



Ability of a montmorillonitic clay to interact with cationic and anionic dyes in aqueous solutions



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ABSTRACT

A montmorillonitic clay in raw and treated forms (size-fractionated, organoclay, Al pillared) was evaluated as adsorbent for cationic (toluidine blue – TB and malachite green – MG) and anionic (Congo red – CR) dyes. A thorough characterization using XRD, SEM-EDS, N₂ adsorption, and FTIR of the considered samples was realized, all highlighting the structural changes after various treatments. UV–VIS analysis demonstrated the interaction between dyes and the adsorbent surface. The investigation of the effects of various experimental parameters using a batch adsorption technique showed that ON has a high adsorption potential for cationic dyes (33 and 39 mg/g in case of TB and MG, respectively). The kinetic study indicated that the adsorption process followed the pseudo-second-order model, while Freundlich isotherm showed a favorable adsorption. The calculated values of Gibbs free energy suggested also that the adsorption is spontaneous and is more favorable at higher temperatures.

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1. Introduction

In the increase need to remove dyes from waste water, low cost and easy available natural materials such as clay minerals were considered as adsorbents [1]. Kaolinite, montmorillonite, clinoptilolite, illite, or modified clays (organoclays, acid-treated) were tested for Congo red, Rhodamine B, methylene blue, malachite green, or heavy metals removal [2–11].

Toluidine blue (TB) is a basic thiazine metachromatic dye with high affinity for acidic tissue components [12]. This dye is mostly used in the dye industry, for medical purposes and in particular as histological special stains to highlight certain components. The chemical formula for TB is C₁₅H₁₆ClN₃S with a molecular weight of 305.82 g/mol. Malachite green (MG) is a triarylmethane cationic dye and is one of the most widely applied dyes. It is used especially as a biological stain, cyanide antidote, oxidation indicator, chemical analysis reagent and also for printing, dyeing, and monitoring [13–15]. The chemical

formula for MG is C₂₃H₂₅ClN₂ with a molecular weight of 364.911 g/mol. Congo red (CR) is a highly water-soluble anionic diazo dye. This dye is used as a laboratory aid in testing for free hydrochloric acid in gastric contents, in the diagnosis of amyloidosis, as an indicator of pH, and also as a histological stain for amyloid. It has a strong affinity to cellulose fibers and thus is employed in textile industry. Also it is a derivative of benzidine and naphthoic acid and metabolizes to carcinogenic products [16]. The chemical formula for CR is C₃₂H₂₂N₆Na₂O₆S₂ with a molecular weight of 696.665 g/mol.

Various physical, chemical, and biological methods, including adsorption, biosorption, ozonation, coagulation/flocculation, photocatalytic degradation, sonochemical degradation, electrochemical degradation, advanced oxidation, membrane filtration, and liquid-liquid extraction have been used for the treatment of dye containing wastewaters [4,17–19]. Adsorption is a very effective separation technique and now it is considered to be superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design and ease of operation [11,20–23]. A commonly-used adsorbent, activated carbon, has a high capacity for the removal of dye/organics, but also is difficult and expensive to regenerate it, which finally will increase the cost of the wastewater treatment [24–26]. This problem could be solved

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by the usage of low cost and efficient alternate materials such as clay minerals [2–6,8–10,27].

In this work, a Romanian bentonite, in raw and treated forms (size-fractionated, Al-pillared, and organoclay) was characterized and tested as adsorbent for cationic (TB, MG) and anionic (CR) dyes removal from aqueous solution in order to evaluate their potential as low cost adsorbents. Also the interaction between the adsorbent surface and dyes was studied using UV–VIS spectrometry. This study is a continuation of previous research related to bentonite deposits from Romania and their possible applications in the removal of pollutants from wastewater [28,29].

2. Materials and methods

2.1. Materials

Raw bentonite sample was collected from a deposit located in Orașul Nou, Satu Mare County, Romania. Bentonite was used in raw and treated form (size-fractionated, organoclay and Al-pillared). Characterization of the bentonite samples and the interaction with the organic compounds (dyes) was realized using X-ray powder diffraction (XRD), scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDS), specific surface area using Brunauer-Emmett-Teller method (BET), Fourier transformed infrared analysis (FT-IR) and ultraviolet, and visible (UV–VIS) spectroscopy.

The TB, MG, and CR dyes were obtained from Sigma Aldrich, LACH-NER, and PENTA respectively and were used as received without any purification.

2.2. Instrumentation

XRD analyses of clay samples were performed using a Rigaku diffractometer, CuK α anticathode. The XRD patterns were recorded with the reflection peaks from 10° to 80° angles, in the following analytic conditions: 40 kV, 44 mA, 2°/min scan rate, step size 0.02. The ICDD Database PDF-2/Release 2012 was used to specify the values of the reflection peaks.

SEM-EDS analyses were performed using Nova Nano SEM 450 and Oxford EDX equipment. 1–3 drops of solution obtained from 2 mg of sample dispersed in 2 mL methanol with 5 min sonication were placed on a Pt coated Si wafer chip and vacuum dried overnight. The working distance was (WD) = 2.1 mm and the voltage HV = 2.00 kV.

N₂ sorption experiments were conducted on a Quantachrome Autosorb-1-1C automated adsorption system. The powders were degassed for 4 h at 250 °C prior to the measurement. The surface areas were calculated using BET method and pore size distributions were calculated using Barrett–Joyner–Halenda (BJH) equation from the desorption branch of the isotherm.

FTIR absorption spectra were recorded using a JASCO 615 FTIR spectrometer 400–4000 cm^{−1} (resolution, 2 cm^{−1}). Analyses were performed on dried samples prepared by encapsulating 1.2 mg of finely grounded particles in 300 mg KBr. In order to be compared, the obtained spectra have been normalized with respect of the most intense band.

Dyes concentration in solution before and after adsorption was measured using a T70+ UV–VIS spectrophotometer PG Instruments Ltd at 633, 618, and 498 nm, which corresponds to the maximum absorbance for TB, MG, and CR, respectively. The UV–VIS measurements samples before and after experiments were measured also on powders using Jasco Model V-550/560/570 Spectrophotometer.

2.3. Adsorbents preparation

All samples were first subjected to a grinding process, followed by a size separation using a 0.2 mm sieve. First treatment employed was size-fractionation. In this case <0.2 μ m fraction of the bentonitic clay was obtained. In order to obtain this fraction, a suspension (solid:liquid ratio = 1:20) of clay stirred for 24 h was separated by centrifugation at 600 rpm; the obtained supernatant was centrifuged again, this time at 7000 rpm; the separated solid sample was then dried at 80 °C for 24 h [29–31]. Size-fractionated sample was obtained in this case, ON-s.

In order to obtain the organoclay, raw, and size-fractionated samples in suspension (solid:liquid ratio = 1:100, 24 h stirring) were contacted with the organic salt under stirring for 2 h. Modified bentonite samples were prepared by adding tetra-*n*-butylammonium bromide to 100% cation exchange capacity of the considered clays (raw and size-fractionated). Treated clay samples were then separated by settling and washed several times until bromide-free with distilled water by centrifugation and finally dried at 60 °C (24 h) [9,29,32]. Organoclays on raw (ON-TBAB) and size-fractionated (ON-s-TBAB) samples were obtained.

The preparation of Al-pillared clays was carried out using dry pillaring method (clay was added as solid to the pillaring solution) [33]. In an AlCl₃ solution (0.2 M) kept at room temperature and stirred vigorously, NaOH solution (0.2 M) was added dropwise until the molar ratio of OH/Al = 2 was reached. The mixture, pillaring solution, was continuously stirred at room temperature for another 24 h. Size-fractionated clay sample was added into the pillaring solution mentioned above in order to obtain an Al/clay ratio of 10 mmol/g. The obtained suspension was continuously stirred for another 24 h at room temperature. The solid was recovered by centrifugation at 5000 rpm and washed until chloride-free, dried at 60 °C and finally calcined at 500 °C for 2 h with a heating rate of 4 °C/min [29,34]. At the end of the above treatment, the ON pillared form on size-fractionated sample was obtained, ON-s-Al.

2.4. Adsorption experiments

Dyes removal experiments were realized in thermostated batch reactor in dynamic regime (3D shaker) at 25 rot/min. Experiments were performed using increasing contact times (15–240 min), dye initial concentrations (10–250 mg/L), solid:liquid ratio (0.02:10–0.25:10 g/mL), and temperatures (20–60 °C). Dye concentrations from solution were determined using the spectrophotometric method. Prior to analysis, aqueous samples were separated by centrifugation at 6000 rpm (Hettich EBA20 centrifuge) in order to completely remove solid particles from the solution. Experiments were conducted in the same conditions for all clay samples (raw and treated) considered.

Amount of dye adsorbed (*q*, mg/g) and removal efficiency (*E*, %) were calculated in order to establish the effectiveness of the considered samples in dyes removal process.

$$q = \frac{(C_0 - C_t)}{w} \times \frac{V}{1000} \text{ (mg/g)} \quad (1)$$

$$E = \frac{C_0 - C_t}{C_0} \times 100(\%) \quad (2)$$

where: *C*₀ is the initial dye concentration in solution (mg/L); *C*_{*t*} is the time *t* dye concentration in solution (mg/L); *V* is the adsorption volume (mL); and *w* is the adsorbent quantity (g).

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