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Use of natural clays for the adsorption of Methylene Blue and Rhodamine-B in seawater

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Abstract

This study investigated the adsorption of Methylene Blue (MB) and Rhodamine-B (RhB) in seawater solution using natural clays (Bentonite, sample SC-02) and the corresponding purified clay (mainly montmorillonite). The adsorption tests were carried out in a batch system, with the adsorbent in powder form (mesh sieve <500 μm). In the adsorption experiments kinetic tests, adsorbent dosage variation, and adsorption isotherms were carried out. The clays were characterized by EDX, XRD, and SEM. The results indicated that clays were very effective in removing synthetic dyes (MB and RhB) in seawater with high removal %. At an adsorbent dosage of $1g_{clay}.L^{-1}$ (weight of clay/volume of synthetic dye solution), natural clay (SC-02) and purified clay achieved the equilibrium of adsorption after 90 minutes for both dyes, recording high removal % 90<. The variation of adsorbent dosage also indicated that low adsorbent dosages are highly effective in reaching high synthetic dye removal, thus the maximum removal (Qe= mg of dye removed per gram of clay; $mg.g^{-1}$) of MB recorded was $217mg.g^{-1}$ (obtained by natural clay), whereas the maximum removal of RhB was 160 $mg.g^{-1}$(obtained by purified clay); both with a dosage of $0.2\ g_{clay}.L^{-1}$. Furthermore, the adsorption isotherms were adjusted to the Langmuir model and Freundlich models. The results of this research showed that the two clays of this work (natural and purified) were highly effective in removing synthetic dyes in seawater. The salinity of the seawater did not affect/hinder the adsorption of RhB and MB.

Keywords: adsorption; Clays; Methilene Blue; Rhodamine-B; Seawater

1. Introduction

The contamination of water bodies by synthetic dyes has become a significant environmental concern due to the widespread use of these chemicals by industries (ex. textile factories). Among many synthetic dyes, Methylene Blue (MB) and Rhodamine B (RhB) are particularly noteworthy due to their variety of applications and potential environmental risks. Methylene Blue (MB) is a synthetic dye widely used in the production of paper, textiles, polyesters, nylon, and even as a biological stain in biological and medical laboratories. Its intense blue color and stability make it a popular choice in these industries. However, its release into the environment, particularly into aquatic ecosystems, can be harmful due to its persistence and potential toxicity. MB dye is known to cause harmful effects on aquatic life, including interference with photosynthesis in aquatic plants and toxicity to fish and other marine organisms. On the other hand, Rhodamine B (RhB) is a reddish synthetic dye belonging to the xanthene family. It is widely used in the textile industry, as well as in printing inks, biological staining, and as a tracer dye in water studies due to its strong fluorescence [1]. Despite its widespread use, RhB is highly toxic, posing significant risks to both aquatic life and human health. Both MB and RhB are cationic dyes, meaning they carry a positive charge, which contributes to their strong binding affinity with negatively charged particles and surfaces. This property, while useful in industrial applications, also means that these dyes can easily bind to aquatic sediments, potentially leading to long-term environmental contamination. Many textile effluents contain high concentrations of synthetic dye and high concentrations of salts, these last usually used to improve the dyeing of the fibers. 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 dye completely [2]. In previous work, it was demonstrated that clays (montmorillonite) are very effective for the removal of synthetic dyes [3]. The present work aimed to study clays as adsorbents for removing MB and RhB in seawater.

2. Experimental

Preparation of adsorbents

A commercially available natural bentonite (clay SC-02) 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 same clay was purified (sample: purified clay) and used as an adsorbent. To obtain the purified clay, the following procedure was carried out: the 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], and the clay was named: purified clay.

Characterization

The crystalline phases of the clays were characterized by X-ray diffraction (XRD) analysis, the chemical composition was determined by Energy Dispersive X-ray Spectroscopy (EDS), and the morphology by Scanning Electron Microscopy (SEM).

Adsorption test

The synthetic dye solutions (Methylene Blue and Rhodamine B) were prepared separately using seawater. The seawater was collected in a remote region, deep sea, on the beach of Guaruja, SP Brazil. Before preparing the dye solution, seawater was filtered with a membrane filter (0.45 microns). In all tests, the initial concentration of MB was 43 $mg.L^{-1}$; whereas the initial concentration of RhB was 35 $mg.L^{-1}$; except for the elaboration of isotherm, where the initial concentrations of each dye varied from 35 to 300 $mg.L^{-1}$.

The adsorption of Methylene Blue (MB) and Rhodamine B (RhB) in solution was carried out individually in a batch system using Erlenmeyer flasks and a magnetic stirrer, maintaining the temperature at 25°C and constant agitation (approx. 500 rpm). The adsorbent dosage (clay/synthetic dye solution volume was varied over 0.1, 0.2, 0.4, 0.6, and 1 ($g_{clay}/L_{dye\ solution}$). The contact time (time of stirrer) was varied over periods of 15, 30, 60, and 90 minutes. After the adsorption tests, the clay was separated by centrifugation at 5000 rpm for 15 minutes. The adsorption efficiency was calculated by the variation in the initial and final concentration of each dye (%) and, Qe factor (mg of dye removed per g of adsorbent, $mg.g^{-1}$). The concentration of dye was monitored by UV-Vis spectrophotometry, using a wavelength of 663 nm for Methylene Blue and 554 nm for Rhodamine B. The Lambert-Beer calibration curves were carried out for Methylene Blue (R^2 = 0.99), and Rhodamine B (R^2 =value of 0.99). All the adsorption tests were carried out in duplicate.

3. Results and Discussion

Characterization: The XRD pattern obtained from X-ray diffraction (XRD) analysis of the purified clay indicated the predominantly presence of Montmorillonite 15A (Mtm-Na: $Na_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_24H_2O$; JCPDS 29-1498 and Mtm-Ca: 13-135), and in a small proportion: Quartz (Qtz: SiO_2; JCPDS: 86-1629), and Cristobalite (Crbt: SiO_2, JCPDS: 76-937). XRD pattern of clay SC-02 showed a similar XRD profile but, as expected, with more presence of Quartz, and Cristobalite. The chemical composition of purified clay determined by EDS is presented in Table 1; these results indicate a high presence of Al, Si, and O elements, consistent with the predominant presence of montmorillonite, which is an aluminosilicate. Figure 1 shows the morphology of the purified clay, which is irregular and typical for clay materials.

Adsorption tests. The results for the kinetic test during adsorption with an adsorbent dosage of 1 $g.L^{-1}$ are shown in Figure 2. In this figure, it was observed that the use of natural clay (principally bentonite, sample SC-02) and purified clay (mainly montmorillonite) was effective in removing the synthetic dyes MB and RhB from seawater. The removal of MB reached values above 90% with both clays, at all observed contact times. The removal of RhB achieved its highest removal percentage with purified clay, peaking at 90% removal after 30 minutes of agitation. With the SC-02 clay, the RhB removal percentage ranged between 70% and 80%. After 90 minutes there was no variation in the concentration of both dyes, therefore, in the next experiments, the time of 90 minutes was established as the time to reach the equilibrium. As very high dye removal values were observed with an adsorbent dosage of 1 $g_{clay}.L^{-1}$, further study of variation of adsorbent dosage was carried out. The variation of adsorbent dosage was varied in 0.2 $g_{clay}.L^{-1}$, 0.4 $g_{clay}.L^{-1}$, 0.6 $g_{clay}.L^{-1}$, 0.8 $g_{clay}.L^{-1}$, and 1 $g_{clay}.L^{-1}$, these results are shown in Figure 3. According to these results, the dosage variation directly influences the value of Qe (Qe = mg of dye per gram of clay; $mg.g^{-1}$); with lower dosages of clays recording the highest Qe values, peaking the maximum value with adsorbent dosage of 0.2 $g_{clay}.L^{-1}$. It is very clear that for all adsorbent variations, the best clay for the removal of MB is clay SC-02 (the sample without purification). By far, the MB has a strong affinity by clay SC-02. On the other hand, purified clay (mainly montmorillonite) showed greater effectiveness in the removal of Rhodamine B, see Figure 3. Considering that montmorillonite generally has a negative surface charge, as previously reported in [3], and also considering that the MB and RhB molecules are cationic dyes, it is possible to affirm that during adsorption over clays, an electrostatic interaction occurs (among Van der Waals forces) between dye molecules and the surface of clay, thus favors the adsorption process of the dyes. This would explain the high dye removal values for MB and RhB.

Adsorption isotherms of RhB over clays were carried out; the adsorption values for pure clay fitted very well to the Langmuir model, with R^2 value of 0.99, whereas the clay SC-02 fitted very well to the Freundlich model, with R^2 value was ~1. This can be related to the presence of impurities on the clay SC-02, which may be favoring the formation of active non-homogeneous energy centers for adsorption (explained by the Freundlich model). The contrary effect may explain the Langmuir isotherm found in pure clay. A similar finding was found during MB adsorption. This study is still under development.

Table 1. Elemental composition of the purified clay.

Elmt	Element	Atomic
	%	%
O K	57.76	71.03
Na K	0.82	0.70
Mg K	1.05	0.85
Al K	6.25	4.56
Si K	30.73	21.53
Ca K	1.00	0.49
Fe K	2.39	0.84
Total	100.00	100.00

Figure 1. Morphology of the purified clay obtained by SEM analysis.

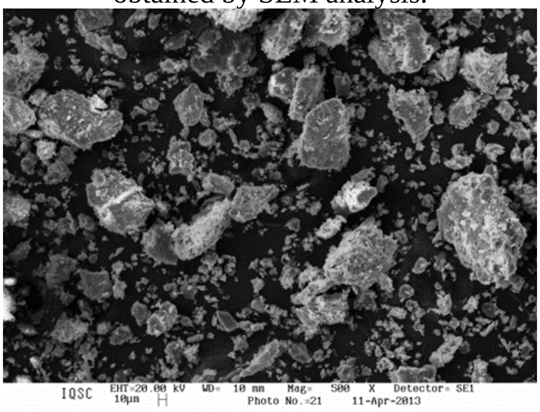


Figure 2. Results of kinetic study during the adsorption of RhB and MB in seawater over clays.

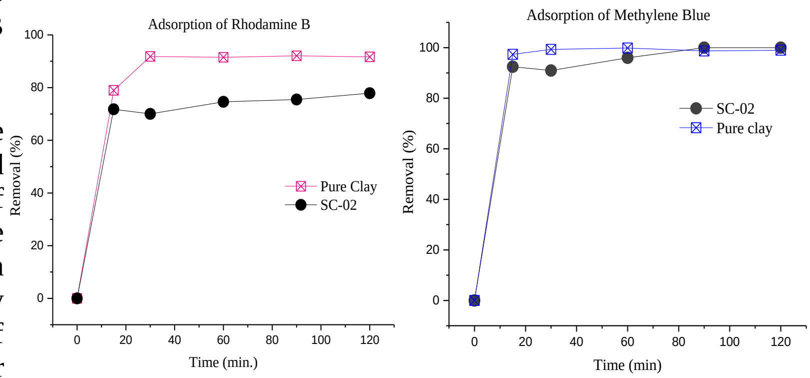
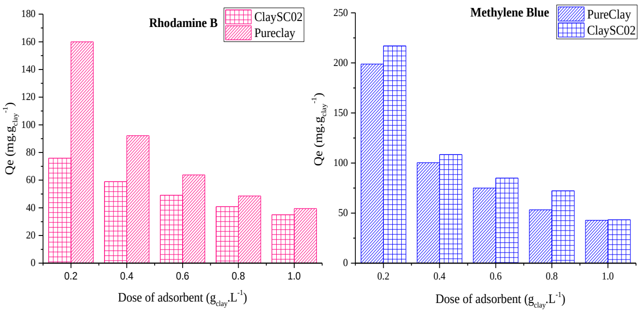


Figure 3. Results of dosage of clay variation during the adsorption of RhB and MB in seawater.



Conclusion

The adsorption tests demonstrated that the natural clays (bentonite and purified montmorillonite) of this work are highly effective in the adsorption of synthetic dyes MB and RhB in seawater.

The purified clay (mainly montmorillonite) showed greater effectiveness in the removal of RhB dye; whereas the natural clay showed a high preference to remove MB. Thus the maximum removal of MB recorded was 217 $mg.g^{-1}$, obtained by natural clay (bentonite), whereas the maximum removal of RhB was 160 $mg.g^{-1}$, obtained by purified clay (mainly montmorillonite); both with a dosage of 0.2 $g_{clay}.L^{-1}$.

These results indicate that the salinity of seawater did not hinder the adsorption of RhB and MB. The adsorption of dyes in seawater using clays is promissory for application in the treatment of effluent with high salinity and color.

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