Removal of rhodamine B in wastewater from the textile industry using geopolymeric material

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Abstract. In this work a geopolymeric material was synthesized by alkaline activation of calcined coal gangue at 700 °C using a solution 1:9 of NaOH:N₂SO₄, as a sorbent to remove rhodamine B from aqueous solutions. X-ray diffraction, fourier-transform infrared spectroscopy and scanning electron microscopy were used to characterize the material structurally and morphologically; removal efficiency and rhodamine B sorption capacity were evaluated by using ultraviolet-visible spectrophotometry. Sorption tests were performed to evaluate the effect of the dose of geopolymeric material and the contact time of this material with rhodamine B solution in a range from 0.5 to 30 hours, interval in which the best sorption was observed. Removal efficiencies and sorption capacity to 80.4% and 1.035 mg/g respectively were found, these values show the usefulness of the material for the removal of rhodamine B in aqueous solution, making it an interesting alternative for water decontamination and object of study for future works. Removal efficiency increased by increasing geopolymer dosage and contact time.

1. Introduction

Industrial discharges on water sources are one of the most damaging and alarming global problem: they cause greater ecological deterioration and impact on human health [1]. Textile industry is a focus of pollution, this one produces 8000 kg/day per fabric and consumes approximately 1.6 million litters of water per day. Mechanical processing of textiles requires a small quantity of water, however, chemical processing operations require a substantial amount of water; after processing, the water used is released as effluent [2] containing, surfactants, chlorine compounds, salts, phosphates, organic products and synthetic dyes [3]. Most synthetic dyes are complex organic molecules and are characterized by high colour intensity, even at low concentrations, and the presence of chromophore groups in their chemical structure that attribute carcinogenic and toxic properties to them [4]. Additionally, dyes can affect photosynthetic activity in aquatic life because of decreased light penetration [5].

Researchers around the world are looking for new alternatives in water conservation due to the demand for drinking water. Geopolymers (GP), also called inorganic polymers, are the product of a process called geopolymerization in which small molecules (oligomers) are combine to form a three-dimensional structure [6]. This process involves dissolution, jellification and condensation reactions that occur simultaneously to form the geopolymeric material which is composed of aluminum and silica interconnected tetrahedrally alternately by sharing all oxygen atoms [7]. GP exhibit many interesting properties, their application as cemenitious materials has been widely studied for their good compressive strength, however, in recent years they have emerged as materials for removal of contaminants in water sources [8]. GP are novel and environmentally friendly alternative sorbent...
materials because it is possible to use industrial wastes as raw materials for their manufacture [9]; these materials represent a low production cost and highly efficient alternative for removal dyes.

Although a wide spectrum of industrial waste can be used for GP manufacture, the most used have been fly ash, metakaolin and red sludge [10]; however, new industrial waste, such as coal gangue (CG), has attracted the attention of researchers for its implementation. CG is the solid waste produced during the coal mining and washing processes, due to its low utilization value is discarded. It is one of the most produced industrial solid waste; it represents between 10% and 25% of crude coal production. Stored in large quantities, it occupies an enormous area of land and, due to the presence of harmful trace elements, causes serious environmental problems by polluting the air, water and soil. In addition, its combustion produces huge quantities of toxic and harmful gases [11]. Its high content of alluminosilicates makes it a potential source for the manufacture of GP: a viable alternative for its use, valorization and reduction of contamination. In this work, a geopolymeric coal gangue material (GPCG) was synthesized and characterized using Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM); its removal efficiency and sorption capacity of rhodamine (RB) in aqueous solutions, was evaluated by using ultraviolet-visible spectrophotometry, to contribute to the preservation and reduction of water pollution rates. Due to its environmental advantages, the efficient removal of RB even in a short period of time, high profitability and the added value of the use of by-products from the coal industry, the manufacture of this geopolymer represents an important contribution to the creation of new materials for innovative applications.

2. Methods

2.1. Preparation of geopolymeric material

CG was calcined at 700 °C for 3 hours. GPCG was synthetized using a mixture of CG and alkaline activators with liquid-solid ratio 1.4 g/mL. Alkaline activators were a mixture 9:1 of sodium silicate (%Na₂O=11.70, % SiO₂=33.30; commercial) and 10 M NaOH (99%; Merck). Alkaline activator solution was added to the calcined CG, mixed and then quickly poured the fresh paste into mold (50 mm x 50 mm x 50 mm). The mixture were cured for 31 hours at 85 °C. Finally, the GPCG was removed from the mold, was milled into fine powder (125 μm) and was kept at room temperature for characterization.

2.2. Characterization

FTIR measurements of the GPCG and calcined CG 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. The GPCG and calcined CG microstructure was evaluated by FESEM using the field emission scanning electron microscope Tescan Mira3. XRD was used to obtain information about the mineralogical composition of the GPGC and calcined CG using the Bruker D8 Advance diffractometer with DaVinci Geometry (40 kV, 40 mA, Cu Ka λ = 1.5406 Å).

2.3. Batch sorption experiments

Sorption tests were carried out to study the influence of contact time and dosage of GPCG on the removal efficiency of RB. For the sorption study, a 10 mg/mL RB stock solution (pH=7.1) was prepared. In this work, 25 mL of RB solution was poured into a 60 mL beaker, the GPCG powder was added to the beaker. The beaker was then sealed and the mixture was shaken at 350 rpm at room temperature for the desired times for de sorption tests. Finally, the GPCG was separated from the RB solution. For the sorption measurements, the concentration of RB remaining in solution was determined by UV spectrophotometry measurements at λ=553 nm using Shimadzu UV-2401 PC instrument. Removal efficiency (RE) and sorption capacity (SC) were calculated at contact times ranging from 0.5 hours to 24 hours and three GM dosage, 0.002 g/mL, 0.008 g/mL and 0.016 g/mL g using the Equation (1) and Equation (2), respectively [12]. Where Cᵢ(mg/L) was the initial concentration RB, Cᵢ(mg/L) was the concentration of RB at time t, m (g) was the dosage of GM and V (L) was the volume of RB solution.
\[
RE(\%) = \frac{100(C_i - C_t)}{C_i}
\]

\[
SC(\frac{mg}{g}) = \frac{V(C_i - C_t)}{m}
\]

3. Results and discussion

3.1. Structural study

For identification of mineralogical phases of GPCG and CG using XRD, the International Diffraction Data Centre (ICDD) PDF-4+ database [13] was used. Figure 1 shows the XRD pattern obtained from the GC, in this pattern three phases were identified: quartz (PDF # 01-075-8322), hematite (PDF # 01-087-1164) and illite (PDF # 00-024-0495) with quartz being the most abundant phase. The presence of the quartz and illite phases suggests the suitability of GC as an aluminosilicate source to synthesize GP.

From Figure 2, where the synthesized GPCG XRD pattern is shown, five mineralogical phases were identified in the GPCG: quartz (PDF #01-070-7344), hematite (PDF # 01-089-0599), muscovite (PDF # 01-089-6880), aluminium oxide silicate (PDF # 04-007-7380) and iron silicide (PDF # 04-011-5925). Appearance of muscovite, aluminium oxide silicate and iron silicide is observed, this new phase are possibly associated with the process of alkaline activation with sodium silicate and sodium hydroxide to which the GC was subjected in the geopolymerization process. Peaks of quartz and hematite raw materials have remained in the XRD pattern although with less intensity. The amorphous hump in the region between 2theta 20 and 30 is reported as a characteristic indicator of the formation of geopolymeric gels. Additionally, intensity diminished at the peaks of the crystalline phases of the precursor material (CG), it is attributed to a partial dissolution of the crystalline phases and possibly also caused by the presence of sodium silicate [14].

FTIR analysis of geopolymeric material and CG are given in Figure 3. FTIR spectra of CG calcined at 700 °C shows several absorption bands of different intensity. The band at 1019 cm\(^{-1}\) is attributed to the symmetric stretching vibration of Si-O-Si. The double band between 800 cm\(^{-1}\)-700 cm\(^{-1}\) correspond to stretching vibration mode of Si-O-Al or Si-O-Si, the band at 559 cm\(^{-1}\) is attributed to the bending vibration mode of Si-O-Al present in illite, and the band at about 452 cm\(^{-1}\) correspond to O-Si-O bending vibrations, all of them characteristic absorption bands of thermally treated CG [15]. FTIR spectrum of the GPCG shows absorption bands similar to those observed in the CG, however, these present variations with respect to their wavelength of appearance, displacement that is mainly attributed to the change in length and angle of the Si-O-Si and Si-O-Al bonds and is interpreted as an indication of geopolymerization [16]. Band in the 1000 cm\(^{-1}\) region is considered as the main band and is mainly
attributed to the quartz crystalline phase present in the CG, this band is displaced to shorter wavelength (976 cm\(^{-1}\)) by the formation and rupture of bonds during geopolymerization. Shift of the absorption band that appeared about 780 cm\(^{-1}\) towards lower wave number (775 cm\(^{-1}\)) is an indication of the participation of quartz in the geopolymerization reaction. Weak absorption band of approximately 1394 cm\(^{-1}\) is attributed to the stretching vibration of the O-C-O, indicative of the presence of sodium bicarbonate caused by the atmospheric carbonation of the geopolymer paste [17].

**Figure 3.** FTIR analysis of GPCG and CG calcined.

FESEM images of the CG and GPCG before and after the RB sorption are shown in Figure 4. Figure 4a shows a flake shape morphology corresponding to the calcined GC. Figure 4b corresponds to the synthesized GPCG. In micrograph the morphological change is evident as a result of the transitions of mineralogical phases inherent to the geopolymerization reaction which are confirmed by the results obtained in XRD, there is evidence of the formation of agglomerates, characteristic of this type of inorganic polymers. However, in some regions, flakes corresponding to GC are observed, indicating that not all the precursor material was geopolymerized. Finally, in Figure 4c, there are no noticeable changes in the morphology of the material, which indicates that even after the RB sorption process the polymer structure remains stable.

![FESEM micrographs at magnifications 10000X of (a) CG calcined (b) GPCG and (c) GPCG after sorption test.](image)

**Figure 4.** FESEM micrographs at magnifications 10000X of (a) CG calcined (b) GPCG and (c) GPCG after sorption test.

### 3.2. Rhodamine sorption tests

The effect of the contact time of the GPCG-RB solution on the absorption of RB at room temperature is shown in Figure 5a. Removal efficiencies from 59.96\% to 80.46\% and sorption capacities from 0.77
mg/g to 1.03 mg/g were obtained. GPCG was found to have a high dye removal capacity even with the lowest contact time (RE=59.96% and SC=0.77 mg/g). In the range of 0.5 hours to 24 hours, removal efficiency and sorption capacity increased as contact time increased; with longer contact time, then more active GPCG sites can interact with dye molecules and thus increase removal capacity. However, increasing the contact time from 24 to 30 hours did not increase RE or SC, a fact that serves as an indication of the saturation of the GPCG in 24 hours. Using a GPCG dose of 0.008 g/mL, the maximum values of RE and SC, 80.46% and 1.035 mg/g respectively, were obtained with 24 hours of contact, a time that is established as optimal to achieve the greatest removal.

Figure 5. (a) Effect of the contact time on the RE and SC. Effect of the GPCG dosage on the (b) RE of RB and (c) the SC of RB.

Effect of GPCG dose on RB removal was evaluated to determine the optimal dose, this results are shown in Figure 5b and Figure 5c. Variation in dosage of GPCG did not have the same effect on both parameters evaluated (RE and SC). As the amount of GPCG increases, the RE also increases; using the higher dose (0.016 g/mL) the best removal efficiencies were obtained. As the amount of sorbent increases, the number of available sorption sites increases, therefore, the amount of RB removed increases. In contrast, the best SC was not obtained with the highest dose of GPCG. SC is related to the amount of RB sipped per unit mass (g), as the amount of GPCG increases the number of sites available to be active sites increases, generating unsaturation of the sorption sites [18]. The highest values for SC were obtained using 0.008 mg/g as the GPCG dose.

4. Conclusions
Alkaline activation of the GC carried out for the synthesis of the GPCG was successful, by means of FTIR, XRD and FESEM the morphological and structural characterization was carried out verifying the appearance of characteristic features of the formation of the inorganic polymer. The GPCG synthesized in this study presented a high capacity of removal of RB from aqueous solutions, even at short periods of contact. The RE and SC increased by increasing the contact time GPCG-RB solution, removal
efficiencies between 59.96% and 80.46% were obtained. Doses of 0.008 g/mL GPCG and 24 hours were established as the optimal dose and sorbent time to achieve the best RB removal. The use of this industrial waste as an alternative for the removal of BR from aqueous solutions represents a great opportunity for the use and valorization of this waste.

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