Adsorption of Cationic Dye onto Silt Dam from Aqueous Solution

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Abstract: *In this work, the potential feasibility of silt dam for removal of malachite green (MG), a cationic dye from aqueous solution was investigated. XRD, MEB and chemical composition analysis were used to characterize the adsorbent material. XRD analysis identified illite as the major clay mineral. The effects of contact time and temperature (298, 303, 313 and 323 K) on the malachite green adsorption have been examined. The results indicated that dye removal was seen to increase with increasing contact time until equilibrium. The experimental isotherm data were analyzed using the Langmuir and Freundlich equations. Data isotherms were good fitted by Freundlich equation. Two kinetic models, the pseudo first order and second-order equations, were selected to follow the adsorption process. Kinetic parameters, rate constants, equilibrium adsorption capacities and correlation coefficients, for each kinetic equation were calculated and discussed. It was shown that the adsorption of malachite green onto adsorbent could be described by the pseudo second-order equation.*

Keywords: *Adsorption; Malachite Green; Kinetic; Silt.*

1. Introduction

The textile industries are the greatest generators of liquid effluent, due to the high quantity of water used in the dyeing processes [1]. Malachite Green (MG) is a cationic dye and widely used for the dyeing of leather, wool and silk, paper, as a food-coloring agent, food additive, in medical disinfectant and fish industries [2]-[3]. The consumption of MG has many adverse effects due to its carcinogenic, genotoxic, mutagenic and teratogenic properties [4]. Many studies have been devoted to the elimination of dyes using several techniques such as biological methods [5], membrane techniques [6]-[7] and the advanced oxidation processes [8]. Adsorption techniques have potential for removing organic and inorganic pollutants from wastewater due to their high efficiency and ability to separate a wide range of compounds [9]. Low-cost adsorbents include natural, agricultural, and industrial by-product wastes. They are attractive because of their abundant availability at low or no cost and their good performance in removing dyes from aqueous solutions. Many adsorbents have been tested to remove malachite green dye from aqueous solutions such as activated carbon [10], chitosan [11], silica gel [12], zeolite [13] and clay [14].

The aim of the present work is to examine the possibility of using the silt to remove the dye. The silt was obtained from Chorfa dam (Mascara, western Algeria). However to characterize the material, we use the XRD, BET and chemical analysis techniques such as point of zero charge (PZC). The effects of various adsorption conditions such as contact time and temperature have been investigated. To fit the adsorption experimental data, we used Langmuir and Freundlich isotherm models. A kinetic study was also evaluated.

2. Materials and Methods

2.1. Adsorbent

The silt used in this investigation was obtained from Chorfa dam in Sig region (Mascara, Algeria). The chemical composition of the raw silt was determined by a Cameca SX-50 electronic microprobe. The grain size of this material was 75 µm. Sample of raw silt was washed with deionized water Milli-Q, dried at 95 °C for 24 h

and sieved. X-ray analyses were performed using INEL CPS 120 diffractometer employing Co Ka radiation. The specific surface area of solid was measured, at 77 K, using the BET N_2 method via an ASAP 2010 instrument (Micromeritics, Norcross, GA, USA).

The point of zero charge of raw silt was determined by the solid addition method [15,16]. The value of finding pH (PZC) is approximately 7.83. This means that in the values of pH lower than the pH (PZC) the surface electric charge of the material will be positive, whereas for the values of pH over the pH (PZC) the electric charge becomes negative.

2.2. Adsorbate

Malachite Green (MG) used in this study was supplied by Merck Chemicals and used without further purification. The chemical formula of MG is: $C_{23}H_{25}N_2Cl$.

2.3. Adsorption Experiment

A malachite green solution was prepared in the range of initial concentrations 10–100 mg/L. For each experiment, 20 ml of dye solution was added to 0.2 g of the raw silt. The suspensions were shaken at room temperature (22 ± 2 °C) for 2 h. The pH was adjusted at 7 by the addition of 0.1 N NaOH or 0.1 N HNO_3 solutions. When the adsorption procedure completed, the mixture was centrifuged to get a supernatant liquid. The residual concentrations of MG were detected using UV-vis spectrophotometer (UV- mini 1240) at λ=615 nm.

3. Results and Discussion

3.1. Characterization of Adsorbent

The raw silt composition is presented in table 1. The result of chemical composition investigation indicates the presence of silica, lime and alumina as major constituents, as well as iron and magnesium oxides. The XRD pattern of the natural sample is given in Figure 1. The silt contains clay minerals, calcite and quartz as main components, with dolomite as accessory mineral. Illite is the dominant clay mineral, the kaolinite is a minority. The specific surface area was found to be 65.57 m^2/g. It is noted that this value is almost the same or higher compared with the surface area of the other materials such as kaolinite [17], montmorillonite [18] and china clay [19].

TABLE I: Chemical composition of raw silt (wt%).

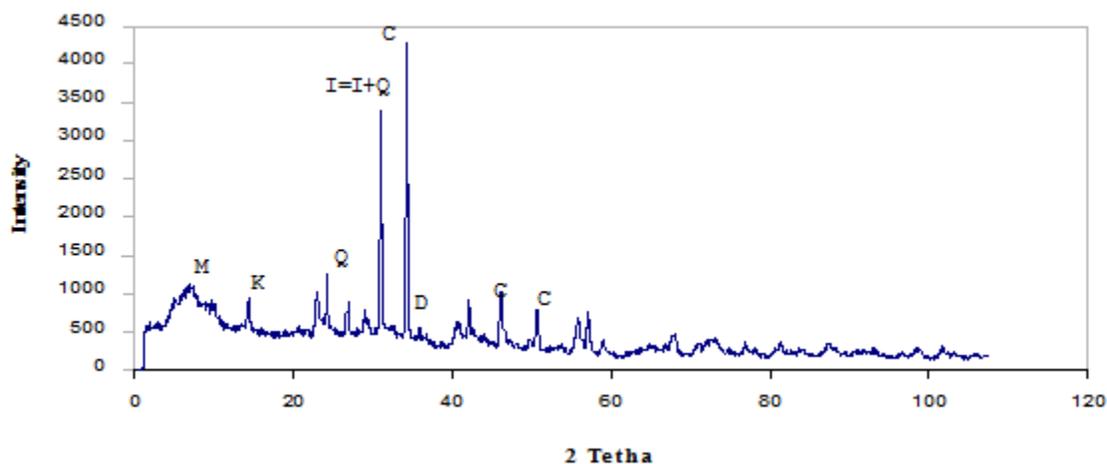| Elements	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Weight loss
Percentage	29,37	18,22	9,12	3,84	1,33	36,46

Fig. 1: XRD patterns for raw silt. Montmorillonite (M), illite (I), kaolinite (K), quartz (Q), calcite (C) and dolomite (D)

3.2. Effect of Contact Time

The uptake of MG as a function of contact time is shown in Figure 2. As illustrated in Figure 2, adsorption of MG increased with rise in contact time up to 50 min. The adsorption process attained equilibrium after 90 min. The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active binding sites on the adsorbent surface In the later stage, the sorption is likely an attachment-controlled process due to less available sorption sites. Similar findings for MG adsorption onto other natural adsorbents have been reported by other investigators [20]–[22].
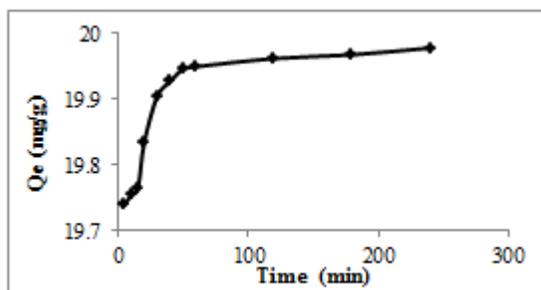
Fig. 2: Effect of contact time on adsorbed amount of GM onto the silt

3.3. Adsorption Isotherms

The relation between the amount adsorbed of MG and its equilibrium concentration in aqueous solution is shown in Figure 3. It can be seen that when the equilibrium concentration of MG increases, the amount adsorbed increases. Using the classification of Giles and al. [23], the experimental isotherm obtained is of type S, indicated cooperative adsorption. The adsorbed amount is 19.5 mg/g. The comparison of the maximum MG adsorption capacities of various sorbents shows that silt has higher adsorption capacity of MG than many of the other adsorbents from aqueous solutions, such as tamarind fruit shell 1.95 mg/g [24], bentonite is 7.72 mg/g [25] and Arundo donax root carbon is 8.69 mg/g [26].
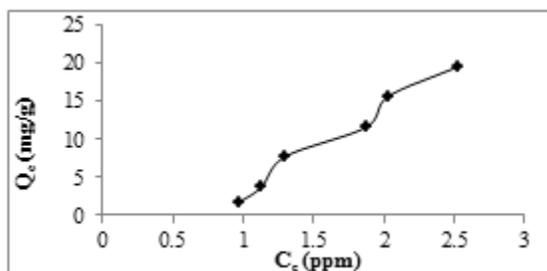
Fig. 3: Green malachite adsorption isotherm on silt at ambient temperature

3.4.Fitting models

The adsorption data of MG have been correlated with the Freundlich and Langmuir models. The linear form of Langmuir's isotherm is given by the following equation [27]-[28].

$$\frac{Q_e}{Q_m} = \frac{K_L C_e}{1 + K_L C_e} \tag{2}$$

Equation (2) can be represented by linear form:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \tag{3}$$

where, Q_e is the amount of MG adsorbed (mg g^{-1}), C_e is the equilibrium concentration of the MG and Q_m and K_L (L/mg) are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively.

When C_e/Q_e was plotted against C_e, straight lines with slope $1/Q_m$ were obtained, indicating that the adsorption of MG on silt follows the Langmuir isotherm. Unfortunately, we have obtained results that are mathematically not consistent with the Langmuir equation. Straights obtained have negative slopes; they have not been presented in this manuscript, although this model has been successfully applied to describe the sorption of MG onto hen feathers [29], indian clay [30] and bentonite [31]. The poor ability of this model to represent the experimental data could have been due to the fact that the Langmuir isotherm does not take into account adsorbate–adsorbate interactions.

The well-known logarithmic form of Freundlich model is given by the following equation [32]:

$$Q_e = K_f C_e^{1/n} \tag{4}$$

Equation (4) can be expressed in linear form:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \tag{5}$$

where K_f and n are Freundlich constants with K_f (mg/g $(L/mg)^{1/n}$) being the sorption capacity of the adsorbent. Index n is the heterogeneity factor [33]-[34].

TABLE II: Freundlich isotherm constants for MG adsorption at different temperatures

T (°C)	K_F	1/n	R^2
30	2,699	1,31	0,99
40	2,545	1,63	0,98
50	3,206	1,98	0,98

Table 2 shows that the experimental data of isotherms at different temperature are suitably described by the Freundlich model, because the value of R^2 is very high (bigger than 0.98). The fitness of the adsorption data to the Freundlich isotherm implies that adsorption of MG onto silt was multilayer adsorption applicable to heterogeneous surfaces. In previous work, the model Freundlich has described better the experimental adsorption data of malachite green onto the soil [35], lignite [36] and the maize cob [37].

3.5. Kinetic studies
3.5.1. Pseudo-first order equation
The linear form of the pseudo-first order rate equation as suggested by Lagergren is given as [38]:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \tag{6}$$

where Q_t is the amount of adsorbate adsorbed (mg/g) at time t, k_1 is the rate constant (min^{-1}) and Q_e the equilibrium adsorption capacity. The values of k_1 and Q_e were determined from the slope and intercept of the plots of $\ln(Q_e - Q_t)$ versus t (figure not shown) and are listed in Table 3 along with the correlation coefficient, R^2.

From the kinetic data in Table 3, it can be seen that the correlation coefficient for the pseudo-first-order kinetic model is very low. Moreover, a large difference between theoretical and experimental equilibrium adsorption capacity, indicating a poor fit of the pseudo-first-order equation to the experimental data.

3.5.2. Pseudo-second order equation
An expression of the pseudo-second order rate based on the solid capacity model is expressed as [39]:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{7}$$

where k_2 is the rate constant for second-order adsorption (g/mg.min). If the plot t/Q_t versus t shows a linear relationship, the second-order kinetic model is applicable. The plot of t/Q_t against t is shown in Figure 4. Contrary to the pseudo-first-order equation, the fitting of the kinetic data in the pseudo-second-order equation

showed excellent linearity with high correlation coefficient ($R^2 = 0.999$). The data obtained for the pseudo-second-order kinetic model is tabulated in Table 3. An analysis of this data suggests that the kinetic of adsorption of MG on silt can be explained more accurately by the pseudo-second-order kinetic model. Furthermore, the calculated Q_e value was found to be quite close to the experimental Q_e value. A similar phenomenon was also observed in adsorption of MG onto bentonite [25], arundo donax root [26] and degreased coffee bean [40].
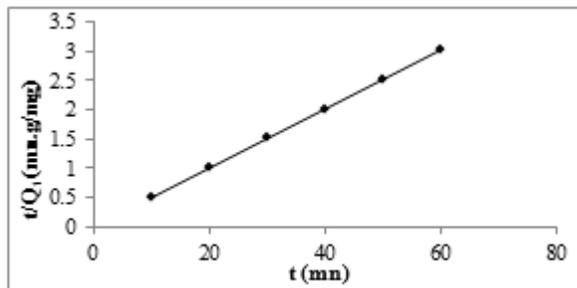

Fig. 4: Pseudo second order kinetic for MG adsorption

TABLE IV: Kinetic models for MG adsorption.

Pseudo-first order		Pseudo-second order	
K_1 (min^{-1})	R^2	K_2 (g.mg^{-1}.min^{-1})	R^2
0,033	0,952	0,357	0,999

4. Conclusion

In this study, natural dam silt of Algerian origin was tested and evaluated as a possible adsorbent for removal of MG, a cationic dye from its aqueous solution. The isotherms exhibited the Freundlich behavior at all temperatures, which indicates a heterogeneous surface binding. The adsorption data showed good agreement with the pseudo-second-order kinetic model. Taking into consideration all the above obtained results, it can be concluded that natural silt can be an alternative economic material to more costly adsorbents used for dye removal in wastewater treatment processes.

5. References

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