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Sono-assisted adsorption of Cristal Violet dye onto Tunisian Smectite Clay: Characterization, kinetics and adsorption isotherms

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ABSTRACT

The present work describes the removal of Crystal violet from aqueous solution by Sono-assisted adsorption on Raw Tunisian Smectite Clay (RSC). This material was purified by dispersion in water and extraction of the fraction with a particle size smaller than 2 µm. the resulting material was characterized by XRD, TEM, BET, surface area and pore volume measurements. Batch studies were carried out to investigate the effect of experimental factors such as contact time (0–60 min), pH (2.5–11), adsorbent dose (0.05–0.3 g/L), and initial dye concentration (12.5–100 mg/L) on the Sono-assisted adsorption of Crystal violet dye. Adsorption kinetics was well fitted by pseudo-second order kinetic model. Langmuir (R^2 = 0.988), Freundlich (R^2 = 0.968), Langmuir–Freundlich (R^2 = 0.997) and Toth (R^2 = 0.999) isotherms were fitted to describe the equilibrium of Crystal violet Sono-assisted adsorption process. The results suggested that Natural Tunisian Smectite Clay is suitable as a sorbent material for Sono-assisted adsorption of Crystal violet dye from aqueous solutions.

1. Introduction

Dyes are common pollutants in the effluents of several industries such as textile manufacturing, leather tanning, cosmetics, paper, food processing, and pharmaceutical industries (Bertolini et al., 2013). Because of their toxicity, carcinogenicity, mutagenic and teratogenic properties they have been a longstanding environmental concern (Debrassi et al., 2012; Bel Hadjltaief et al., 2013; Fabryanty et al., 2017). Several physicochemical methods i.e., adsorption, chemical oxidation, coagulation, flocculation and advanced oxidation are currently available for the treatment of dye-colored wastewater (Bel Hadjltaief et al., 2018).

Adsorption has been a particular attention among the worldwide researchers due to its high efficiency, lower operating cost and simple operation process (Eloussaief et al., 2013; Hamza et al., 2015). Finding new adsorbent materials to improve removal efficiency has always been the important issue in adsorption. The most important commercial adsorbents are activated carbon, silica, resins, clays, zeolites and activated alumina (Bel Hadjltaief et al., 2017). In particular, abundant natural clay is considered as low cost adsorbents and widely applied in various water purification processes due to their easy availability, eco-friendly, non-toxic, huge surface area and presence of several types of active sites on the surface (Chaari et al., 2015; Sdiri et al., 2016). Our groups have reported the application of the natural Tunisian clays such as kaolinite, montmorillonite, halloysite, smectite, bentonite, and sepiolite in the adsorption of phenols (Bel Hadjltaief et al., 2017), heavy metals (Eloussaief et al., 2011, 2009), dyes (Chaari et al., 2015), volatile organic compound (Dammak et al., 2015a; Jarraya et al., 2010), in the purification of industrial phosphoric acid (Hamza et al., 2016; Khoualdia et al., 2017) and also used in dry reforming of methane at moderate temperatures (Liu et al., 2016).

Recently, the combination of ultrasound irradiation and adsorption process has received much more attention (Asfaram et al., 2017a, 2017b; Jorfi et al., 2017). The advantage may be related to more acceleration in chemical reactions and mass transfer as a result of acoustic cavitation (formation, growth and collapse of cavitation bubbles in a liquid) and creation of new adsorption sites on adsorbent (Ansari et al., 2016; Bagheri et al., 2017; Milenković et al., 2013). The combination between ultrasound irradiation and adsorption leads to increase the efficiency and also decrease the cost of dye adsorption (Soltani et al., 2016; Jorfi et al., 2017; Roosta et al., 2014; Saad et al., 2017). The effects of ultrasonic irradiation on adsorption of various pollutants have been studied recently and reported different outcomes. For example Jorfi and coworkers (2017) prepared a novel adsorbent silica nanopowder (SNP)/milk vetch-derived charcoal (MVDC) nanocomposite. This material exhibited considerably the uptake of Basic Red 46 (BR46) dye was higher in the absence of US than in the presence. The sono-assisted adsorption process shows significant improvements such as the

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reduced adsorbent quantity, increased efficiency and reduced contact time (Jorfi et al., 2017). In a subsequent work, and co-workers were also investigated the effect of ultrasound on adsorption of brilliant green (BG) and malachite green (MG) on Mn-doped Fe_3O_4-nanoparticle-loaded activated carbon, and they found the same conclusions (Asfaram et al., 2017a, 2017b).

To date, the use of natural clay as an adsorbent in Ultrasonic-assisted adsorption of organic dyes has been never considered. To our knowledge, this paper is the first study that investigates the adsorption of Cristal Violet, as a model organic dye, on natural Tunisian clay in the presence of ultrasound irradiation at ambient temperature. The influence of key operational parameters, such as pH, adsorbent amount and initial dye concentration has been considered. The kinetic parameters were calculated to determine the adsorption mechanism. The Langmuir, Freundlich, Langmuir–Freundlich and Toth models were applied to determine the correlation between the isotherm models and experimental data. The regenerability and reusability of the adsorbent were also evaluated.

2. Materials and methods

2.1. Preparation of adsorbent and adsorbate

The natural clay used in this work has been taken from the deposit of Jebal Cherahil located in the central-west of Tunisia from the area of Kairouan (Bel Hadjltaief et al., 2013). The natural clay was first purified by dispersion in water, decantation, and extraction of the fraction with a particle size smaller than 2 µm. The resulting solid was dried at 60 °C, ground to 80 mesh, and kept in a sealed vessel. The chemical composition of RSC was found to be as follows: 42.4% SiO_2, 16.82% Al_2O_3, 7.7% Fe_2O_3, 4.9% CaO, 4.50% MgO, 2.5% Na_2O, 0.5% K_2O and 18.17% loss of ignition. Crystal violet, ($C_{25}H_{30}N_3Cl$) (CI Classification number: 42555; CAS number: 548-62-9) (Qualigens India) was used without further purification (Ameur et al., 2017). A stock solution of the dye containing 200 mg/L was prepared by dissolving the required amount of dye in double distilled water. Solutions for adsorption experiments were made from the stock solution by appropriate dilution.

2.2. Characterization of adsorbent

Several techniques were employed for the characterization of natural Tunisian Clay. The chemical composition and structural features of the RSC was analyzed by means of X-ray fluorescence (XRF, ARL® 9800 XP spectrometer). The identification of the different phases of this material was performed through the XRD analysis. An X-ray diffractometer (Philips PW 1710, Japan) was used with CuK_α (λ = 1.54056 Å) radiation over a range of 2θ angles from 10 to 60, with a step size of 0.02°/s. The morphology of RSC was studied using High Resolution Transmission Electron Microscopy (HRTEM, JEOL JEM 2011). The specific surface area was determined by nitrogen adsorption at − 196 °C on a surface area and porosity analyzer ASAP 2020 V 3,04 H (Micromeritics).

2.3. Adsorption and Sono-assisted adsorption experiments

Studies of Cristal Violet adsorption onto natural Tunisian Clay were carried out using batch technique due to its simplicity and reliability. On the Sono-assisted adsorption was performed using an ultrasonic bath with a frequency of 50 Hz and a nominal power of 230 W (ULTRASONIC CLEANER USC-T, USC300T). The bath has dimensions 15 × 15 × 15 cm^3. Adsorption was carried using a magnetic stirrer (FALC stirrer, 20 W, 50/60 Hz) with 300 rpm at ambient temperature.

All batch adsorption experiments were carried out in 150 ml Erlenmeyer flasks by mixing a fixed amount of adsorbent with 100 ml of aqueous dye solution. After well-established intervals of time, the adsorbent was separated from the dye solution by filtration.

The dye concentration from the filtrate was determined by a Shimadzu 160 A UV–visible spectrophotometer, at the maximal adsorption wavelength of MG, λ_{max} = 578 nm (Ameur et al., 2017).

The concentration of dye, adsorbed by adsorbent was calculated from the difference between the initial and the final concentration of dye solution obtained before and after contact between the adsorbent and the synthetic dye solution.

Percentage removal of the CV dye and the amount of CV dye adsorbed per unit mass of the adsorbent (mg/g) at equilibrium are obtained by Eqs. (1) and (2) respectively (Ahmad, 2009).

$$\text{Removal efficiency}(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$\text{Adsorption capacity}(mg/g) = q_e = (C_0 - C_e) \times \frac{V}{m} \quad (2)$$

where C_0 (mg/L), C_t (mg/L) and C_e (mg/L) are the concentrations of the dye initially, at time t and at equilibrium, respectively, q_e is adsorption capacity (mg/g), V is the volume of the CV solution (L) and m is the mass of natural clay (g).

3. Result and discussion

3.1. Physicochemical characterization

The X-ray diffraction (XRD) pattern and morphological observations by TEM of the RSC were shown in Fig. 1a. The crystalline structure of the RSC identified by XRD measurements showed that clay is composed mainly of smectite (S), kaolinite (K) and illite (I) (Bel Hadjltaief et al., 2013). These minerals are characterized by their (001) basal reflections at 14.5, 10.1, and 7.15 Å, respectively. The main impurity in the raw clay is quartz, as indicated by the sharp (101) basal reflection at 3.34 Å. TEM image further confirm that structure is characteristic of smectite clay and the basal d-spacing smectite was 15.4 Å.

Nitrogen adsorption-desorption for the clay sample follow a type-IV isotherm (IUPAC) with a tight hysteresis loop at high relative pressures, p/p0 = 0.4–0.9, which points to the presence of mesopores (Bel Hadjltaief et al., 2016). The specific surface area (S_{BET}), average pore size by BET, and total pore volume of the RSC obtained from N_2 adsorption-desorption isotherms were 74 m^2/g, 15 Å, and 0.19 cm^3/g, respectively. Investigation of the pore size distribution using Barrett-Joyner-Halenda (BJH) analysis showed that the pore size distribution was in the mesopore range (5–50 nm).

FTIR analysis was conducted to evaluate the roles of functional groups on the clay surface in the adsorption process. Fig. 1b shows the FTIR spectra of the RCS before and after dye sono-adsorption. In the raw clay, the presence of OH stretching vibration of the structural hydroxyl groups in the clay and water molecules at 3630 and 3340 cm^{-1} as well a typical band of the silicate components appear between 1200 and 400 cm^{-1}.

3.2. Effect of contact time: comparative study

Batch experiments were carried on, in order to investigate the efficiency of adsorption and Sono-assisted adsorption processes of crystal violet dye removal. For this, the initial dye concentration, adsorbent dosage and contact time were adjusted to 50 mg/L, 0.5 g/L and 60 min, respectively. As seen in Fig. 2 the efficiency of adsorption and Sono-assisted adsorption on smectite clay were obtained to be 71.9% and 100%, respectively. Furthermore, the results sign that removal proceeds faster using sono-adsorption than adsorption process. The efficiency of CV removal increases quickly after less than 20 min in the first case; whereas it takes more than 60 min to full removal in the second case. Fig. 2b reports a picture of color change in the reaction solution during the adsorption and Sono-assisted adsorption processes that indicated Sono-assisted adsorption is very faster than adsorption, after 30 min