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Adsorption of Congo Red using Ti/Al-pillared clays .

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Abstract

The present work aimed to synthesize clays pillared with Ti and Al and verify the efficiency in the removal of the anionic diazo dye Congo Red. The kinetic equilibrium, the catalyst dosage, and adsorption isotherms were studied in the adsorption experiments. The adsorbents were characterized by XRD, SEM/EDS, BET, and FTIR. The results for the adsorption tests indicated that the equilibrium time was 90 minutes, and the amounts of dye removed (mg) per gram of adsorbent (Q_e) were 23.4; 35.1 and 26.0 mg.g $^{-1}$ for clays montmorillonite, Ti-PILC, and Al-PILC, respectively. In the study of the kinetics of the adsorption process, the adsorption on Al-PILC fitted very well to the pseudo-first-order, whereas the adsorption on montmorillonite and Ti-PILC fitted to the pseudo-second-order. The best adsorbent dosage for Congo Red removal for montmorillonite and Ti-PILC was 0.5 g.L $^{-1}$, and for Al-PILC was 1 g.L $^{-1}$. The adsorption over all clays was better described by the Langmuir isotherm. EDS analyses showed that the expected composition of the clays was mainly montmorillonite. The clays demonstrated a high potential for Congo Red removal, being the titanium-pillared clay (Ti-PILC) the most promising. The best adsorbent was regenerated and used up to three times, recording good stability and utility to remove Congo Red dye.

Keywords: adsorption; Clays; Pillared-clay, Congo-Red Dye; montmorillointe; water

1. Introduction

Textiles, food, and tanneries industries use synthetic dyes in their production processes and generate large amounts of effluents containing various organic and toxic reactive dyes, that cause negative impacts on the environment and human health. One of these synthetic dyes is Congo Red ($C_{32}H_{22}N_6Na_2O_6S_2$), which is an anionic diazo dye based on benzidine, derived from azo naphthalene acid, its molecular structure is shown in Fig. 1, which is also called [1-naphthalenesulfonic acid, 3,3'-(4,4'-biphenylenebis(azo)) bis(4-amino-) disodium salt].

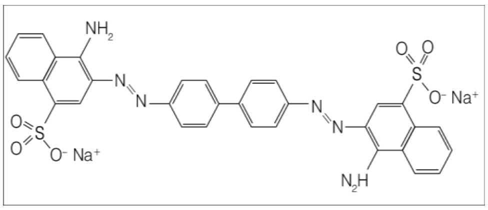

Figure 1: Molecular structure of Congo red dye.

Congo Red (CR) dye causes allergic reactions and generates benzidine as a metabolic product, a human carcinogenic compound [1]. Improper management of industrial effluents containing Congo red can cause major environmental problems because its high stability, complex structure, and carcinogenic effects. Therefore, it is of great importance to remove it from wastewater. It is a challenge to accomplish this task because the techniques used to date cannot degrade it or remove it easily from wastewater [2]. The water treatment of textile dyes includes filtration, precipitation, and coagulation, among other processes, that in many cases are not very effective in removing the textile dyes completely [2]. The adsorption process is well-known as promising for wastewater treatment. Montmorillonite is a clay material with the capacity to exchange cations because it has ions and minerals between its lamellae. In previous work, it was demonstrated that clays (montmorillonite) are very effective for the removal of synthetic dyes such as Rhodamine B [3]. The present research aimed to study clays as adsorbents for removing CR dye using pillared clays, including their regeneration and reutilization.

2. Experimental

Preparation of adsorbents

A commercially available natural bentonite was used for this study. Bentonite is a natural clay that contains between 80 to 90% montmorillonite, with the remainder being impurities (feldspar, quartz, mica, and organic matter, among others). This clay was purified (LG sample) and used subsequently, to make pillared clays. To obtain the purified clay, the following procedure was carried out: the commercially available bentonite was ground and sieved (mesh size <500 µm) to remove larger particles. Then, a controlled sedimentation process was applied to separate the montmorillonite fraction (≤ 2 µm) from the mentioned impurities. The sedimentation was performed following the detailed steps in reference [4].

Preparation of Aluminum and Titanium pillared clay.

The purified clay obtained previously (LG sample) was homo-ionized in a NaCl solution (2M) and stirred for 24 hours. The solid fraction was separated by centrifugation, washed (until the Cl^- ions were eliminated), and dried in an oven (60ºC). The pillarization of the clay with Ti and Al was carried out following the details reported previously in [5]. For the preparation of Al-pillarization solution, solutions of NaOH (0.2 M) and $AlCl_3$ (0.1 M) were mixed, keeping a molar ratio of 2OH/Al, and Al/clay ratio of 4 $mmol.g^{-1}$. Similarly, for the preparation of Ti-pillarization solution, titanium butoxide and HCl (6 M) were used to obtain a concentration of 10 mmol Ti/g_{clay}. The samples were named Al-PILC, Ti-PILC, according to the pillar used in each case, and LG for the purified clay without pillar (montmorillonite).

Characterization

The crystalline phases of the clays were characterized by X-ray diffraction (XRD) analysis, Energy Dispersive X-ray Spectroscopy (EDS), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and BET surface area.

Adsorption test

The adsorption of Congo Red (CR) in aqueous solution was carried out individually in a batch system using Erlenmeyer glass flasks and a magnetic stirrer, maintaining the temperature at 25°C and constant stirrer (500 rpm). The experiments were carried out aiming to study the adsorption kinetics (equilibrium time, min.) and the variation of the adsorbent dosage (grams of clay/volume of CR dye solution; $g_{clay}.L_{dye\ solution}^{-1}$) and adsorption isotherms. For the two first, the initial CR concentration was 40 ppm, at the natural pH of the CR solution. The adsorption isotherms were performed with solutions at different concentrations (100, 200, 300, 400, and 500 ppm) with a natural pH of the solution. After the adsorption process, the clay and dye solution were separated by centrifugation (5000 rpm) for 15 minutes. The adsorption efficiency was calculated by the variation in the initial and final concentration of each dye (Removal %) and, Qe factor (mg of dye removed per g of adsorbent; $mg_{dye}.g_{clay}^{-1}$). The CR concentration was monitored by UV spectrophotometry, using a wavelength of 498 nm. The Lambert-Beer calibration curves were carried out previously ($R^2 = 0.999$). All the adsorption tests were carried out in duplicate.

3. Results and Discussion

Characterization. *EDS results:* Elemental investigation by EDS showed the expected composition of montmorillonite clays, which are an aluminosilicate rich in Al, Si, O, Na, Mg, Ca, Fe, and Ti in smaller presence. The incorporation of Al and Ti in the pillared clays was detected by the increase in the elemental percentage of these in the composition of the Al-PILC and Ti-PILC clays, respectively. *XRD results:* Fig. 2 shows the XRD patterns of the LG-PILC, Ti-PILC, and Al-PILC clays. It is possible to identify in the XRD pattern of LG-PILC the presence of peaks characteristic for the presence of montmorillonite and cristobalite. In the XRD patterns of Al-PILC and Ti-PILC clays there is no presence of cristobalite, most likely due to the calcination process at 300° C for 2 hours during the preparation of the pillars, that was sufficient to destabilize and eliminate the cristobalite crystals [6]. According to the XRD patterns of Al-PILC and Ti-PILC clays, the characteristic peaks of montmorillonite were preserved, but the Ti-PILC sample shows wider and less intensity of these peaks, showing a more amorphous feature when compared to the other clays.

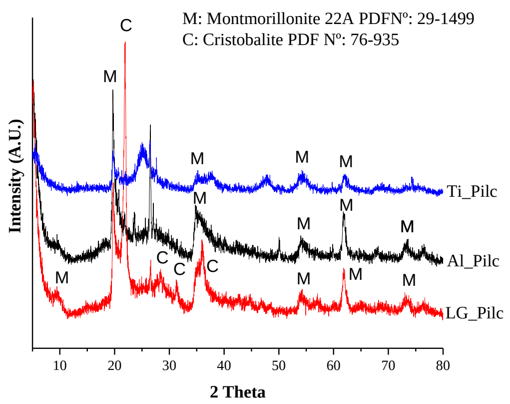

Figure 2. XRD diffratogram of clays

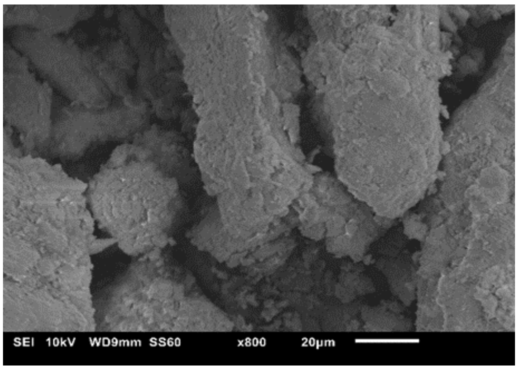

Figure 3. SEM image of the morphology of LG clay.

SEM analysis. In Figure 3 we can observe the morphology of LG clay obtained by SEM, it contains clusters of particles with irregular shapes, and the images of the other clays are very similar. *BET analysis.* According to these analyses, there was an increase of surface from LG (176.5 $m^2.g^{-1}$) to Ti-PILC (240.0 $m^2.g^{-1}$). Curiously, the contrary effect was observed in Al-PILC, as there was a reduction in the surface area of Al-PILC (169.5 $m^2.g^{-1}$) compared to LG-PILC (176.5 $m^2.g^{-1}$). The highest surface area values of the Ti-PILC clay may be related to the atomic radius of Ti, because it is larger than Al, then it can form larger pillars. Also, Ti-PILC has the largest volume of micropores overall.

Adsorption tests. Figure 4a shows the results of the kinetic tests. As can be seen, the adsorption reached equilibrium in 90 minutes, and the amount of Congo Red dye adsorbed by the LG, Ti-PILC, and Al-PILC clays (expressed as Qe = milligram of dye per gram of clay, $mg.g^{-1}$) were 23.4, 35.1, and 26.0 $mg.g^{-1}$ respectively. The pseudo-first-order kinetic model was better suited for the Al-PILC clay (R^2 = 0.9747), whereas the pseudo-second-order model was better suited for the LG and Ti-PILC clays, with R^2 values of 0.9929 and 0.997, respectively. The influence of the adsorbent dosage for dye removal (grams of adsorbent/liter of dye solution) was also studied; the results are shown in Figure 4b; 0.5 $g_{clay}.L^{-1}$ was the best dosage for the LG and Ti-PILC clays; and 1 $g_{clay}.L^{-1}$ for Al-PILC. To investigate the adsorption mechanisms, adsorption isotherm tests were performed, and the isotherm profiles obtained for each sample best suited the Langmuir model with the following R^2 values: 0.845; 0.9874 and 0.7003 for the LG, Ti-PILC, and Al-PILC clays, respectively. These R^2 values are like other reported in the literature for clay materials. The Langmuir model assumes homogeneous adsorption forming a monolayer of adsorbate on the surface of the adsorbent without interaction between dye molecules and there is only the interaction of one active site per dye molecule. The pillared clay with Ti (Ti-PILC) was shown to be superior to other clays for the removal of Congo Red dye. This may be because of its superior surface area (240 $m^2.g^{-1}$) when compared to the other clays. Also, it is possible that the addition of Ti modified the surface charge of the clay surface (montmorillonite clay has a negative surface charge [2]), and, the titanium pillars formed larger spacing in the interlayer region of the clays (larger pillars), since the atomic radius of Ti is larger than that of Al. Considering that montmorillonite generally has a negative surface charge, as previously reported in [2], and also considering that the Congo Red molecules are anionic dyes, it is possible to affirm that during adsorption over clays, electrostatic interaction among Van der Waals forces are involved in the adsorption of Congo Red dye molecules on the surface of the clays. Adesina et al [3] studied the TiO_2/clay materials, and, they observed that the addition of TiO_2 raised the pH_{PZC} to around pH 6-7, unlike pure montmorillonite which presents a net negative surface charge (in the entire pH range). This may indicate that the Ti-PILC clay has a more neutral surface charge than the other clays, thus favoring the adsorption of the dye. Modification of the clay surface by the addition of Ti influences adsorption and can favor the forces of attraction between Congo Red (anionic dye) and the clay surface. Furthermore, obviously, textural properties of clay such as surface area are the principal influence on the adsorption process of the dyes. All these explanations would explain the high dye removal values for Ti-PILC.

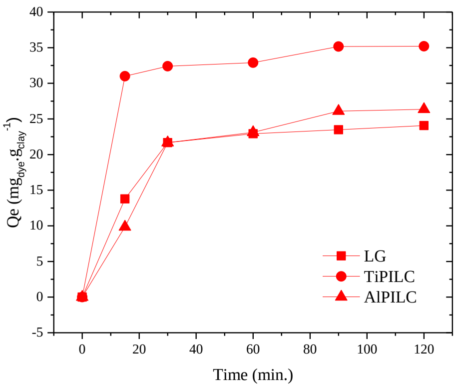

Figure 4a: Dye removal expressed in Qe (mg. dye per gram of clay) over time (min.).

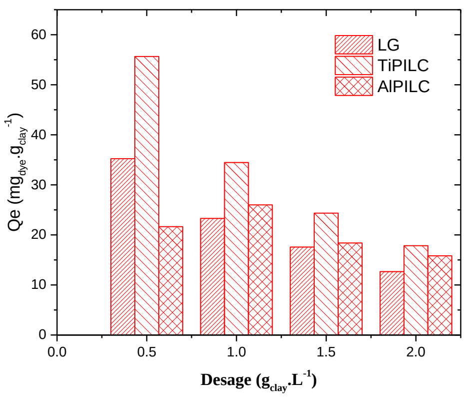

Figure 2b: Effect of adsorbent dosage ($g._{clay}$/L).

Reutilization: Clays were used up to four times. The best clay (Ti-PILC) showed a decrease in the percentage of dye removal of 49.84%; 61.34%, and 63.52% in the second, third, and fourth use respectively when compared to the first use.

Conclusion

All clays studied in this work removed Congo Red in an equilibrium time of 90 minutes and the adsorption occurs according to the Langmuir model. The best dosage for montmorillonite and pillared clay Ti-PILC was 0.5 $g_{clay}.L^{-1}$; and 1 $g_{clay}.L^{-1}$ for Al-PILC. The Ti-PILC clay was the adsorbent as recorded the best performance in the removal of Congo Red, owing to its superior surface area (240 $m^2.g^{-1}$), and probably due to the formation of larger interlayer spacings (larger pillars), since the atomic radius of Ti is larger than that of Al and possible modifications in the surface charge of the clay, thus favoring the adsorption of the dye. The Al-PILC and LG clays had lower performances and very similar kinetic behavior, each other, indicating that the pillarization with Al pillars did not affect the adsorption of Congo Red dye. These clays can be reutilized, at the beginning, up to four times.

Acknowledgments

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