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Study of malachite green adsorption by organically modified clay using a batch method

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ABSTRACT

The adsorption of toxic dye malachite green from aqueous effluents by organically modified clay was studied in a batch system. The organoclay (OC) used was prepared by the intercalation of cationic surfactant hexadecyltrimethylammonium bromide in a Mexican montmorillonite. The effects of initial dye concentration, temperature, pH, and contact time were investigated. The OC showed a high dye removal (99.6%) from an initial dye concentration of 60 mg L^{-1} at pH 6 and 25°C . The adsorption capacity was independent of pH and increased with the temperature. Equilibrium data were well fitted by Langmuir adsorption model. The rate of sorption was adjusted to a pseudo second-order kinetic model.

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1. Introduction

Malachite green (MG) is a synthetic dye (Fig. 1) which is widely used as biocide in the aquaculture as well as a dye in textile industry. It is also applied as a food coloring agent, food additive, medical disinfectant and anthelmintic [1,2]. However, despite its wide use, MG represents a risk to the consumers of treated fish because its adverse effects on the immune and reproductive systems, carcinogenic, genotoxic, mutagenic and teratogenic properties. For these reasons and because that this colorant is highly accumulative within edible fish tissues, a zero tolerance has been established. The United States and the European Council have imposed a strict ban on the use of malachite green in all categories of food-producing fish [3]. In addition to this, discharge of MG into the hydrosphere can cause environmental degradation as it gives undesirable color to water and reduces sunlight penetration [1–4]. Therefore, it is important to remove MG from aqueous effluents before they are discharged into bodies of water. Many methods have been developed for color removal such as electrocoagulation, flotation, chemical oxidation, filtration, ion-exchange, ozonation, membrane separation and microbial degradation [5]. Adsorption processes are

gaining wider acceptance due to their high efficiency and ability to separate a wide range of compounds from liquids and, although commercial activated carbon is a preferred adsorbent for dyes removal its cost and regeneration are elevated [6]. Therefore, much research concerning adsorbents from natural sources such as clays, zeolites, and other low-cost and available solid materials to remove dyes from wastewater has been undertaken [1,5,7–10]. Clay minerals are suitable for adsorption process due to their large specific surface area and nanometer-scale size. For example, the expandable montmorillonite clay is composed of two silica tetrahedral sheets with an octahedral alumina sheet. The montmorillonite surface is negatively charged due to isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and, Mg^{2+} for Al^{3+} in the octahedral layer. The negative charge is balanced by exchangeable cations such as Na, K, Ca and Mg in the lattice structure. In the presence of water these cations are hydrated therefore the clay surface is hydrophilic [11]. Recent progress in the synthesis of nanostructured materials offers an opportunity to modify surface properties of natural clays in order to increase their adsorption capacity for organic compounds. The organoclays (OCs) are prepared by introducing cationic surfactant molecules (e.g. hexadecyltrimethylammonium, HDTMA) into the interlamellar space of a clay (e.g. montmorillonite) through ion exchange, changing the surface properties of the natural clay from hydrophilic to hydrophobic [11]. The OCs are investigated for removal of a wide variety of organic compounds because of their unique sorption capacities. For example, phenol and derivatives

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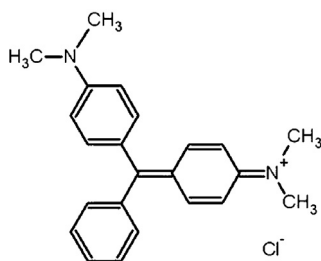


Fig. 1. Structure of malachite green: 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N,N-dimethylaniline [1].

[12,13]; tannins [14], naringin [15], dyes such as Methyl Orange [16], Reactive Red 141 [17], Reactive Blue 19 [18], Crystal Violet [19], Congo Red [20] and Direct Red 2 [21], among others.

Given the above, the objective of the present work was to study the adsorption capacity of a prepared OC to evaluate its applicability to remove an ionic organic dye from aqueous solutions. The effects of concentration of solute, temperature, contact time, and pH on the MG adsorption were also studied.

2. Materials and methods

The host clay utilized was a montmorillonite from northern Mexico supplied by Arcillas Industriales de Durango, S.A., and the surfactant HDTMA $C_{19}H_{42}BrN$ (99% pure) was purchased from Sigma–Aldrich Chemical Co. The MG dye $C_{23}H_{25}ClN_2$ (96% pure) was purchased from Sigma–Aldrich Chemical. The OC was obtained by adding amounts of surfactant equivalent to 100% of the value of the cation exchange capacity of the host clay. The procedure used to prepare and characterize the OC was described in a previous paper by Arellano-Cárdenas et al. [15]. The characterization of the OC by X-ray diffraction and nitrogen gas adsorption, showed a basal spacing $d(001)$ of 2.012 nm, BET specific surface area of $9.3 \text{ m}^2 \text{ g}^{-1}$, and an average pore diameter of 11.35 nm. The point of zero charge (pH_{PZC}) of the OC was of 8.0, as determined by potentiometric method. The pH was measured by a Hanna HI 2210 pH-meter. The MG concentration in aqueous solution was determined using a Thermo Scientific Genesys 10 UV spectrophotometer.

2.1. Batch adsorption experiments

The adsorption of MG on the OC was carried out using a batch process [22]. A series of flasks containing 0.2 g of the OC, 0.025 L of the solution of MG (concentration ranging from 10 to 500 mg L^{-1}), and pH 6 were equilibrated in a temperature-controlled, water-bath shaker at 25°C for 24 h. Preliminary experiments showed that the sorption was completed within 12 h, but to ensure that the equilibrium was attained, a 24 h time period was used. After the equilibrium was reached, the suspensions were filtered through Whatman No. 42 filter paper. The remaining solutions were analyzed for the concentration of residual MG by spectrophotometry at 424 nm.

The specific amount of solute adsorbed was calculated using the following mass balance Eq. (1):

$$q_e = (C_0 - C_e) \left(\frac{V}{W} \right) \quad (1)$$

where q_e is the adsorption capacity of the adsorbent at equilibrium (mg g^{-1}); C_0 and C_e are the initial and equilibrium concentrations of solute, respectively (mg L^{-1}); V is the volume of the aqueous solution (L) and W is the mass of adsorbent used (g). Adsorption experiments were also conducted at two additional temperatures, 40 and 60°C , as described above. To determine the influence of pH, the adsorption experiments were carried out using 0.2 g of the OC,

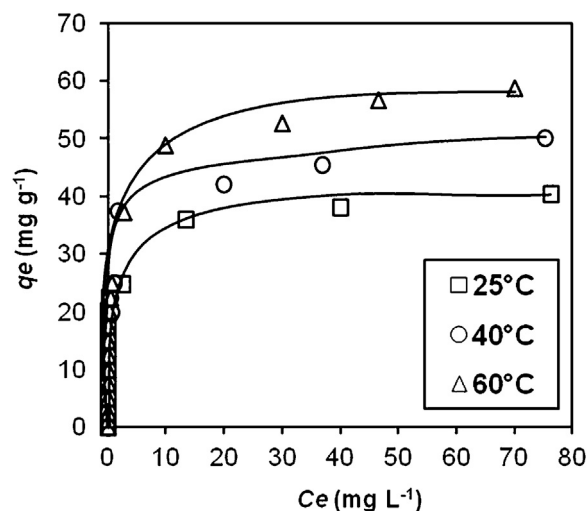


Fig. 2. Malachite green adsorption isotherms on the organoclay obtained at different temperatures (contact time 24 h and pH 6).

0.025 L of MG solution with an initial concentration of 60 mg L^{-1} at 25°C , for 24 h. The pH of the solutions was carefully adjusted between 2 and 10 with 0.1N HCl or NaOH by using a pH meter. The MG concentration in aqueous solution was determined at 424 nm in the pH range of 2–7, and at 383 nm for pHs values of 8–10. The kinetic studies were performed using 0.2 g of the OC, 0.025 L of MG solution with initial concentration of 60 mg L^{-1} , pH 6, at temperatures of 25, 40 and 60°C , for 24 h. The reported results are the average of triplicate measurements.

3. Results and discussion

3.1. Adsorption isotherms

The adsorption isotherms were obtained by plotting the amount of MG adsorbed by the solid phase (OC) q_e (mg g^{-1}), against MG liquid phase concentration at equilibrium C_e (mg L^{-1}) (Fig. 2). The isotherms obtained at different temperatures display an H-type shape according to the Giles et al. [23] classification, which indicates that the MG has such high affinity for the OC that in solutions with relative low concentration ($<60 \text{ mg L}^{-1}$) it was completely adsorbed. Therefore, the initial part of the isotherms was vertical. The plateau reached after indicating the formation of the monolayer.

The OC had an affinity for MG despite that its surface area ($9.3 \text{ m}^2 \text{ g}^{-1}$) was smaller than other adsorbents, therefore the distribution and arrangement of the intercalated surfactant in the OC was responsible for the adsorption efficiency rather than the BET-N_2 surface area.

3.2. Effect of temperature

It is also observed in Fig. 2 that the adsorption capacity increased from 40.5 to 59 mg g^{-1} for an increase in the temperature from 25 to 60°C , therefore the process was endothermic, indicating that several kinds of interactions could be between the OC and the dye, such as hydrophobic links between non-polar parts of the MG molecules and the alkyl chains of the intercalated surfactant, Van der Waals forces, ion–dipole interactions, and even chemical bonding. The endothermic adsorption of dyes has been reported for the cationic dye Crystal Violet [19], Direct Red 2 [21], and Congo Red [20] by HDTMA-montmorillonite.

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