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## Nanoclay as Adsorbent: Evaluation for Removing Dyes Used in the Textile Industry

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### Abstract

The dyes commonly used in the textile industry have structural resonant valence distribution, within a complex molecule, which determines the color of the dyes. The coloring is produced by chromospheres holding radiation in UV-visible range. Besides coloring, these compounds can be found in waste water and cause serious problems in living organisms, because their biodegradation products may be a source of toxic substances such as amines, which are generated from the characteristic azo chromospheres groups in most of the dyes. Current treatments for color removal from hazardous waste from these materials are complex and costly, for this reason some industries do not treat the wastes generated during the staining step. The aim of this study is to evaluate the use of nanoclay as adsorbents for dye used in the textile industry. The dyes used in this work are commercially known as: Orange GR, Black GN and African Brown. Nanoclay was obtained by bentonite treated with organic cation. The retention of the dye was evaluated by measurements in the UV-visible spectrum by using a HP-8354 equipment.

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## 1. Introduction

In recent years, new materials with technological application have been developed in the field of nanoscience and nanotechnology, understanding these terms as the design, characterization, production and application of structures, devices and systems by means of controlling shape and size at the nanoscale. Nanotechnology is the most promising discipline for its impact on many sectors, its scope covers from medicine, construction, ceramics, metallurgy, textiles, food, etc. In addition to the commercial and industrial applications, these materials are widely used in the field of environmental remediation; due to the effects derived mainly from the particle size. Nanomaterials can be obtained synthetically through complex processes, like physical processing, chemical and physicochemical processing and from natural raw materials. This is the case of nanoclays, modified clays which are controlled by manipulating the nanometer level with a specific design of the structure for each application. In this paper we study the behavior of nanoclay in the adsorption process of textile azo dyes. In the overall context of the dye industry, synthetic azo dyes constitute about half of the world, of which between 15% and 50% are remaining and are spilled into the environment as waste. These wastes may produce harmful compounds for living organism due to a mutation of the azo chromospheres to carcinogenic amines in addition to interfering with the photosynthetic activity of some aquatic plants by the presence of aromatic groups, metals, chlorides, between others.

## 2. Methodology

For adsorption tests of textile dyes, nanoclay prepared from bentonite clay from Neuquén province (Z) was used. The bentonite was rich in smectite as it was determined by X-Ray diffraction. Nanoclay was prepared by treatment of the bentonite with an organic cation referred as hexadecyltrimethylammonium (HDTMA), (Zo). Placing organic cations in the cation exchange sites of the clay material surface properties are significantly modified. Image 1 shows the molecular structure of the organic salt with which the nanomaterial was prepared from the clay.

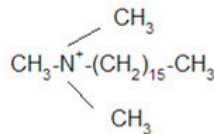


Fig. 1. Molecule HDTMA

Dyes selected for the experiments were: Orange GR (O), Black GN (N) and African Brown (M), they were prepared in distilled water dilution at concentration of 50 ppm. The chemical structures of two textile dyes can be seen in Figure 2.

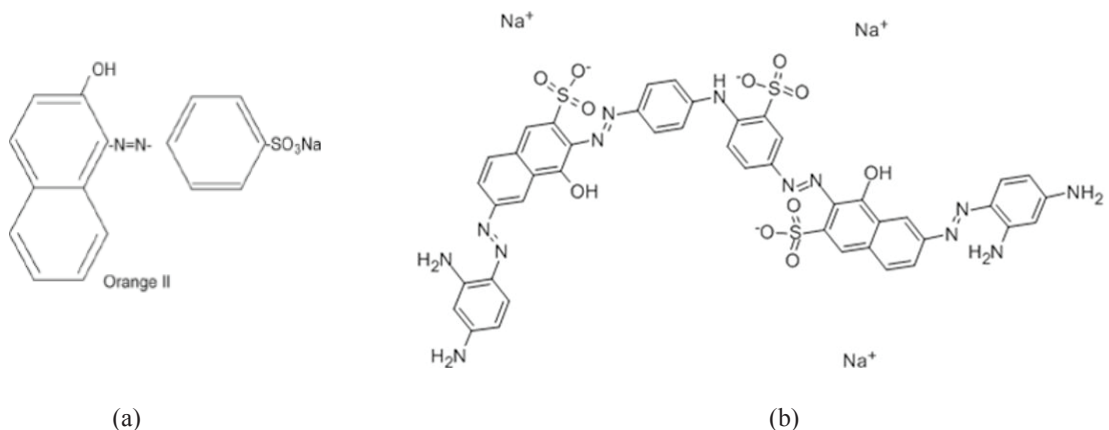


Fig. 2. (a) Orange GR; (b) Black GN

The molecule belonging to the sample O has an azo group (N=N), an aromatic ring and naphthalene next to  $\text{SO}_3^-$  while the dye N has structure with five azo groups plus terminal amino functional groups and thiosulphate as aryl groups naphthalene and benzenes are observed.

Black dye azo chromospheres GN owns and sulfone groups (O=S=O), and as functional structures amines and sodium cations, aromatic structures are seen as benzene and naphthalene rings.

The dye molecule known commercially as African Brown is not exposed because lacks the identification code on the International Registration of colorants known as Colour Index. However UV-visible analysis thereof presents an adsorption band at 450nm which is consistent to the azo chromospheres group, of interest in this study for its ability to mutate to carcinogenic compounds in aqueous solution.

Solutions thereof to evaluate the retention of the dye solids were analyzed using a UV-visible equipment. The initial solutions and the supernatants recovered after contact with the nanoclays (O, N and M) were prepared in distilled water at a dilution of 50 ppm and designated O50, N50 and M50.

The solids were placed in contact with dye solutions prepared in ratios of 0.20 and 0.50% natural clay/dye solution and ratios of 0.02, 0.05, 0.10 and 0.20% nanoclay/dye solution.

### 3. Results and Discussion

#### 3.1. Adsorbents

Diffraction patterns of the adsorbent employed (Z), can be seen in Figure 3. In this you can observe the smectite group as mineralogical component of phyllosilicates and diffraction peaks of gypsum, feldspar and quartz in the rock as impurities.

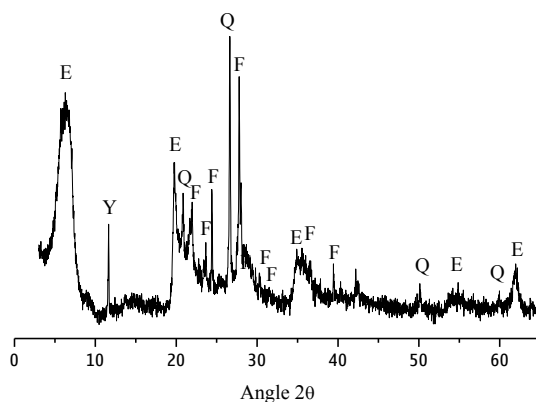


Fig. 3. XRD sample Z

Figure 4 shows the spacing  $d_{001}$  of clay Z and nanoclay Zo, and in it is evidenced the modification of native sample after treatment with the cation HDTMA, in which the spacing shifted from 1.41nm to 2.03 nm, indicating the displacement of exchangeable cations for the organic cation interlayer spacing in smectite clay.

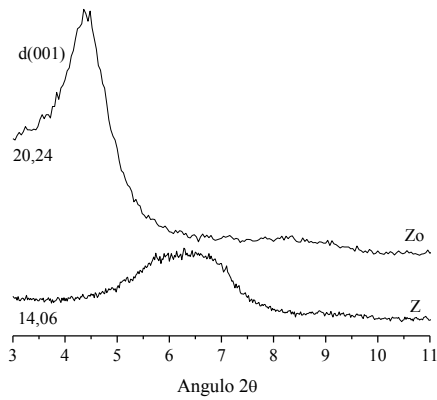


Fig. 4. Comparison space d001 sample Z and Zo

### 3.2. Adsorption tests

Figure 5 presents the UV-visible spectra of the supernatants resulting from the adsorptions of black dyes, orange and brown (N50, O50 and M50) in contact with the natural bentonite solids in varying proportions. It can be seen that the natural material lacks the ability to retain the colorants.

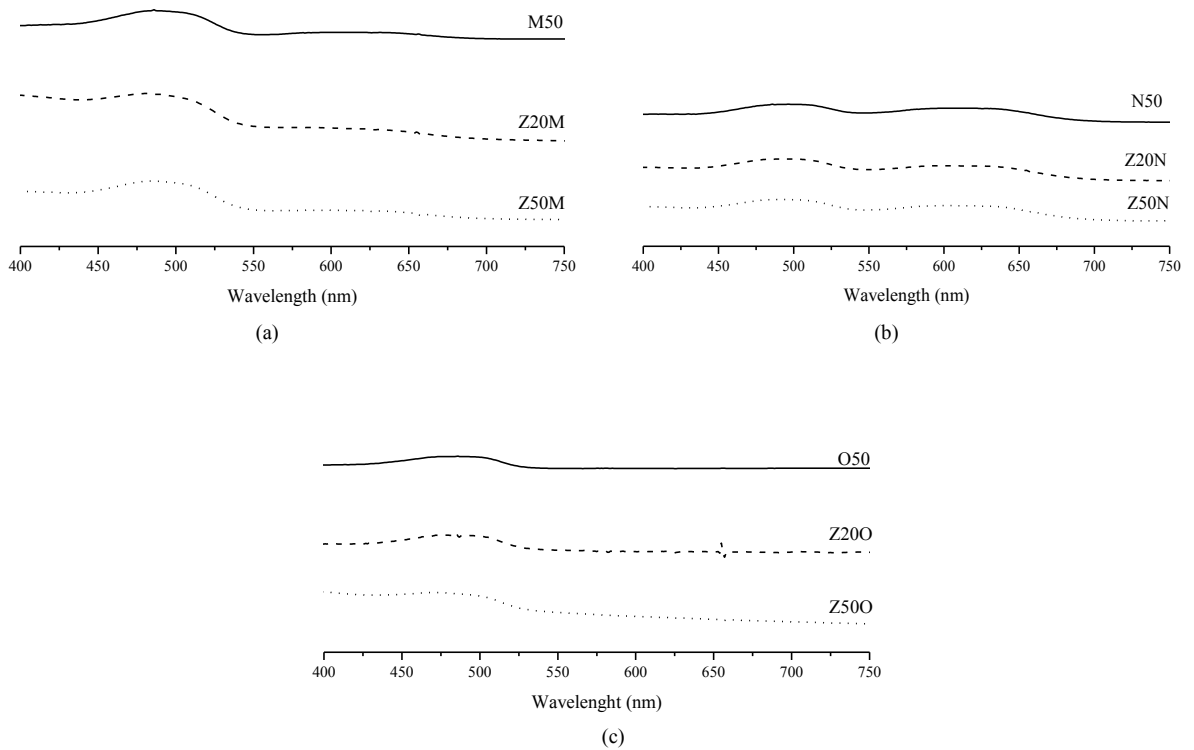


Fig. 5. Uv-visible dye solutions on initial concentrations and the supernatants after the tests performed with the native adsorbent. a) Z with M; b) Z with N and c) Z with O

Figure 6 shows the UV characterization of the supernatants obtained after contacting the dye solutions with the modified clays. It is concluded that the nanoclay is capable of adsorbing the azo dyes at the concentrations considered in this study. The treated nanoclay shows a large retention (in the same operating conditions) of Black dye, followed by the Orange and then Brown.

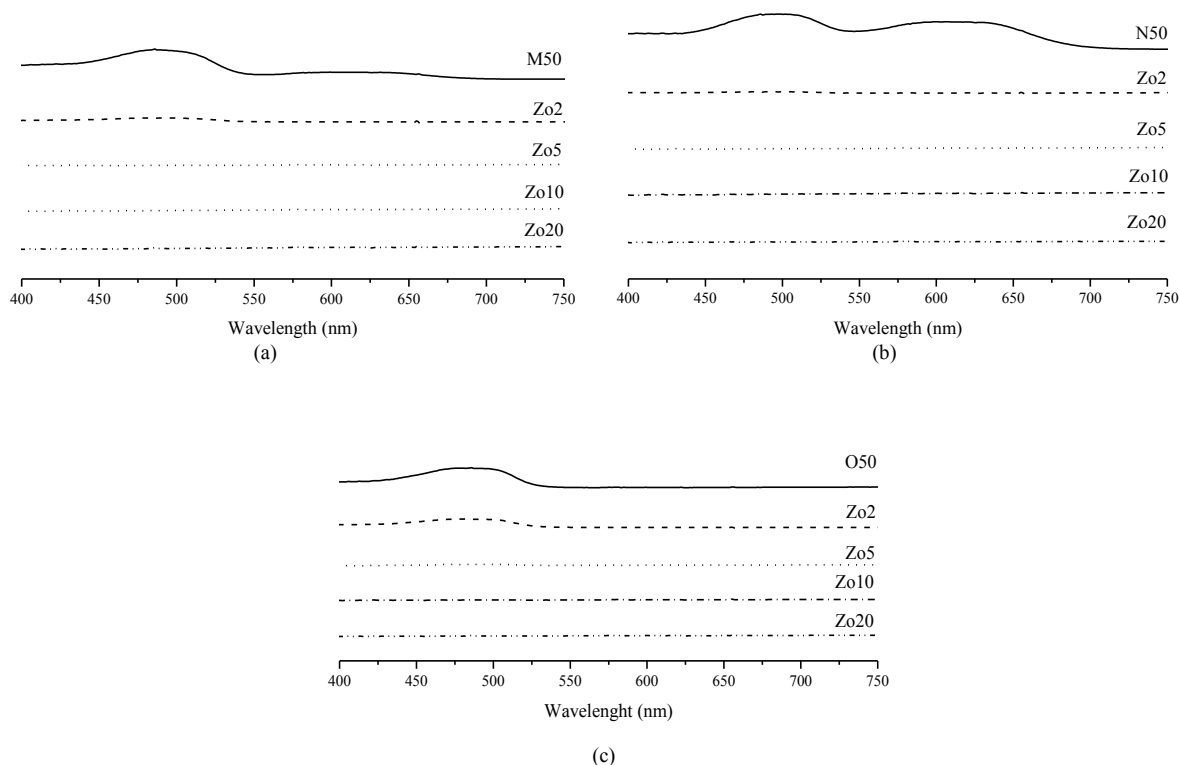


Fig. 6. UV-visible dye solutions on initial concentrations and the supernatants after studies with nanoclay:

a) Zo with M; b) Zo with N and c) Zo with O.

#### 4. Conclusions

The dyes studied, Brown, Orange and Black, show a satisfactory retention onto the nanoadsorbents considered, even in relationships 2% solid/liquid.

The natural substrate (clay Z), lacks the ability to adsorb organic dye molecules naturally. This may be due to competition from loads that arise between the functional groups of the adsorbent/substrate (negative charges) and the functional groups contained in the molecular structures of the dyes M, N and O.

The organic treatment of the sample Z causes a significant change of the interlayer spacing. This charge benefits the retention process of azo dyes tested.

In order to understand the behavior and the phenomena that occur during the adsorption of organic dyes in contact with nanomaterials, it is necessary to extend the study to other dyes with different structural characteristics as well as analyze this adsorbent with alternative organic treatments in order to determine the best conditions according to the adsorbents treated.

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