarado-Quintana, PhD[3]
[1]Universidad Privada del Norte, Perú, *cinthya.alvarado@upn.edu.pe*
[2]Universidad Nacional de Trujillo, Perú, susan.0693@gmail.com
[3]Universidad Nacional de Trujillo, Perú, halvarado@unitru.edu.pe

Abstract*– The objective of this research was to determine the influence of the percentage of rice husk ash (CCA) and the concentration of the alkaline activator on the removal of chromium ions from geopolymer filters based on metakaolin (MK), due to the high toxicity generated by the chromium on health and the environment. The geopolymer was prepared by mixing activated rice husk ash at different percentages (0%, 10%, 20%, 30%) with kaolin at different molarities of sodium hydroxide (10M, 12M, 14M); subsequently, spheres of 4 mm in diameter were formed; was placed in the oven at a temperature of 110℃ for 24 hours after 1 day of cooling, the same samples were placed in the oven at a temperature of 900℃ for a time of half an hour to achieve sintering of the geopolymer. The results obtained through the adsorption process indicate that the highest percentage of chromium (VI) removal is achieved when the geopolymer is made up of metakaolin with 30% rice husk ash with an alkaline activator concentration (NaOH) of 14M with a time of 3 hours, being 54.42% the percentage of removal of chromium VI ions. This study concludes that the higher the percentage of CCA and the higher the molarity of the alkaline activator (NaOH), the higher the percentage of removal of chromium ions.

Keywords—geopolymer, metakaolin, adsorption, chromium

I. INTRODUCTION

Over the years, due to increasing industrialization and technological scientific development, different sources of pollution have been generated, which have worsened the health of the planet and that of those who inhabit it. The increasing pollution of urban and industrial wastewater by toxic metal ions causes significant environmental pollution.[1]

In Peru, there are 438 formally registered companies in the leather industry, of which: 30.1% are concentrated in Lima, 29.5% in Arequipa, 24.2% in La Libertad, 3.2% in Cusco, 2.7% in Junín, and 10.3% in the rest of the country. [2]

Various socio-economic activities are developed in the La Libertad region; such as agriculture, commerce, mining, industry, and others. The tanneries are within the industrial category, which are places where tanning is carried out, a process that turns animal skins into leather. In the province of Trujillo there are 140 registered tanneries distributed in the districts of El Porvenir, La Esperanza, Florencia de Mora, Moche, Trujillo, Huanchaco, Laredo and Víctor Larco, where the highest percentage is found in La Esperanza and El Porvenir. [2]

The tanneries in the Porvenir district represent an important part of an industrial sector that is key to regional development; however, these industries are highly polluting due to the discharge into the environment of high contents of organic matter and effluents with sulfur, chloride, and trivalent chromium in concentrations that reach toxic levels.[3]

Of all the pollutants emitted by a tannery, one of the most problematic is chrome. Since chromium (III) tanning salts are usually produced from chromium (VI) salts, it is common for tanning inputs to still contain trace amounts of chromium (VI). This means that the shavings and leather remains that are discarded by the company, as well as the effluents, may contain small concentrations of chromium (VI) in addition to the large concentrations of the primary component of chromium (III).[4]

All chromium species are toxic, but not with the same intensity. Of the two forms of chromium, the more toxic is chromium (VI), as it is capable of causing fatal consequences at concentrations up to 100 times lower than those of chromium (III). Chromium (VI) is on the list of the 129 most critical contaminants. This is considered carcinogenic and mutagenic, it can also cause damage to the kidneys, lungs, skin lacerations, etc. The leather tanning process requires a large amount of water that involves 2 processes: Ribera and tanning, therefore over the years ways have been sought to mitigate this impact, tanneries must comply with the maximum permissible limit of total chromium of 0.5 mg/L and chromium (VI) (unfiltered sample) 0.1 mg/L with pH of 6.5-8.5 but the permissible limits of inorganic and organic chemical parameters of the regulation of the quality of water for human consumption of total chromium is 0.050 mg/L with a pH of 6.5 to 8.5.[5], [6]

Chromium is a dangerous substance that is transported in water and can be absorbed by plants, so its entry into living organisms, not only locally but regionally, occurs mainly through water resources and food. When this substance enters organisms either by ingestion, contact, or inhalation, it generates very harmful genetic, mutagenic and carcinogenic effects. In this way, the high levels of chromium in the wastewater generated in tanneries that implement chrome tanning procedures represent a threat to living organisms.[7]

There are numerous traditional methods such as precipitation, ion exchange, membrane filtration, electrodeposition, and adsorption; they present significant imperfections such as high chemical and energy requirements, formation of dangerous sludge, and high cost on large scales, the variable options are the use of agricultural by-products and clays; such as rice husk ash and metakaolin.[8], [9]

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Rice husk is a lignocellulosic plant tissue made up of 85% organic material, represented by cellulose, lignin, D-xylose, and small amounts of D-galactose[2]. When rice husk is subjected to high temperatures, it produces ash between 13 and 29% of the initial weight, consisting mainly of silica between 87 and 97% because it does not dissociate when burned, and small amounts of inorganic salts, which is why it is used for ash with a decontamination alternative since, thanks to its physicochemical characteristics, it promises to be a good heavy metal adsorbent.[1]

Metakaolin is an activated silica-aluminous material that is obtained by calcining at 650 - 800°C a clay called kaolin, from the dehydroxylation of kaolin, which is a very pure white clay produced by the calcination of pure kaolinite (Al_2O_3. $2SiO_2.2H_2O$), in a controlled temperature range that allows its dehydroxylation and, therefore, the obtaining of a product with a high amorphousness.[8], [9]

This research is focused on the study of the use of new materials such as rice husk ash and metakaolin for the removal of chromium (VI) from industrial effluents as a process to mitigate the impact on the environment, reducing the percentage of chromium (VI) in wastewater. from the tanning stage through the formation of thermally treated geopolymer grains to obtain reusable water that is within the maximum permissible limits.[6], [10]

Reference [8] investigated the replacement of metakaolin (MK) with rice husk ash (RHA) in the production of alkali-activated binders or geopolymers. The influence of RHA addition on compression and flexural strength, as well as the water absorption and the apparent porosity, were determined in terms of the percentage of RHA in the mixture and the molar proportions of the mixtures. Changes in the microstructure of geopolymer matrices with the addition of RHA.

Reference [11] synthesized a highly amorphous geopolymer from residual coal fly ash to be used as an adsorbent for Pb(II) removal from wastewater. The effect of various parameters including geopolymer dosage, initial concentration, contact time, pH, and temperature on lead adsorption was investigated. The main components of the ash used in the present study were SiO_2, Al_2O_3, and Fe_2O_3, which represent 91.53% by weight of its mass. The synthesized geopolymer was found to have a higher lead ion removal capacity compared to raw coal fly ash. The removal efficiency increases with increasing geopolymer dose, contact time, temperature, and decreasing initial Pb (II) concentration. The optimal removal efficiency was obtained at pH 5. The adsorption isotherm study indicated that the Langmuir isotherm model is more suitable for the experimental data than the Freundlich model. It was also found that the adsorption process is endothermic and more favorable at higher temperatures.

Geopolymers are obtained from the mixture in optimal proportions of a mineral-based on SiO_2 and Al_2O_3 (precursor) with a chemical agent (alkaline activator), which promotes a series of reactions that lead to the formation of a product with cementitious characteristics. One of the widely used precursors in this type of technology is heat-treated kaolinitic clays, which have a high reactivity as a consequence of their vitreous nature [12]–[14].

They are alkaline aluminosilicates that form tetrahedral units, through random bonds formed thanks to silicon and aluminum, and hydrated alkaline cations such as K^+ or Na^+ located in the holes [15]–[17]. Alkali activation (or geopolymer) technology is an important tool in promoting the circular economy, as it is a method to convert many inorganic wastes into useful products [18], [19].

II. MATERIAL AND METHODS

A. *Material*

The raw materials used in the investigation were: Rice husk from the Huanchaco mill - Trujillo - Peru. White kaolin (trilaminar clay) from Huamachuco, Sánchez Carrión, La Libertad – Peru.

The materials selected as raw material were characterized, as they were acquired, for which the following tests were carried out: Granulometric analysis by hydrometry, the specific gravity of the solids, liquid limit (LL), and plastic limit (LP). Likewise, a dilatometry test was carried out to determine the maximum temperature at which the kaolin should be worked, before its vitrification. Differential thermal analysis (DTA) was also carried out to determine the activation temperature of the kaolin and thermal gravimetric analysis (TG) to determine the amount in grams that are lost in calcination. Finally, scanning electron microscopy (SEM) was performed to determine its microstructure.

B. *Experimental procedure*

The different molarities (10M, 12M, and 14M) were prepared; for 14M with 56 g of NaOH, 12M with 48 g of NaOH, and 10M with 40 g of NaOH, the different molarities were mixed each in 100 ml of distilled water and placed on the magnetic stirrer until completely diluted.

The unburned rice husk was washed to remove all impurities, then it was dried at room temperature, and then burned in an oven at a temperature of 700 °C for 6 hours, then the material was removed to grind it in a grinding mill. balls for a time of 4 hours.

The calcination of the kaolin to transform it to the metastable state was carried out at around 682°C in the electric furnace for 2 hours, according to the results obtained from the DTA.

Rice husk ash (CCA) and metakaolin with NaOH activator (10M, 12M, and 14M) were mixed manually after obtaining a workable mass, and spheres with an approximate diameter of 4mm were formed (Figure 1) for each molarity and each percentage of rice husk ash (0%, 10%, 20%, 30%), then each sample was placed in different containers to be distinguished, it was placed in the oven at a temperature of 110 ° C for 24 hours after 1 day of cooling, the same samples were placed in the oven at a temperature of 900 ° C for a time of half an hour to achieve sintering.

Finally, to carry out the chromium ion removal test, a recirculation circuit was used with an 8W non-submersible pump with a capacity of 50 L/h, which was coupled to a PVC piping system. The percentage of chromium (VI) removed could be measured with a high-performance double beam T80 UV-Visible spectrophotometer with a wavelength of 540nm.

Fig. 1 Geopolymer filters based on rice husk ash and metakaolin with a size of 4 mm.

III. RESULTS

A. Characterization of raw materials

The characterization was carried out to determine the characteristics that the clays have, in their natural state, and to know at what temperature the calcination can be carried out.

In Figure 2, the differential thermal analysis (DTA) is shown, which shows four endothermic peaks. In the DTA curve, it is observed that there is no pronounced phase change, that is, only a partial phase change since the peaks are not pronounced, compared to the first peak, which indicates the loss of water.

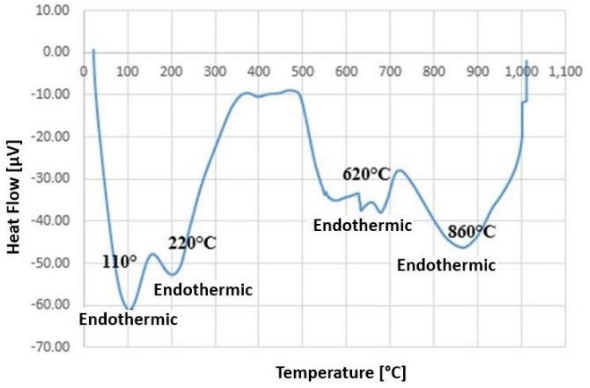

Fig. 2 Differential thermal analysis (DTA) of kaolin, sieved at 200 mesh.

The DTA curve records the heat absorbed (endothermic), as the temperature increases, in said curve four predominant peaks are observed, the first of these approximately at 110°C, to which the loss of adsorbed water is attributed; the second is around 220°C, which is due to decomposition of organic matter or adsorbed water and interlaminar water. Subsequently, an important predominant endothermic peak is shown at 620°C, announcing a possible phase transition, which corresponds to the decomposition of the mineral and the elimination of the hydroxyl groups as water, in other words, at this temperature the chemical water present is eliminated. in the sample, and finally the last endothermic peak at 860°C. In other words, this analysis is shows us an endothermic peak between 520 °C and 680 °C, characteristic of kaolinite decomposition and chemical water loss, combined as follows:

$$3(Al_2O_3.2SiO_2.2H_2O) \rightarrow 3(Al_2O_3.2SiO_2) + 6\ H_2O \qquad (1)$$

Figure 3 shows the thermogravimetric analysis (TG) of kaolin, which shows a constant mass loss, from approximately 27.50 grams to a value of 24 grams. In addition, an endothermic peak at 520°C and 820°C can be observed.

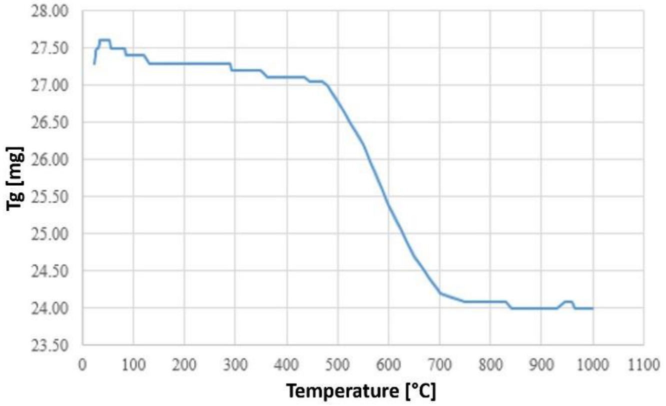

Fig. 3 Thermal gravimetric analysis (TG) of kaolin, sieved at 200 mesh.

For the characterization of the rice husk ash, a dry rice husk sample was taken and taken to the laboratory to obtain its calcination temperature.

Figure 4 presents the DTA thermal analysis, which shows four endothermic peaks. In the DTA curve, it is observed that there is no pronounced phase change, that is, only a partial phase change since the peaks are not pronounced, compared to the first peak, which indicates the loss of water.

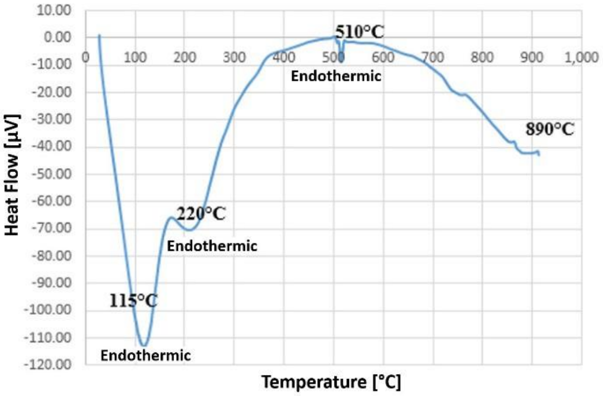

Fig. 4 Differential thermal analysis (DTA) of rice husk ash.

Figure 4 shows two endothermic peaks around 115°C and 220°C, later a slight peak of thermal absorption at 510°C is shown, which is a temperature of structural change and the characteristics of the material.

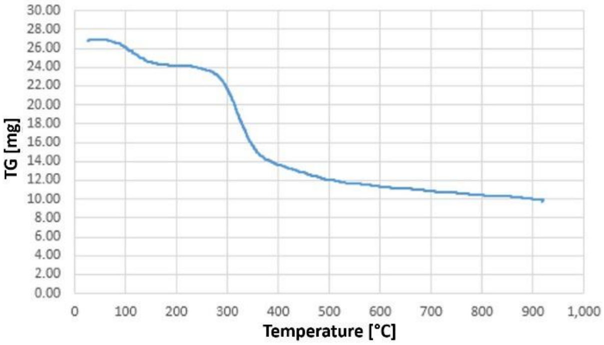

Fig. 5 Thermal gravimetric analysis (TG) of rice husk,

Figure 5 shows two falls of the mass, the first occurs in the range between 30°C and 170°C where we find a weight loss of the sample, and the second occurs between 250°C and 370°C where it occurs. the loss of CO_2, subsequently the fall is gradual and slow until it loses a total of 49% of its initial mass approximately when its maximum test temperature has been reached.

Dilatometry is the most suitable technique to reveal the thermal behavior of kaolin. Figure 6 shows the optimum calcination temperature.

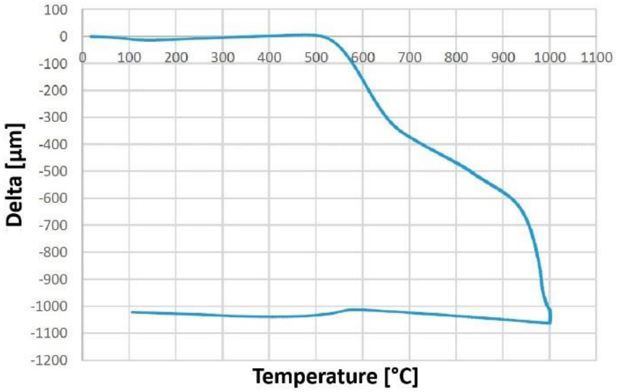

Fig. 6 Kaolin dilatometry, sieved in #200 mesh.

Figure 6 shows the contraction stage that starts from room temperature to approximately 500°C, due to the loss of water from the sample, from 650°C to 800°C of temperature a transformation of its crystalline structure by breaking the Van der Waals bonds (OH^-) that join the silica tetrahedrons, SiO_2, and the alumina octahedra, Al_2O_3, that is, by losing the combined water due to thermal action, the crystalline structure of kaolin is destroyed.

B. *Chrome removal results*

Figure 7 and Figure 8 represent the microstructure of geopolymers based on metakaolin and CCA activated with NaOH. at 14M it presents a greater quantity of aluminosilicate crystals.

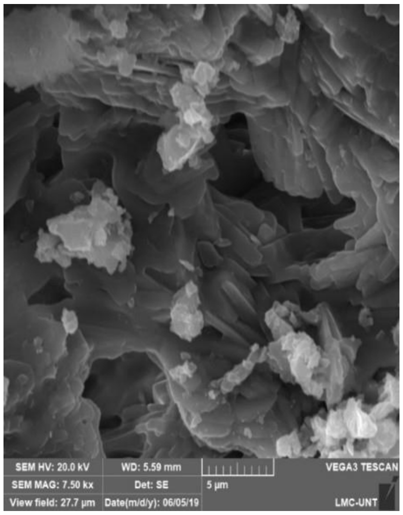

Fig. 7 SEM micrographs at 30% CCA with activation at 12M NaOH

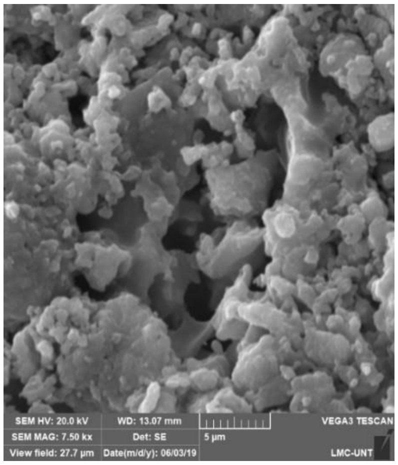

Fig. 8 SEM micrographs at 30% CCA with activation at 14M NaOH

The porosity in the geopolymer is not homogeneous, as can be seen in both figures; this is reflected in figure 9, the values of the 30% CCA geopolymers with 14 M NaOH activation are higher than when it is activated at 12 M NaOH, it can be verified that the amount of aluminosilicate crystals is greater at 30% CCA with 14M NaOH activation; This proves that the greater the molar activation, the greater the adsorption. This is due to the ionic exchange between the anions $HCrO_4^-$ and CrO_4^{2-}, Being negatively charged compounds, where the surface of the adsorbent geopolymer has a positive charge, this corroborates what was said by reference [20], Na^+ counteracts the negative charge formed by AlO_4. The geopolymers produced are composed of SiO_2, Al_2O_3, and Fe_2O_3 mainly, kaolin contains 51.5% SiO_2, 49.5% Al_2O_3, and 0.5% Fe_2O_3 while CCA contains 98.0% SiO_2 and 0.5% Al_2O_3, these compounds play a fundamental role in the adsorption of chromium as shown in references [21]–[23] where the adsorption of chromium with CCA is greater than 73% while in the reference [24], shows the chromium adsorption with kaolin is 16% and metakaolin has an adsorption capacity of 19.9 mg/g, this justifies the result obtained by the geopolymers with maximum chromium adsorption of 54.42% and a minimum of 47.64%, in addition to being negatively or positively charged the geopolymer depends on the pH of the solution, the solution has an initial pH equal to 5, therefore the charge of the adsorbent elements is positive, these are responsible for the adsorption of chromium in the solution, especially rust or iron and alumina, which will have a highly positive surface.

In figure 9, the percentage of CCA vs. the percentage of removal of chromium (VI) at different molarities of NaOH (10M, 12M, and 14M) is represented, resulting in a curve of greater adsorption at 14M; It is observed that the activation of the geopolymer with 14M NaOH has a chromium (VI) removal percentage with a minimum of 48.49 and a maximum of 54.42%, the geopolymer activated with 12M NaOH has a chromium (VI) removal percentage of 49.46% and the geopolymer activated with 10 M NaOH has a chromium (VI) removal percentage of 47.64%, the geopolymer activated with 12 M NaOH allows adsorption of chromium (VI) greater than the activation with 10 M NaOH; the lowest adsorption of chromium (VI) occurred when the activation of the geopolymer is at 10 M NaOH. The chromium adsorption capacity of the geopolymer is related to the porosity, contact surface, and amount of filter material.

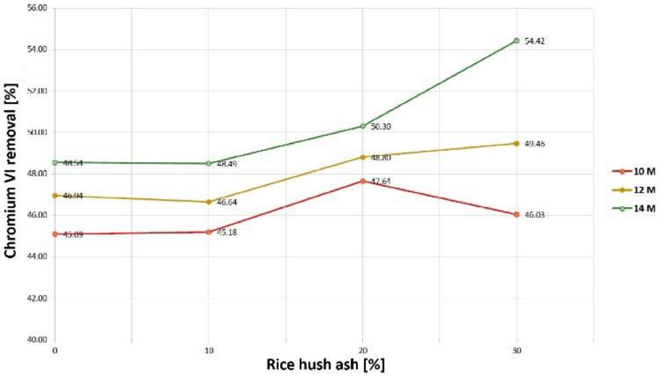

Fig. 9 Chromium (VI) removal as a function of RHA percentage

Both the original pH of the potassium dichromate solution of the mother solution was measured with a value of 5, and the pH value after finishing the adsorption tests, giving higher pH values those activated with 14M sodium hydroxide having a higher pH value at 7.72 and lower pH value at 7.44; for geopolymers activated with 12 M NaOH, they have a maximum pH value of 7.47 and a minimum pH value of 7.34, in addition to lower pH values than those activated with 10 M NaOH, having a maximum pH value of 7.40 and a lower pH value 7.14. This shows that the higher the removal percentage, the higher the pH value, respectively. This affects the surface charge of the fly ash, due to the increase in the initial pH of 5, which contains predominantly $HCrO^{4-}$, which produces a change in the chromium species to CrO_4^{-2}, which is present at pH values greater than 6.5. The results obtained here have the same trend as the reference [24]. Where the percentage of removal is directly influenced by the pH of the solution, as the percentage of removal of chromium (VI) ions increases, the pH of the solution also increases for the different molarities of activation; at higher solution pH (effluents) the adsorption process is more difficult due to the charges present in the geopolymer (CrO_4^{-2}) due to changes in pH and elements on the surface reduces the negative zones in the geopolymer.

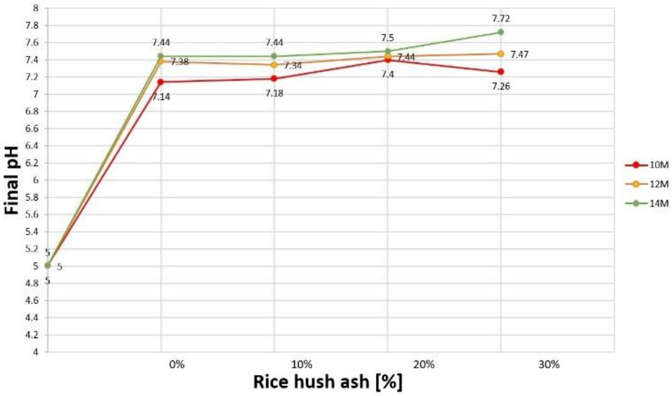

Fig. 10 Final pH as a function of RHA percentage

IV. CONCLUSION

The addition of rice husk ash greatly increased the adsorption on the removal of chromium (VI) ions from metakaolin-based geopolymeric filters. The optimal conditions for geopolymeric filters based on binary mixtures (metakaolin + rice husk ash) alkali-activated with NaOH at different molarities were developed. It was determined that the best chromium (VI) ion adsorption capacity is at 30% addition of rice husk with a molarity of activation with sodium hydroxide is at 14M, giving an adsorption result of 54.42% removal. The influence of the molarity of the activator (sodium hydroxide) plays an important role because it generates a high efficiency in the conversion of the solid material to form a network of polysisialates.

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