Effects of synthesis conditions on sorption capacity methylene blue of coal gangue based geopolymer

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Abstract. In this work, coal gangue from the department of Cesar, Colombia, was used in the synthesis of a geopolymer by alkaline activation. The effect of the variation of the geopolymerization temperature and of four parameters on the composition of the activating solution was evaluated: SiO$_2$/Al$_2$O$_3$, SiO$_2$/Na$_2$O, NaOH concentration and amount of H$_2$O$_2$. The geopolymer was characterized structurally by X-Ray diffraction and Fourier transform infrared spectroscopy. The sorption properties of methylene blue in aqueous solutions of geopolymer were studied through ultraviolet-visible spectrophotometry. Effects of various parameters such as pH value, geopolymer dose and initial concentration on the sorption capacity were studied. The adsorption kinetics and adsorption isotherm fitted well with the pseudo-second order model and Langmuir model, respectively. In the kinetic study it was evidenced that the adsorption equilibrium time was reached quickly, therefore this material constitutes a viable alternative for water decontamination.

1. Introduction

Dyes are substances widely used industrially for their ability to impart color, however, after the colouring processes, are discharged as effluent into the water sources, one of the industries that generates the greatest pollution of dyes is the textile industry [1]. The presence of this type of substance in the water causes a decrease in photosynthetic activity, causing serious ecological damage and the most alarming thing is that most of the colorants are carcinogenic and mutagenic for both animals and human beings [2].

Multiple strategies have been designed for the removal of dyes, mainly due to the worldwide need for drinking water and the high resistance of dyes to degradation [3,4]. In recent years, new emerging materials have been studied for environmental remediation. Geopolymers are materials with excellent mechanical properties, low-manufacturing costs and allow the use of industrial waste as raw material. These materials, besides exhibiting good properties as Pozzolanic materials [5], have also been studied as sorbent materials for water decontamination [6].

The process of geopolymerization by alkaline activation can be described mainly in the following steps: (1) dissolution of the aluminosilicate source, (2) speciation and equilibrium of aluminate and silicate, (3) gelification, (4) reorganization, and (5) polymerization and hardening [7]. The study of the effect of the composition and conditions of geopolymer synthesis have been studied for different applications [8-10] because in the alkaline activation of aluminosilicate materials, the nature of the activating solution is very important since the composition of the alkali activating solution is vital to
dissolve the Si and Al atoms to form precursors of geopolymerization and affects microstructure and material properties [11].

In this work, coal gangue (CG), a waste material generated during coal extraction processes that presents potential hazards, was used to synthesize a geopolymer (GP) by alkaline activation. Coal gangue geopolymer (CGGP) synthesis, its use in the removal of methylene blue (MB) and the study of its sorption process, is an important contribution in the search for efficient and environmentally friendly methods for water decontamination and represents an interesting alternative, viable for its high percentages of removal in short periods of time and use of a by-product produced in large quantities in the coal industry.

2. Methods

2.1. Synthesis of coal gangue geopolymer

For the determination of the effect of the synthesis conditions on the MB sorption capacity of the CGGP, two values were used for each of the variables to be studied: geopolymerization temperatures of 70 °C and 90 °C, SiO$_2$/Al$_2$O$_3$ ratio of 3.3 and 4.5, SiO$_2$/Na$_2$O ratio of 1.7 and 2.0, NaOH 8 M and 12 M, and amount of H$_2$O of 0 and 1.5 mL. Thus, 32 specimens were synthesized, each with different synthesis conditions using the established values. Initially, calcined (700 °C for 10 hours) and milled (125 μm) CG was mechanically mixed with Al$_2$O$_3$ (99%; Merck), then the activating solution of NaOH and sodium silicate (99%; Merck, %Na$_2$O = 13.3, %SiO$_2$ = 27) was added and mixed quickly. Once homogeneity was achieved in the mixture, it was deposited in metal molds and cured for 31 hours at the designated temperature. Finally, it was removed from the mold, milled into fine powder (125 μm) and stored at room temperature for further characterization and sorption tests.

2.2. Methylene blue removal study

Studies on removal of MB were carried out with ultraviolet-visible spectrophotometry (UV-VIS) using QLS UV5800 PC instrument, the concentration of MB remaining in solution was determined at λ = 664 nm. Batch sorption experiments to determine the best synthesis conditions were performed at room temperature, 25 mL of AM solution of known concentration (25 ppm) prepared from the solid MB (99%; Merck) were taken and 0.05 g of CGGP powder (125 mM) was added, the mixture was shaken at 200 rpm for 24 hours. Finally, the CGGP was separated from the solution and the amount of dye remaining was quantified. The MB sorption capacity (q$_t$) of the CGGP was calculated using Equation (1) [4], where C$_0$ (mg/L) was the initial concentration MB, C$_t$ (mg/L) was the concentration of MB at time t, V (L) was the volume of MB solution and m (g) was the dosage of GPCG.

$$ q_t (\text{mg/g}) = \frac{V(C_0 - C_t)}{m} $$ (1)

2.2.1. Effects of some parameters on methylene blue sorption. The effect of pH, adsorbent dose and initial concentration of MB was studied by varying these parameters for two of the synthesized CGGP: one of them with the highest qt and the other one with opposite synthesis conditions for comparison (see Table 1). The effect of pH was studied on 25 mL of 25 ppm MB solution with 0.05 g of CGGP, then pH was adjusted from 2 to 13 using NaOH and HCl solutions. The effect of the initial MB concentration was studied with solutions of different concentrations (5 ppm to 50 ppm), 0.05 g of CGGP was added in 25 mL of these solutions. Finally, to study the effect of CGGP dosage on MB sorption, 0.01 g - 0.2 g CGGP were added to 25 mL of 25 ppm solution of MB. A contact time of 12 hours at room temperature was used in all these tests.

2.2.2. Adsorption kinetics. For the determination of adsorption kinetics, 0.15 g of CGGP was added to 200 mL of MB solution of initial concentration of 40 ppm. Aliquots of 13 ml were taken at different
times, the UV-VIS analysis was performed for the MB quantification. Data were adjusted to the pseudo first order and pseudo second order kinetic models and the isothermal models of Langmuir and Flory-Huggins.

2.3. Characterization

FTIR measurements of the CGGP, CGGP after sorption and calcined CG were carried out with Bruker Tensor 2 spectrometer in attenuated total reflectance mode in the wavenumber range of 400 cm\(^{-1}\) - 4000 cm\(^{-1}\) and 32 scans. The Bruker D8 Advance diffractometer with DaVinci Geometry (40 kV, 40 mA, Cu Ka \(\lambda = 1.5406 \text{ Å}\)) was used to obtain information about the mineralogical composition of the CG, CGGP and CGGP after of sorption.

3. Results and discussion

Statistically it was not established that a variable or its combination significantly affects the response variable (qt) in the range studied, all the CGGP obtained had a very similar qt value (11.90 mg/g - 12.34 mg/g). However, a structural study and sorption tests were performed with the CGGP with the highest qt obtained, coal gangue geopolymer (GPCG 1), and a second material, coal gangue geopolymer (GPCG 2), whose synthesis conditions differed in the synthesis parameters, to evaluate its behavior (qt) with respect to variations in pH, the dose of CGGP and the concentration of the initial MB solution. Table 1 shows the synthesis conditions of the two materials.

|          | SiO\(_2\)/Al\(_2\)O\(_3\) | SiO\(_2\)/Na\(_2\)O | NaOH (M) | H\(_2\)O\(_2\) (mL) | Temperature (°C) | qt (mg/g) |
|----------|--------------------------|---------------------|----------|---------------------|-----------------|-----------|
| GPCG 1   | 3.3                      | 2.0                 | 12       | 0.15                | 90              | 12.34     |
| GPCG 2   | 4.5                      | 1.7                 | 8        | 0.0                 | 90              | 12.27     |

3.1. Structural characterization

Figure 1 shows the diffractograms corresponding to the precursor of geopolymerization (coal gangue), GPCG 1 and GPCG 2. Using the International Diffraction Data Centre (ICDD) PDF 4+ database [12], presence of seven crystallographic phases was identified: quartz #PDF 01-089-1961, muscovite #PDF 01-073-9857, phengite #PDF 04-013-6129, albite # PDF 01-084-0752, microcline #PDF 00-001-0705, hematite #PDF 00-033-0664, anatase #PDF 00-021-1272.

Figure 1. X-ray diffraction pattern of CG.

On all diffractograms, similar crystallographic phases are observed with variations in their intensity, with quartz peaks being the main and most intense. The presence of quartz, phengite and muscovite makes CG an excellent source of aluminosilicates for geopolymerization. When comparing the XRD pattern of GPCG 1 and GCGP 2 with that of the CG, a decrease in the intensity of the peaks corresponding to phases such as phengite, muscovite, microcline and albite is observed, this decrease is
attributable to the dissolution of these phases in the geopolymerization process. However, other characteristic peaks of CG remaining in the XRD patterns of the geopolymers, did not decrease in intensity compared to the XRD patterns of the GC, demonstrating that some crystalline phases of CG do not participate in the geopolymerization process and act as internal fillers in the geopolymer structure [13]. By observing the diffraction pattern of GPCG 1 and GPCG 2 it is not possible to establish considerable differences in their structure. Figure 2 shows the diffraction pattern of the geopolymer before and after contacting an AM solution: GPCG 1 and GPCG-ABS, respectively. No shift change of intensity or disappearance of the peaks was observed, this suggests that the CGGP does not change its structure after sorption and exhibits the stability of the material for its applicability in this type of process.

![Figure 2. X-ray diffraction pattern of CGGP.](image)

Infrared spectra shown in Figure 3, corresponds to the calcined CG, the geopolymer synthesized before (GPCG 1) and after the sorption of MB (GPCG 1-ABS). The FTIR spectrum of the calcined CG, reveals presence of characteristic bands of this type of material. The band at 987 cm$^{-1}$ is attributed to the symmetric stretching vibration of Si–O–Si. The band approximately at 679 cm$^{-1}$ is the stretching vibration mode of Si–O–Al, the band at 543 cm$^{-1}$ correspond to the bending vibration mode of Si-O-Al, the band at 466 cm$^{-1}$ is attributed to O-Si-O bending vibration and the double band around of at 750 cm$^{-1}$ is attributed to stretching vibration of Si-O-T, where T can be Al or Si.

![Figure 3. FTIR spectrum of CG, GPCG 1 and GPCG-ABS.](image)

In the spectrum corresponding to GPCG 1, absorption bands similar to those of its precursor (CG) are evidenced with small shifts towards smaller wavelengths, a fact that is interpreted as evidence of geopolymerization where the angle and length of the Si-O-Si and Si-O-Al bonds change. Absorption band present in 1400 cm$^{-1}$ is attributed to the stretching vibration of the O-C-O, product of atmospheric
carbonation and the band in the region of 3250 cm\(^{-1}\) corresponds to the water remaining in the material after the geopolymerization process. [14]. The spectrum taken from the geopolymer after the sorption of AM, does not allow elucidating a structural change of the material, the same bands of absorption are observed, disappearing only that caused by carbonation.

3.2. Effect of pH, adsorbent dosage and initial concentration of methylene blue

The effect of pH variation in the range 2 to 13 on the sorption of MB, a basic (cationic) dye, has been studied. The functional oxygen groups on the surface of the geopolymer appear to play an important role in the dye adsorption process [6]. As the pH of the dye solution increased, the association of MB cations with the most negatively charged site could easily occur, which increased their removal.

In Figure 4(a), the two geopolymers exhibited the same trend, the lowest sorption was found at pH 2, for the other pH values higher qt values were obtained, with the GPCG1 showing higher sorption in all cases. Figure 4(b) shows the effect of the CGGP dose on the qt of MB. The highest value for qt was obtained by using the least amount of CGGP (0.01 g). An increase in the amount of CGGP added in the sorption test, causes a decrease in its qt, this is attributable to a phenomenon of unsaturation that occurs in the material. qt is a parameter related to the amount of MB sipped per unit of sorbent mass, increasing the amount of CGGP also increases the number of sites available to be active sites, generating an unsaturation in the sorption sites [15]. Figure 4(c) shows the variation in sorption capacity due to the effect of the initial concentration of MB solution in the range of 5 ppm to 50 ppm. Sorption capacity generally depends on the relationship between the initial dye concentration and the available sites on an adsorbent surface [16], the increase in qt as the concentration of MB increases leads to the conclusion that the CGGP adsorption sites are not saturated. Even using a solution of 50 ppm MB, pores are still available in the material and therefore the sorption capacity is increasing.

Figure 4. (a) Effect of pH on the qt of MB. (b) Effect of the CGGP dosage on the qt of MB, and (c) the effect of initial concentration on the qt of MB.

3.3. Adsorption kinetics

The test developed to determine quantitatively the MB removal by CGGP is shown in Figure 5, where the variation of the qt of GPCG 1 is observed when the contact time with the solution increases, from this information the kinetic study was carried out.

Figure 5. Effect of contact time on the qt of MB.
Adsorption kinetics test was only performed for GPCG 1 because this was the material with the best sorption. It can be observed that the qt variation begins to be almost constant from approximately 120 minutes of contact, which allows to infer that the adsorption equilibrium time is reached quickly. The parameters of the kinetic models were determined from experimental data with the help of linear curve fitting. Pseudo-first and pseudo-second order models were evaluated for the adsorption kinetic study and the Langmuir and Flory-Huggins isotherms were employed for the adsorption equilibrium study. To establish the fit with the pseudo-first order model, ln (qₚ - qₜ) vs t was plotted, from the slope and intersection of the curve it was determined the value of Kₚ and qₑ (see Table 2). In Equation (2), the mathematical expression that governs this model is shown, where qₑ is the capacity of sorption in equilibrium (mg/g), Kₚ the constant of pseudo first order of the model (min⁻¹) and t is time. Likewise, the value of qₑ and the change constant for the pseudo-second order model (Kₛ) were determined and its adjustment of the experimental data was evaluated by graphing t/qₑ vs t (see Table 2), in Equation (3) is shown the mathematical expression that describes this model, where qₑ also represents the capacity of sorption in equilibrium [16]. These results have shown that the experimental data do not match the pseudo-first-order kinetic model; they fit better with the pseudo-second-order model.

\[
\log \log \left(\frac{q_e - q_t}{q_e}\right) = \log(q_e) - \frac{k_p}{2.303}t
\]  

\[
\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e}t
\]

The isothermal model of Flory-Huggins is described by the expression of Equation (4). To evaluate the fit of experimental data with this model, log (θ / Cₒ) vs log (1 - θ) was plotted, where theta indicates the degree of coverage of the surface of the adsorbent (θ = 1 - Cₑ/Cₒ) [17]. To determine the adsorption isotherms of Langmuir, Cₑ/qₑ vs Cₑ was plotted. In general, the Langmuir model shapes the adsorption process using the expression shown in Equation (5), where qₑ is the amount of MB adsorbed on the CGGP surface at equilibrium, Cₑ is the MB equilibrium concentration (mg/L), Kᵢ is the Langmuir adsorption constant, and qₑ is the maximum adsorption capacity of the adsorbent (mg/g). Table 2 shows the value of the parameters obtained for each of the isotherms.

\[
\log \log \left(\frac{\theta}{C_o}\right) = \log K_{FH} - n_{FH} \ast \log (1 - \theta)
\]

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

Langmuir's model presented the best fit to experimental data, this model assumes that adsorption occurs on a homogeneous adsorbent surface, furthermore it is assumed that only a monolayer surface coverage is produced, all surface sites are equivalent, and the adsorbed molecules are immobile [18]. The adjustment of the data suggests that it is a chemisorption, attributed to the active sites generated by the negative aluminum on the surface of the material and the cationic nature of the MB.

| Table 2. Parameters determined for the kinetic models evaluated for GPCG 1. |
|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| **Model**         | **R²**            | **qₑ** (mg/g)    | **Kᵢ** (g/mg*min) | **Kₛ** (g/mg*min) | **Kₑ** (L/mg)    | **nₑ** (L/mg)     | **Kₘ** (L/mg)     | **qₑ** (mg/g)    |
| Pseudo first order| 0.812             | 20.77            | 0.095             | -                 | -                 | -                 | -                 | -                 |
| Pseudo second order| 0.997             | 49.75            | -                 | 0.005             | -                 | -                 | -                 | -                 |
| Flory-Huggins isotherm | 0.897             | -                | -                 | -                 | 5.171             | 0.224             | -                 | -                 |
| Langmuir isotherm  | 0.995             | -                | -                 | -                 | -                 | -                 | 1.343             | 25.51             |
4. Conclusions
The coal gangue based geopolymer synthesized by alkaline activation was investigated as a low cost and readily available absorbent for the removal of methylene blue from aqueous solutions. No noticeable improvement in the sorption capacity of the geopolymer was observed due to variation in the composition of the activating solution and temperature in the range studied. The increase in pH and initial dye concentration indicated a positive effect on removal efficiency, while negative effects on sorption capacity were noted when geopolymer dosage were increased. Experimental results obtained were better adjusted to the isotherm of Langmuir. Pseudo-second order kinetic model was better adjusted to the kinetics obtained. It was evidenced that the coal gangue based geopolymer can be exploited as a promising low-cost absorbent for the removal of methylene blue, especially for its high sorption capacity in periods of time less than 2 hours.

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