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Research Paper

Adsorption of methylene blue, crystal violet and congo red from binary and ternary systems with natural clay: Kinetic, isotherm, and thermodynamic

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ABSTRACT

The adsorption of Methylene Blue (BM), Crystal Violet (CV) and Congo Red (CR) onto natural clay from Agadir region in the binary and ternary system was carried out. All the parameters influencing the adsorption of three dyes were studied namely effect of percentage, contact times (20–120 min), initial dye concentration (100–600 mg L^{-1}), temperature (22–50 °C), and dye solution pH (2–12). The obtained results showed that the adsorption of MB, CV, and CR is highly dependent on the initial dye concentration, the temperature, and the dye solution pH. The kinetic study was performed by applying two kinetic models, the pseudo-first-order and the pseudo second-order. According to the obtained results, the pseudo-second-order model is better described the adsorption of dyes onto natural clay. The adsorption isotherms were studied such as Langmuir, Freundlich, the obtained results indicate that the adsorption followed the Langmuir model with correlation coefficients which are very close to 1. The maximum adsorption capacities for three dyes are 202.13 mg g^{-1} for MB (MB + CV), 289.59 mg g^{-1} for MB (MB + CR), 281.31 mg g^{-1} for MB (MB + CV + CR), 179.28 mg g^{-1} for CV (CV + MB), 289 mg g^{-1} for CV (CV + CR), 280.61 mg g^{-1} for CV (CV g MB + CR), 253.53 mg g^{-1} for CR (CR + MB), 240.06 mg g^{-1} for CR (CR + CV) and 264.54 mg g^{-1} for CR (CR + MB + CV). The thermodynamic study showed that the adsorption of dyes in the binary and ternary system is spontaneous, physical and endothermic.

1. Introduction

The presence of dyes in textile effluents can pose a serious environmental menace when they are discharged into biosphere without previous treatment or with an insufficient level of treatment [1–4]. Treatment will therefore be essential to remove these dyes which are harmful to the environment [5–7]. Several techniques have been developed to remove dyes from wastewater such as coagulation/flocculation [8,9], oxidation/ozonation [10], membrane separation [11,12], photodegradation [13] et biological process [14], but most of these conventional methods are beginning to prove insufficient for simple and effective treatment, in addition they are very expensive [15]. It is necessary to think about effective techniques and inexpensive. Adsorption onto activated carbon has been recognized as one of the best techniques for the treatment polluted water by organic and inorganic materials, because the activated carbon has a high adsorption capacity due to its large surface area [16,17], but activated carbon remains very expensive and onerous [18]. Consequently, the treatment of water by adsorption onto natural materials such as clays responds to this constraint in an efficient and economical manner. Clays are now considered as interesting adsorbent materials, due to their low-cost, their abundance in nature, their small size (less than 2 μm), their high specific surface area, high cation exchange capacity and high chemical stability [19,20]. Consequently, these minerals are considered as natural wells to be facing to organic and inorganic pollutants.

Our main objective is to apply our support as an effective adsorbent to treat textile effluents, which contains different types of dyes namely cationic, anionic, and neutral. In this context, we have tested the effectiveness of our adsorbent which has several advantages such as its availability and low cost because it requires no treatment, in the mixture of dyes in a binary and ternary system. In our work, we chose three dyes, Methylene Blue, Crystal Violet (cationic type), and Congo Red (anionic type) as model dyes (Fig. 1), because of their harmful effects on health and the environment. Methylene Blue is much used in textile, printing, dyeing wood and strainers for medicinal surgery [21–23]. Crystal Violet dye is widely used in coloring paper, cotton and silk [24], it is also employed in animal and veterinary medicine as a biological stain [25]. Congo Red is employed as colorants in textiles, printing,

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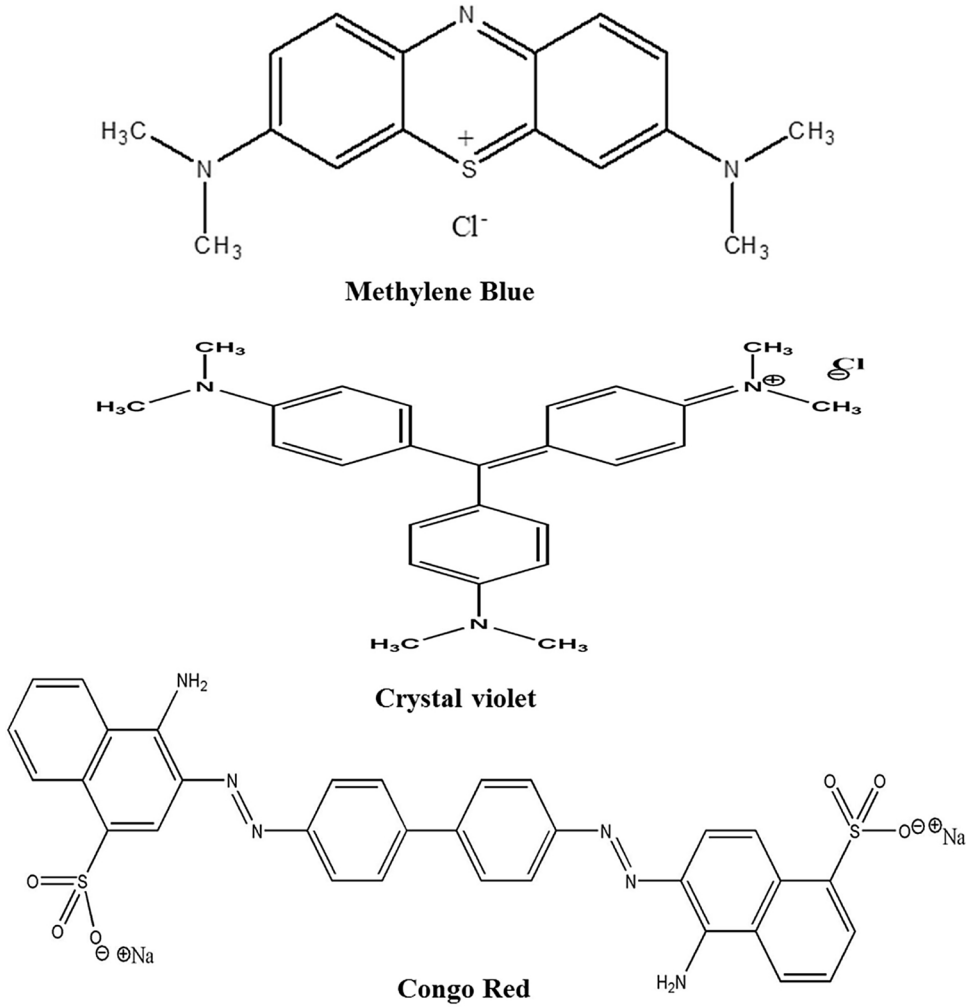

Fig. 1. Chemical structures of dyes used.

dyeing, paper, and plastic industries and also as the indicator of pH [26–28]. This dye can cause cancer, vomiting, jaundice, skin irritation, diarrhea in human beings [29–35]. For this reason, we have carried out the adsorption of MB, CV, and CR onto the clay to evaluate the behavior of these three dyes in binary and ternary mixtures. We studied all the parameters influencing the adsorption of these dyes in the mixtures such as the percentage effect, the contact time, the initial dye concentration, the temperature and the initial dye solution pH. The adsorption isotherms, kinetic models and thermodynamic study were performed to describe the mechanism involved in the adsorption process.

2. Materials and methods

2.1. Materials

The natural clay was collected from Agadir region and was crushed to obtain clay with a diameter less than 50 μm [36]. Methylene Blue (MB) is a cationic dye, the molecular formula $C_{16}H_{18}ClN_3S{\cdot}3H_2O$, a molar mass of 373.90 g mol $^{-1}$ and a maximum absorbance is equal 661 nm. Crystal Violet (CV) is a cationic dye, the chemical formula $C_{25}H_{30}ClN_3$, a molar mass 407.979 g mol^{-1}, and a maximum absorbance is 589.5 nm. Congo Red (CR) is an anionic diazo dye, the chemical formula $C_{32}H_{22}N_6Na_2O_6S_2$, a molar mass 696.66 g mol^{-1} and a maximum absorbance is 498 nm. These three dyes were purchased from Sigma-Aldrich and used without purification.

2.2. Characterization

According to our previous study [36,37], the results of the analyzes are:

The X-ray diffractogram shows that the natural clay is characterized by the presence of the dolomite phase which is the majority. This phase is confirmed by the existence of intense peaks at 21.6°, 24.01°, 30.89°, 33,46°, 37.3°, 41.11°, 43.77°, 44.85°, 49 0.21°, 50.5°, 51.06°, 58.92° (in 2θ) which may be attributable to the Miller indices:(101) (012) (104) (006) (110) (113) (021) (202) (024) (018) (116) (211), by comparison with the standard JCPDS N°. 36-0426 (corresponding to the dolomite). In addition, this diffractogram also shows the existence of a minority phase corresponding to silica, whose peaks 26.64°, 35.98°, 50.13°, 56.80° (in 2θ) attributable to the Miller indices (101) (110) (112) (103) which is in accordance with standards JCPDS N°. 33–1161(Fig. 2) [36].

The FTIR spectrum shows some characteristic bands of the silica in the zone 1250–700 cm^{-1}. Indeed, the bands appear at 1250 and 1000 cm $^{-1}$ are due to the stretching mode of Si-O and Si-O-Si respectively. Silica is also justified by an intense peak at 1099 cm^{-1} due to Si-O-Si stretching vibration. In addition, the bands appear at 791 and 728 cm^{-1} and at 474 cm^{-1} are attributed to the Si-O stretching vibration. It remains to be noted that the absorption spectra located at 3423 cm^{-1} (medium intensity) and 1638 cm^{-1} correspond to the hydroxyl group OH and the deformation of the H_2O molecules respectively (Fig. 2) [36].

SEM analysis shows that this sample is characterized by the presence of particles having different sizes and uniform morphology. The