Evaluation of the methyl violet sorption capacity in waters with a bentonite based geopolymer material

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Abstract. In this study, bentonite geopolymer was used as a sorbent to remove methyl violet in aqueous solutions. Several parameters such as pH, sorbent dose and initial sorbate concentration were evaluated. The greater sorption effectiveness of bentonite geopolymer is observed at pH 2-3, and the greater sorption capacity of methyl violet by bentonite geopolymer occurs when the sorbent/sorbate ratio decreases. The study of sorption kinetics showed that the data fit the pseudo-second order model, where much of the sorption occurs during the first hour of contact, it was shown that the process prefers diffusion between pores. Sorption was adjusted to the isotherm of Langmuir, which indicated that the sorption is preferentially in monolayer. Bentonite geopolymer proved to be an excellent candidate for removal of methyl violet in aqueous bodies.

1. Introduction

Environmental pollution is one of the biggest problems facing the world today and is increasing as the years go by. Industrial discharges into water sources are one of the world's most damaging and alarming problems: they cause further ecological degradation and a greater impact on human health [1]. The World Bank estimates that 17-20% of industrial water pollution comes from dyeing and textile treatment, identifying 72 toxic products, 30 of which cannot be eliminated [2]. Most synthetic dyes are chromophore organic structures, to which toxic and carcinogenic properties are attributed [3]. In addition, dyes may affect photosynthetic activity in aquatic life due to decreased light penetration [4].

Bentonite is the product of devitrification, hydration and hydrolysis of the vitreous phase of certain lavas, ashes and tuff, for this reason it is composed mainly of montmorillonite, a mineral of the silicate group; as well as crystalline forms of quartz and different mineralogical phases of aluminosilicates [5]. These structural and compositional characteristics promote it as an excellent precursor for bentonite-based geopolymers. Bentonite-based geopolymers have been studied not only for their mechanical properties to replace cement-type materials, but also for their adsorbent properties, which are largely bound by the porosity of the material [6]. In the study carried out by Maleki, et.al, the adsorption of heavy metals with geopolymers synthesized from bentonite [7] was evaluated, on the other hand, in the study carried out by Ramakrishna the absorbing capacity of bentonite to remove dyes was studied, demonstrating excellent results [8].

In this work, a geopolymeric bentonite material (GPB), synthesized and characterized in the “Laboratorio de Química Orgánica y Biomolecular (LQOBio)” removal efficiency and sorption capacity of methyl violet (MV) in aqueous solutions, was evaluated by using ultraviolet-visible (UV-VIS)
spectroscopy, to contribute to the preservation and reduction of water pollution rates, some sorption parameters were evaluated and the sorption kinetics of the material was studied.

2. Materials and methods

2.1. Reagents

GPB was used without any previous treatment, except for the reduction of its size through grinding and sieving with a Mesh 200. This solid was synthesized and characterized by LQOBio [9], the diffraction pattern obtained by X-ray diffraction (XRD) technique is shown in Figure 1 and it is quantitative in Table 1, analyses performed for verification of what was reported by LQOBio.

![Figure 1. XRD Pattern of GPB and GPBabs.](image)

**Table 1. Quantitative XRD of GPB.**

| PDF No.      | Name               | Symbol | Quantitative |
|--------------|--------------------|--------|--------------|
| 01-083-2465  | Low quartz         | Qz     | 42.3%        |
| 01-072-1245  | Albite             | Ab     | 18.2%        |
| 01-071-0956  | Orthoclase         | Or     | 8.9%         |
| 01-072-1503  | Muscovite          | Ms     | 7.6%         |
| 01-078-1064  | Trolite            | Tro    | 7.1%         |
| 01-076-8291  | Montmorillonite    | Mnt    | 4.9%         |
| 01-077-0135  | Microcline         | Mc     | 2.9%         |
| 01-083-0971  | Kaolinite 1A       | Kln    | 2.8%         |
| 01-075-8790  | Clinohlorite       | Clc    | 2.3%         |
| 01-071-5088  | Calcite            | Cal    | 1.5%         |
| 01-083-0736  | Magnesium-ferri-hornblende | Mhb | 1.5%         |

Methyl violet (MV) was supplied by Merck KGaA (Germany) and was used as a sorbate in the present study; the MV is used as indicator, changes his colour from yellow to blue-violet in a pH range of 0.0-2.0 [10] and its solubility changes in aqueous medium as the pH increases. For the sorption assays in this job, the MV was diluted in distilled water at the desired concentration.

2.2. Batch sorption experiments

Sorption tests were carried out to study the removal capacity of MV by the GPB, for which the pH, initial concentration of MV and dose of GPB were evaluated. For the sorption study, a 10 mg/mL MV stock solution (pH = 7.0) was prepared. In this work, 25 mL of MV solution was poured into a 60 mL beaker, the GPB powder was added to the beaker. The beaker was then sealed, and the mixture was shaken at 200 rpm at room temperature for 12 hours. Finally, the GPB was separated from the MV solution by seepage. For sorption measurements, the concentration of MV remaining in solution was
determined by UV spectrophotometry measurements at $\lambda = 590$ nm using Shimadzu UV-2401 PC instrument. Removal efficiency (RE) and sorption capacity (SC) were calculated using Equation (1) and Equation (2) respectively, where $C_i$ (mg/L) was the initial concentration MV, $C_t$ (mg/L) was the concentration of MV at time $t$, $m$ (g) was the dosage of GM and $V$ (L) was the volume of MV solution.

$$\text{RE(\%)} = \frac{100(C_i - C_t)}{C_i}$$

$$\text{SC}(\text{mg/g}) = \frac{V(C_i - C_t)}{m}$$

For the pH study, it was varied from 2 to 12. For the GPB dose study the range was 25 mg - 200 mg and for the initial MV concentration study the range was 5 mg/L - 1000 mg/L.

2.3. Kinetic study

The kinetic study was performed with the best conditions established in the previous trials, pH 2, dose of GPB 500 mg and initial concentration of MV 10 mg/L; with a volume of MV of 250 mL, agitation of 750 RPM at room temperature. Concentration of MV remaining in solution was determined by UV-VIS measurements at $\lambda = 590$ nm at time intervals from 10 min to 720 min and determining the RE and SC. It was evaluated from the kinetic models of sorption and the isotherms of Langmuir and Freundlich, models.

2.4. Characterization

Fourier-transform infrared (FTIR) spectroscopy measurements of the GPB and Geopolymer after sorption (GPBabs) were carried out with Bruker Tensor 2 spectrometer, in attenuated total reflectance (ATR) mode in the wavenumber range of 400 cm$^{-1}$ - 4000 cm$^{-1}$ and 32 scans. XRD was used to obtain information about the mineralogical composition of the GPB and GPBabs using the Bruker D8 Advance diffractometer with DaVinci Geometry (40 kV, 40 mA, Cu Ka $\lambda = 1.5406$ Å).

3. Results and discussion

3.1. Methyl violet sorption test

3.1.1. Effect of pH. In this study the effect of pH on the sorption capacity of MV by the GPB was evaluated, since it has been demonstrated that in dyes such as MV the pH can alter its solubility, on the other hand interactions of hydroxyl ions and/or hydronium ions with the structure of the dye and sorbent can change the kinetics of sorption [11].

Figure 2(a) shows how the sorption capacity of the GPB decreases as the pH of the solution increases, a fact that is corroborated by Figure 2(b) where the efficiency of MV removal in the solution decreases. In both cases, the sorption loss is stabilized at an alkaline pH, close to pH 8, and then increases slightly. This behavior may be mainly due to the decrease in solubility of the MV in water as the pH of the solution increases, however the increase in SC and RE in alkaline pH may be due to precipitation of the MV that is not quantified in the concentration of the solution after the sorption. On the other hand, acid pH can generate active sites in the polymer structure by neutralizing remaining hydroxyl groups in the material and allowing the access of MV molecules in the active sites of the GPB.

3.1.2. Effect of geopolymer bentonite dosage. The effect of the GPB dose on the MV sorption is shown in Figure 2(c) and Figure 2(d) where it is observed that the sorption capacity of the GPB decreases as the dose of the same increases, until it stabilizes at a sorption capacity of approximately 1 mg/g GPB; this indicates that the active sites of the material seem to compete among themselves to establish contact with the sorbate, promoting its capacity of sorption of the same one [12]. On the other hand the removal efficiency increases up to a geopolymer dose of 125 mg and then decreases, the growth of the removal efficiency occurs, because although the removal capacity of the geopolymer decreases, the
sorbent/sorbate ratio is high, however, as this ratio increases, there is greater competition between the active sites, causing the desorption of the sorbate after 125 mg of sorbent.

3.1.3. Effect of initial methyl violet concentration. The effect of the initial concentration of MV in solution is shown in Figure 2(e) and Figure 2(f), it can be observed that as the concentration of MV increases, the sorption capacity of GPB also increases, which reinforces what is observed in the geopolymer dose effect, as the concentration of sorbate increases, the competitiveness between the active sorbent sites decreases, thus, as the sorbent/sorbate ratio decreases, the sorbent capacity of the GPB increases. As shown in Figure 2(f), as absorption capacity increases, no apparent change in removal efficiency is observed and excellent results are obtained in all cases, demonstrating the material's good ability to remove MV in high concentration.

![Figure 2](image_url)

**Figure 2.** Effect of variables in the sorption of MV by GPB. (a) SC vs pH (b) RE vs pH (c) SC vs dosage of sorbate and (d) RE vs dosage of sorbate (e) SC vs initial MV concentration y (f) RE vs initial MV concentration.

3.2. Sorption kinetic study

The parameters of the kinetic models were determined from experimental data with the help of linear curve fitting, these data can be seen in Figure 3. Pseudo-first, pseudo-second order and Intra-particle diffusion models were evaluated for the adsorption kinetic study and the Langmuir and Flory-Huggins isotherms were employed for the adsorption equilibrium study.

The adjustment of the pseudo-first order model for the experimental data was made by means of the graphic representation of \( \ln(q_e-q_t) \) vs \( t \), from the slope and intersection of this model and together with Equation (3) the value of \( K_f \) and \( q_e \) was determined (see Table 2), where \( q_e \) is the capacity of sorption in equilibrium (mg/g), \( K_f \) the constant of pseudo first order of the model (min\(^{-1}\)) and \( t \) is time. Although the data did not have the best fit with the pseudo-first order model, the \( K_f \) value obtained by the curve is close to that found by Dogan and Alkan [13] who obtained a value of 0.273 min\(^{-1}\) for MV with perlite, demonstrating similar sorption kinetics.

In the same way, the pseudo-second order model was adjusted for the experimental data by means of the graph of \( t/q_e \) vs \( t \), from the slope and intersection of this model and together with Equation (4) the value of \( K_s \) and \( q_e \) was determined (see Table 2), where \( q_e \) is the capacity of sorption in equilibrium
(mg/g), $K_s$ the constant of pseudo-second order of the model (min$^{-1}$) and $t$ is time. The sorption of MV with GPB has a better fit to the pseudo-second order model, unlike the previous model, the values of $h$ and $K_s$ show that the initial sorption ($t_0$) is low with a mean sorption rate, corresponding to the data, where it is observed that the greatest sorption occurs during the first hour of contact.

$$\log(q_e - q) = \log(q_e) - \frac{k_f t}{2.303}$$  \hspace{1cm} (3)  \\
$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e}$$  \hspace{1cm} (4)

Finally, the intra-particular diffusion model was adjusted for the experimental data by means of the graphic representation of $q_t$ vs $t^{1/2}$, from the slope and intersection of this model and together with Equation (5) the value of $K_{id}$ was determined (see Table 2). Where $K_{id}$ the constant of pseudo-second order of the model (min$^{-1}$) and $t$ is time (Figure 4) [14]. The low correlation in the intra-particle diffusion model shows that there is no diffusion sorption in the pores of the material, which may be due to the fact that geopolymerization is a little homogeneous process, the generation of non-homogeneous pores by this type of synthesis may cause low diffusion in the same.

$$q_t = k_{id} \cdot t^2 + C$$  \hspace{1cm} (5)

**Table 2.** Kinetic parameters for the removal of MV by GPB.

| Dye  | $k_f$ (min$^{-1}$) | $q_e$ (mg/g) | $R^2$ |
|------|-----------------|-------------|-------|
| MV   | 0.1299          | 4.95        | 0.847 |

| Dye  | $K_s$ (g/mg*min) | $h$ (mg/g*min) | $R^2$ |
|------|-----------------|---------------|-------|
| MV   | 0.0207          | 0.0954        | 0.999 |

| Dye  | $K_{id}$ (g/mg*min) | $R^2$ |
|------|---------------------|-------|
| MV   | 0.0150              | 0.6918 |

3.3. Sorption equilibrium study
The isothermal model of Freundlich is described by the expression of Equation (6), where $q_e$ is the amount of MV adsorbed on the GPB surface at equilibrium, $C_e$ is the MV equilibrium concentration (mg/L), $K_f$ is the Freundlich adsorption constant. To evaluate the fit of experimental data with this model, $ln(q_e)$ vs $ln(C_e)$ was plotted [15]. To determine the adsorption isotherms of Langmuir, $C_e$ vs $C_e$ was plotted. The Langmuir model is described by the expression of Equation (7), where $q_e$ is the amount of MV adsorbed on the GPB surface at equilibrium, $C_e$ is the MV equilibrium concentration.
(mg/L), $K_L$ is the Langmuir adsorption constant, and $q_m$ is the maximum adsorption capacity of the adsorbent (mg/g).

$$\ln (q_e) = \ln(kf) + \frac{1}{n} \ln(Ce) \quad (6)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (7)$$

The results of the adjustment of each isotherm with the sorption data are shown in Table 3; Figure 5 shows the plot of $C_e/q_e$ vs $q_e$. It is observed that there is a greater fit to the Langmuir model, which indicates that sorption is given preferentially through chemisorption, through stronger links or interactions, this in correspondence with what was found in the study of kinetics, where sorption is given in the first hour of contact with an with a slower than expected speed, it also explains why sorption does not have a good correspondence with a diffusion model, since it has preference to have a monolayer sorption through strong interactions [16]. However, it is expected that in a such model the initial sorption velocity and the initial absorbed quantity are higher than they are (will be the highest), this effect may be due to the surface homogeneity of the material, which can be described thanks to the geopolymerization process.

### Table 3. Isotherm parameters for removal of MV by GPB.

| Isotherm   | $K_f$ (mg/g)/(mg/L)$^1/n$ | $1/n$ | $K_L$ (L/mg) | $q_m$ (mg/g) | $R^2$ |
|------------|--------------------------|-------|--------------|--------------|-------|
| Freundlich | 4.7364                   | 0.0109| --           | --           | 0.9896|
| Lagnmuir   | --                       | --    | 13.2486      | 4.3630       | 0.9997|

**Figure 5.** Lagmuir isotherm plots for removal of MV by GPB.

3.4. **Characterization of geopolymer bentonite after sorption**

Figure 1 show the characterization by XRD of GBP after sorption assays, which indicate that there is no apparent changes in the material. In diffraction profile, there is a decrease in crystallinity on the part of the solid, but no shifts in the signals or the sighting of a new phase or the disappearance of phases are observed.

4. **Conclusions**

The present study showed the ability of GBP to remove MV in aqueous solutions. The effect of different parameters on the sorption of MV by the GPB was evaluated, it was found that at low pH (2-4) the greater capacity of sorption by the material is observed, in the same way it was found that the greater relation sorbent/sorbate, greater is the capacity of sorption of the GPB The kinetic study showed that the sorption of MV by the GPB follows a pseudo-second order model with a mean sorption at the onset of contact, a process that occurs during the first hour. The sorption conforms to the Langmuir model, indicating that sorption occurs through strong interactions and explaining that sorption occurs during the first hour of contact. GPB proves to be a good candidate for the removal of MV in aqueous sources.
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