Feasibility of polyurethane-supported bentonite clay modified with Nb_2O_5 catalyst for degradation dye textile by photocatalysis

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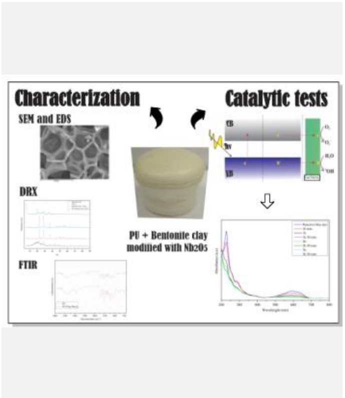


Water pollution caused by textile dyes is of high environmental concern, due to the complex removal and/or degradation of these compounds. Thus, the search for heterogeneous catalysts for dye degradation increases being low-cost materials with abundant global reserves as a potential alternative to be applied to advanced oxidative processes. In this study, bentonite clay was modified with Nb_2O_5, supported on polyurethane foam (PU/Clay-Nb), and evaluated as a catalyst for the degradation of textile blue dye by photocatalysis. The PU/Clay-Nb was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (DRX), Scanning electron microscopy, and energy dispersive spectroscopy (SEM-EDS). The results showed that the polyurethane efficiently supports bentonite clay modified with Nb_2O_5. The photocatalytic degradation of reactive textile blue using PU/Clay-Nb showed a good discoloration efficiency (up to 88 %) in 3h of reaction. The PU/Clay-Nb is a simple and reusable alternative catalyst for textile degradation by photocatalysis.

Introduction

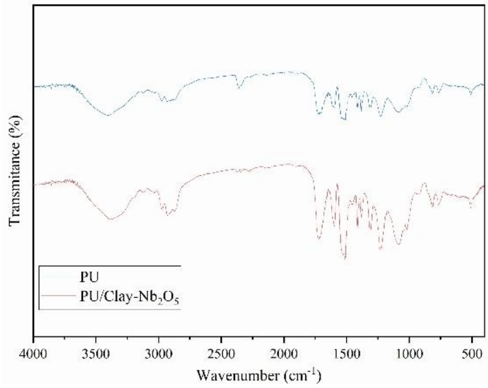
The growth in population and the rapid development of industries have caused severe environmental damage, mainly water contamination, due to inadequate disposal of organic compounds without any type of treatment, such as textile dyes [1]. Thus, it increases the search for materials of low cost, with abundant world reserves, that can be applied in advanced oxidative processes (AOPs) for degradation of these contaminants. The bentonite clay represents an interesting alternative to their composition and properties: high adsorption capacity, cation exchange capacity, and swelling.[2] The clay mineral also supports semiconductors, such as Nb_2O_5, presenting excellent photocatalytic activity.[3] Bentonite clay and Nb_2O_5 materials have abundant reserves and show good photocatalytic efficiency but present a low mechanical resistance and difficulty in recovering the catalyst from the aqueous medium. Therefore, Polyurethane (PU) is a viable alternative to avoid such limitations because of its high mechanical resistance and ease of reuse.[4] In particular, recent studies have shown that materials applied to photocatalysts using inorganic catalytic polymer systems have obtained promising results.[5] This study proposes polyurethane-based support for bentonite clay modified with Nb_2O_5 for the degradation of textile dyes via photocatalysis.

Material and Methods

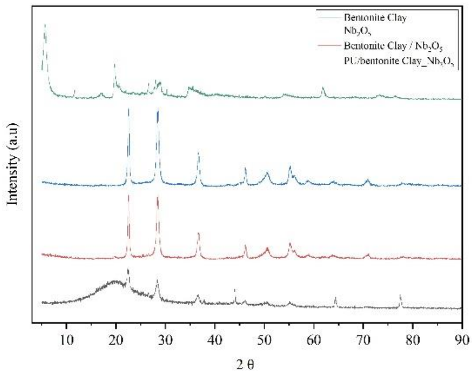
The polyurethane foam was obtained by formulated polyol and diphenylmethane 4.4' diisocyanate from the "*one shot*" method, adding Nb_2O_5-modified bentonite clay. The bentonite clay was modified according to Lacerda *et al*., 2020.[3] The PU/Clay-Nb foams were characterized using FTIR, DRX, and SEM-EDS techniques. Degradation, adsorption, and photolysis tests were carried out in a 250 mL photocatalytic jacketed glass reactor with reactive blue dye (30 mg L^{-1}). The mass of PU/Clay-Nb used was ~2.2 g, being 9% of bentonite Clay-Nb. The substrate was irradiated using a 125W mercury vapor lamp vertically positioned on the photochemical reactor through a quartz bulb. The absorbance was measured in a spectral range of 200 nm to 800 nm with a UV-Vis spectrophotometer.

Results and Discussion

The spectra obtained via FTIR for PU/Clay-Nb (Fig. 1a) show bands at 3300, 1712, 1305, and 1222 cm^{-1}, which refer to N-H, C=O, C-N, and C-O, respectively. Bands referring to the Si-O stretch and Si-O-Si and Al-O-Si angular deformation were found at 1083, 462, and 521 cm^{-1}, respectively. In addition, Nb-O-Nb bands were observed at 619 cm^{-1}. The diffractogram obtained for the bentonite clay, Nb_2O_5, Bentonite clay/Nb_2O_5, and PU/Clay-Nb samples (Fig. 1b) presents peaks at 5.7° belonging to d001 characteristically found for bentonite clays; the peaks at 22° d001, 28° d100, 36° 101 and 46° d002 refer to the orthorhombic structure of the Nb_2O_5. After modification of bentonite clay and synthesis of PU/Clay-Nb , it is possible to observe a decrease in the characteristic clay peak, indicating that the Nb_2O_5 was immobilized on the clay surface. Furthermore, the distinctive peaks of Nb_2O_5 were also observed after synthesizing the PU/Clay-Nb, indicating that the bentonite clay modified with Nb was successfully supported on PU. The images obtained using SEM for PU/Clay-Nb (Fig. 2) show large particle edges and morphologies broadly reported for the polyurethane. Also, tiny agglomerate particles are observed on PU, possibly particles of the modified bentonite clay. The image also presents the mapping of the Si, Al, O, highlighting elements of the clay minerals. C and Nb are also mapped by EDS. The efficiency of the PU/Clay-Nb system on photodegradation was tested with blue textile dye. The results suggest a band decrease at the maximum absorption (594 nm), responsible for the dye color and an intrinsical band for aromatic groups (200-300 nm), which disappears almost totally after three hours of degradation.



(a)



(b)

Figure 1. (a)- Pu and PU/Clay-Nb_2O_5 FTIR spectra , and **(b)** DRX for bentonite clay, Nb_2O_5, Bentonite Clay/ Nb_2O_5, and PU/Clay-Nb_2O_5.

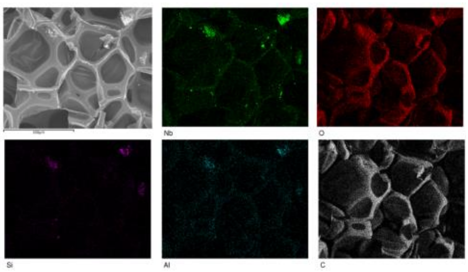


Figure 2. SEM-EDS images and mapping of PU/Clay-Nb_2O_5

The best degradation ratio using the PU/Clay-Nb system as a catalyst in the absence of oxygen peroxide was 88 % after 3 hours of reaction (Fig 3). The catalyst was also reused under the same conditions, achieving, after 3 hours of reaction, a 77% discoloration efficiency (Fig.3). Additional tests were performed to verify the influence of the effect of UV radiation (photolysis) and adsorption on the reactive blue dye on the system surface. The results indicate 17 % and 24 % of discoloration efficiency for photolysis and adsorption tests (Fig. 3), respectively.

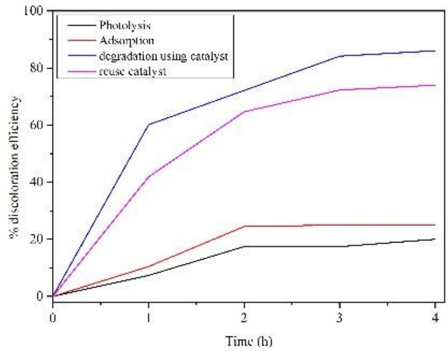


Figure 3. Discoloration efficiency for photolysis, adsorption, and photocatalysis using PU/Clay-Nb catalyst and reuse catalyst tests.

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Conclusions

The support for bentonite clay modified with Nb_2O_5 based Polyurethane was successful. The system PU/Clay-Nb was used as a catalyst for the reactive blue dye by photocatalysis and show high discoloration efficiency, being 88% in 3 hours of reaction. Still the reutilization of catalyst promotes 77% of discoloration efficiency in the same reaction time. Thus, the proposed PU/Clay-Nb is a simple, low-cost, and efficient alternative catalyst for degradation of textile dyes by photocatalyst.

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