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Modeling and analysis of dynamic malachite green adsorption onto natural clay

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Abstract

A continuous fixed bed (column) study was carried out by using natural clay of Safi as an adsorbent for the removal of malachite green dye, from aqueous solutions. The effects of the operation conditions of the fixed bed on the breakthrough curve were investigated using continuous-flow column operation by varying the bed height (0.15–0.3 m) and the feed concentrations (160 – 260 mg/l). Breakthrough analysis revealed that early saturation and lower MG removal takes place at higher flow rate and at higher concentrations.

Adams- Bohart was applied to experimental data to determine the characteristic parameters of the column that are useful for process design. the Adams- Bohart model was only used to predict the initial part of the dynamic process. An attempt has also been made to model the data generated from column studies using the empirical relationship based on Bohart–Adams model, the bed depth service time analysis (BDST) model was applied at different concentrations to predict the breakthrough curves. The model is found suitable for describing the adsorption process of the dynamic behaviour of the MG column and the data were in good agreement with BDST model.

1. Introduction

The worldwide high level of dye production and their extensive use in many applications generates coloured wastewaters which cause severe water pollution [1]. In effect, the discharge of contaminents such as dyes in the environment is worrying for both toxicological and esthetical reasons as damage the quality of the receiving streams and is toxic to food chain organisms [2]. Thus, dyeing wastewater may damage the ecosystem of receiving water, and the environment in total, due to the carcinogenic, mutagenic, and allergenic characteristics of dyes. The treatment of such a toxic wastewater is necessary to avoid environmental contamination [3].

Malachite green (MG) is an N-methylated diaminotriphenyl methane dye, which is known to be highly toxic to mammalian cells and to act as a tumour enhancing agent. However, despite the large amount of data on its toxic effects, it is still used in aquaculture and other industries [4].
One of the effective methods to remove color is to use an adsorbent to adsorb the dye molecules, which removes the colour from water [5].
Adsorption process is an innovative and economical alternative due to its performance and ease of operation [3]. Although activated carbons have been most widely used as adsorbents in wastewater treatment processes [6], clay material have been increasingly receiving much attention because it is promising low cost adsorbent [7].
The focus of this research was to evaluate the adsorption potential of the Moroccan crude clay in removing MG from aqueous solutions through batch and fixed bed. Experiments were conducted to optimize the system variables and to evaluate the adsorption capacity of MG onto clay. Dynamic experiments were performed to obtain breakthrough curves of dye through a fixed bed packed with raw Moroccan clay mixed with sand.

2. Experiments

2.1. Materiel

2.1.1 Adsorbate

The dye, malachite green oxalate, C.I. Basic Green 4, C.I. Classification Number 42.000, chemical formula $C_{27}H_{27}N_2O_6$, MW= 463.5 g/mol, λ_{max} = 618 nm (measured value) was used without purification. The chemical structure of malachite green oxalate is shown in Figure 1.

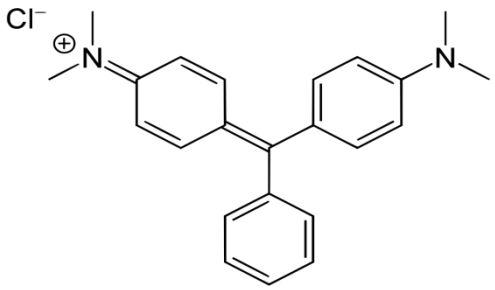

Figure 1: molecular structure of malachite green (MG)

2.1.2. Adsorbent materiel

2.1.2.1. The raw Moroccan clay

The Raw clay used in this work is collected from a natural basin in the region of Safi (Morocco), crushed and sieved to <0.08 µm size fraction. Then, it was dried at 105°C for 24h and used for further experiments. The chemical composition of this clay is: 53.11% SiO_2, 16.95% Al_2O_3, 5.94% Fe_2O_3, 3.51% CaO, 2.51% MgO, 0.2% SO_3, 4.64% K_2O, 0.26% Na_2O, 0.09% P_2O_5 [8].

2.1.3. Characterization of the RC:

The chemical composition of the adsorbent was determined by using Philips X' Cem X-ray fluorescence spectrometer (XRF).
Mineralogical identification was performed by XRD in Siemens D500 diffractometer using a 106 CuKα radiation (λ = 1.5406 Å), produced under conditions of 40 kV and 20 mA.

2.2. Methods

2.2.2. Dynamic studies

The behaviour of Moroccan clay in a fixed-bed column operation at room temperature was studied to determine the breakthrough point. Continuous flow adsorption studies were conducted in a glass column made of Pyrex glass tube of 2 cm inner diameter and 30 cm height which was filled

with mixed adsorbent: clay and sand mixtures. The adsorbent-sand mixtures were prepared by mixing adsorbent clays with quartz sand (3%wt of clay) in order to avoid clogging phenomenon.
A known quantity of mixed adsorbent was packed between a layer of 5 mm size glass beads in order to provide a uniform flow of the solution through the column and filter paper at the end of the column in order to prevent the escape of the clay. A known quantity of the clay mixed with the sand with quartz sand (3%wt of clay) was packed in the column to yield the desired bed height of the adsorbent (15 - 30 cm). Dye solution of known concentrations (160, 210 and 260 mg/l) at pH 6.5 was pumped upward through the column at a desired flow rate (4 ml/min). The MG solution was pumped from the bottom of the column to the top at a desired flow rate using a peristaltic pump. The MG solutions at the outlet of the column were collected at regular time intervals and the concentration was measured using a spectrophotometer [GBC (ajax, ontorio) UV/visible 9 [**9**] at 618 nm. The concentration of solution passing through the columns was monitored continually by collecting manually the samples in volumetric flasks. All the experiments were carried out at room temperature (25 ± 1°C). The breakthrough curves were constructed as C_t vs. time.

2.2.2. 1. The Adams–Bohart model

Bohart and Adams established the fundamental equations that describe the relationship between C_r, C_0 and time in an open system for the adsorption of MG. In spite of the fact that the original studies of Adams–Bohart were performed with the gas–charcoal adsorption system, its overall approach can be applied successfully in quantitative description of other systems. [10]. the model proposed assumes that the adsorption rate is proportional to both the residual capacity of the Moroccan clay and the concentration of the sorbing species. The mass transfer rates obey the following equations:

$$\frac{\partial q}{\partial t} = -k_{AB} q C_b \qquad (5)$$

$$\frac{\partial C_b}{\partial Z} = -\left(\frac{k_{AB}}{U_0}\right) q C_b \qquad (6)$$

k_{AB} is the kinetic constant (L mg^{-1} min^{-1}), C_b the bulk MG concentration in the solution in the column (mg L^{-1}), q represents the MG concentration in the solid phase in the column at any time (mg L^{-1}), U_0 the superficial velocity (cm min^{-1}) and Z is the height of the column (cm). For the solution of these differential equations system two assumptions are made: $t \rightarrow \infty$ and $q \rightarrow N_0$, (where N_0 is the saturation concentration (mg L^{-1})). When the differential equations system is solved, the following equation is obtained with parameters k_{AB} and N_0 [11]:

$$\text{Log}\frac{C}{C_0} = KC_0 t - KN_0\frac{Z}{U} \qquad (7)$$

C_0 and C are the inlet and outlet MG concentrations (mg L^{-1}), respectively. From this equation, values describing the characteristic operational parameters of the column can be determined from a plot of ln C/C_0 versus t at a given bed height and flow rate.

3. Results and discussion

3.1. Characterization of adsorbent:

The crude clay composition is presented in Table 1. SiO_2 and Al_2O_3 are the major constituents of the clay with other oxides present in trace amounts. The mineralogical composition of the crude clay, originally from a natural basin in the region of Safi (Morocco), was determined from X-ray diffractogram (Figure 2).

Element	Percentage (%)
SiO_2	53.11
Al_2O_3	16.95
Fe_2O_3	5.94
CaO	3.51
MgO	2.51
SO_3	0.2
K_2O	4.64
Na_2O	0.26
P_2O_5	0.09

Table 1: Mineralogical composition of the Crude Clay

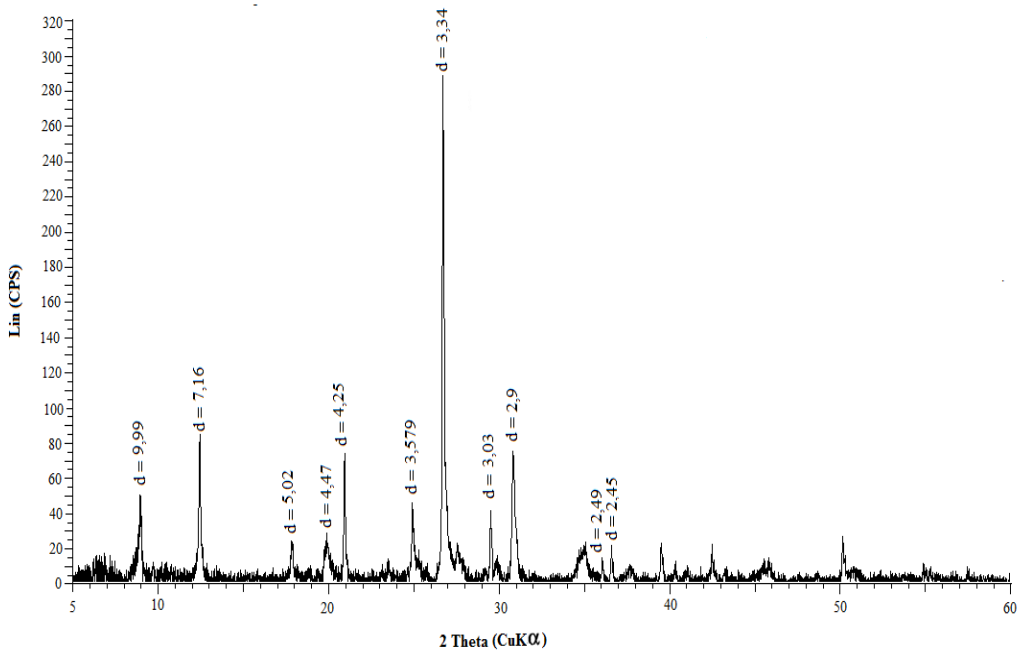

Figure 2: X-ray diffractometer analysis for the Crude Clay

The following mineral phases were identified: quartz, illite, kaolinite, dolomite and calcite. The predominant peaks found in the crude clay were 9.99 Å, 7.16 Å, 5.02 Å, 4.47 Å, 4.25 Å, 3.579 Å, 3.34 Å, 3.03 Å and 2.9 Å which correspond to illite, kaolinite, illite, kaolinite, quartz, kaolinite, quartz+illite, calcite and dolomite.

3.3. Results of dynamics adsorption studies

The results of MG adsorption on the mixed sand and clay using a continuous system were presented in the form of breakthrough curves which showed the loading behaviours of MG to be

adsorbed from the solution expressed in terms of residual concentration as a function of time (C_r vs. t). The breakthrough time (t_b) for the column operation was defined as the time when the effluent concentration (C_e) of MG dye reached 3% of the dye concentration (C_f).

3.3.1 Effect of initial dye concentration

The The change in the initial MG concentration has a significant effect on breakthrough curve as illustrated in Fig 3.

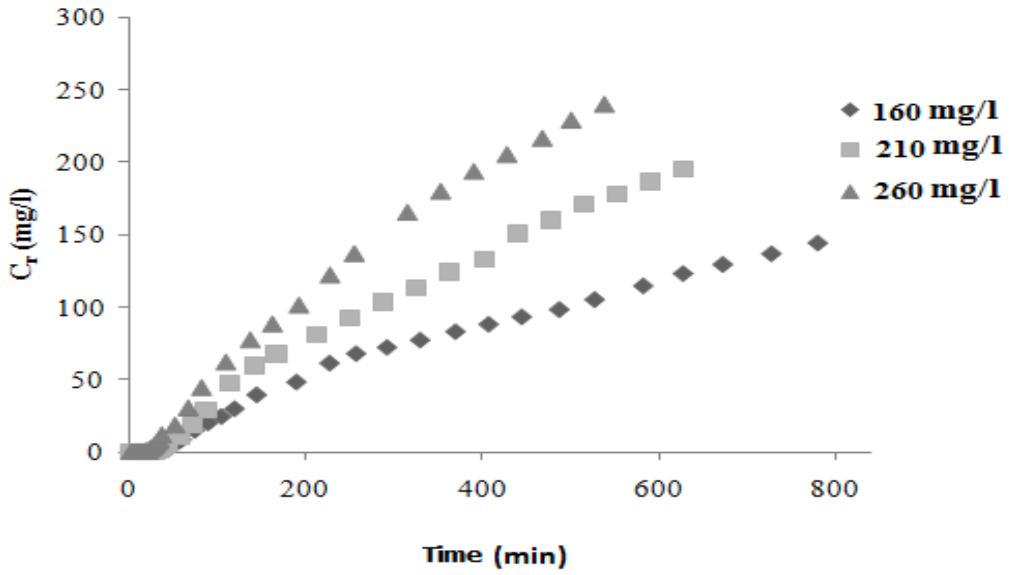

Figure 3: Break through curve for different dye concentration at constant bed height of 0.3 m and hydraulic loading rate of 4 ml/min

It shows the resulting breakthrough curves for MG at different inlet concentrations. It can be seen from this figure that there was a period of time where the residual MG concentration remained zero and then the residual concentration of the dye started to increase. The larger the initial dye concentration, the steeper is the slope of break through curve and smaller is the breakthrough time [12]. A decrease in breakthrough and the exhaustion time at higher initial concentration may be due to the rapid exhaustion of the sorption sites. Also the saturation of the bed is faster at higher MG concentration.

These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time, or in other words, the diffusion process is concentration dependent. As the dye concentration increases, dye loading rate increases, but so does the driving force for mass transfer, which in a decrease in the adsorption zone length. The net effect is an appreciable increase in adsorption capacity [12] as presented in Table 2.

Similar trends were obtained for Adsorption of basic dye using activated carbon [2], removal of lead II by using treated granular activated carbon [12], Adsorption of Brilliant Green dye from aqueous solution onto red clay [3].

3.3.2 Effect of bed height (adsorbent mass)

The influences of the fixed bed height, on the breakthrough curves were studied. for four bed heights of 15cm, 20cm, 25cm and 30 cm at dye concentrations of 160, 210 and 260 mg/l and at the hydraulic loading rate of 4 ml/min. Fig. 4, 5 and 6 show the breakthrough curve obtained for MG adsorption on the crude clay.

	Z (cm)	K (l/mg.min)	N_0 (mg/g)	R^2
C = 160 mg/l	15	0.0011	9.83	0.99
	20	0.001	10.50	0.96
	25	0.0008	11.07	0.94
	30	0.0005	12.40	0.95
C = 210 mg/l	15	0.00086	11.19	0.98
	20	0.0008	12.16	0.96
	25	0.0006	12.42	0.98
	30	0.0006	13.47	0.97
C = 260 mg/l	15	0.0006	11.94	0.98
	20	0.0006	12.61	0.96
	25	0.0006	13.1	0.97
	30	0.0004	14.34	0.98

Table 2: Parameters predicted from the Adams–Bohart andWolborska models at different inlet MG concentrations and bed height

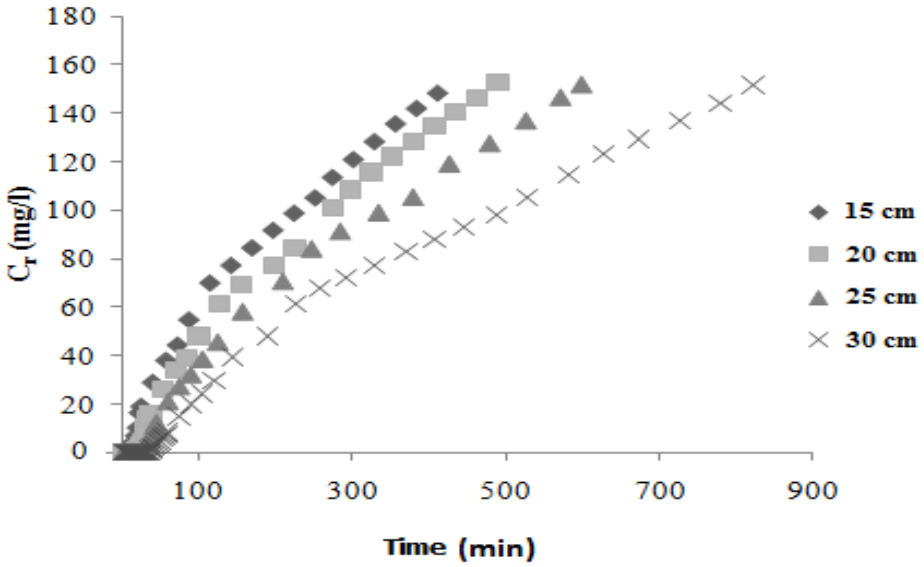

Figure 4: Breakthrough curves for MG adsorption on natural clay at different bed heights (initial dye concentration = 160 mg/l, flow rate = 4 ml/min, temperature = 25 ± 1°C)

As expected, the breakthrough point decreases with decreasing the bed height and increasing bed height increases the breakthrough time. The mass transfer zone in a fixed bed travels from the entrance of the bed and progresses towards the exit. Hence, for the same influent MG concentration and fixed bed conditions, an increase in the bed height results in a longer distance for the mass transfer zone to reach the exit and therefore an increase in the breakthrough time [13]. A higher MG uptake was also observed at a higher bed height due to the increase in the specific surface of the crude clay which provided more fixation binding sites for the dye to adsorb. The

increase in the adsorbent mass in a higher bed provided a greater service area which would lead to an increase in the volume of the solution treated [2].

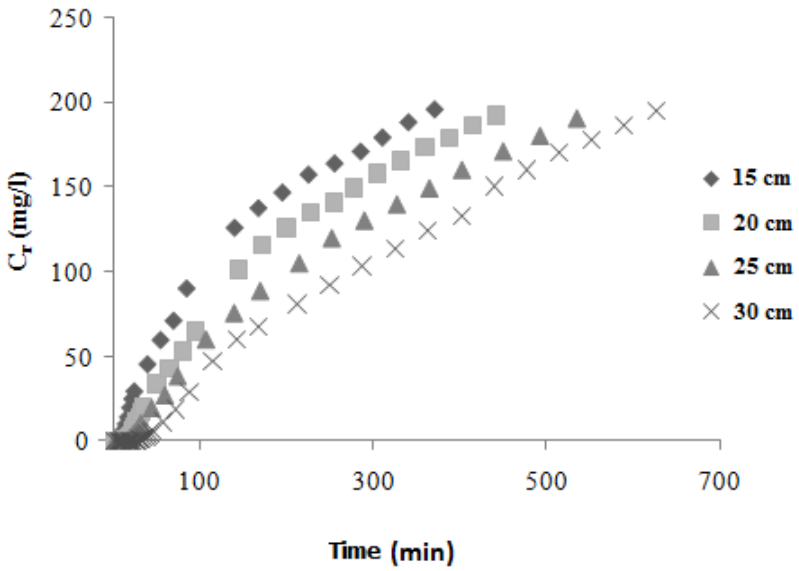

Figure 5: Breakthrough curves for MG adsorption on natural clay at different bed heights (initial dye concentration = 210 mg/l, flow rate = 4 ml/min, temperature = 25 ± 1°C)

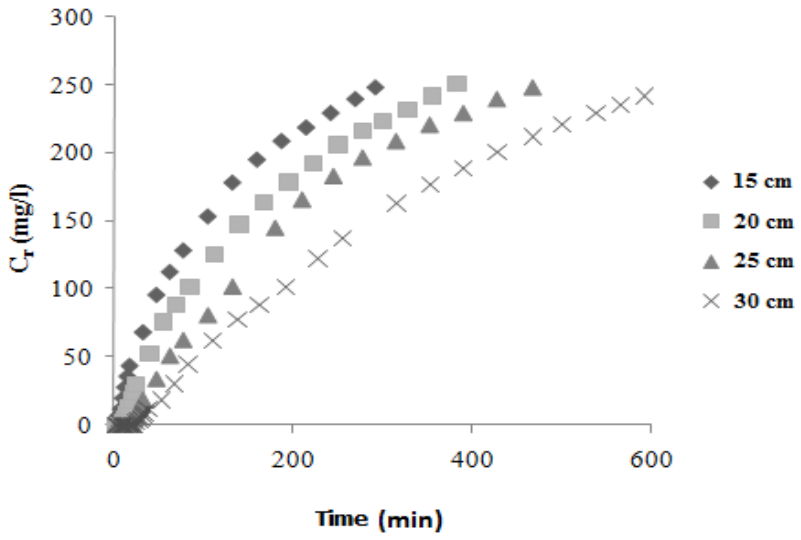

Figure 6: Breakthrough curves for MG adsorption on natural clay at different bed heights (initial dye concentration = 260 mg/l, flow rate = 4 ml/min, temperature = 25 ± 1°C)

Similar trends were obtained for Adsorption of basic dye using activated carbon [2], removal of lead II by using treated granular activated carbon [12], dye removal by low cost adsorbent [1], Adsorption of Brilliant Green dye from aqueous solution onto red clay [3].

3.3.3 Bed depth service time model

Bohart and Adams [14] developed an equation to describe the relationship between service time (t) and bed height (Z) for a fixed bed adsorber. Service time is referring to the time utilized by the adsorption column to reach the breakthrough point with specific saturation percentage, and it was related to adsorption operating conditions as:

$$\text{Log}\frac{C}{C_0} = KC_0t - KN_0\frac{Z}{U}$$

Hutchins [15] proposed a linear relationship to this equation, to become:

$$t = \frac{N_0}{C_0}\left[L - \frac{U}{KN_0}\text{Log}\left(\frac{C_0}{C_t} - 1\right)\right]$$

The service time and bed height are correlated with the process parameters (N_0 and k) and initial dye concentration, feed flow rate and effluent composition.
The results are listed in table 3.

Cc (mg/1)	160	210	260
q_{max} (mg/g)	9.48	11.52	12.74

Table 3: Column adsorption capacity, $Q_{0.3}$ at break through concentrations

It is expected from this table that the adsorption capacity increases with increasing initial dye concentration. As the dye concentration increases, dye loading rate increases, but so does the driving force for mass transfer, which in a decrease in the adsorption zone length [12].

Conclusion

Moroccan clay shows an interesting capacity in separating malachite green from water. The objective of this work was to study the dependence of adsorption on adsorbent and adsorbate (MG) characteristics by means of both batch and column studies. Conclusions from the present study are as follows:

For The batch adsorption process, The Redlich–Peterson isotherm is the best fit model for the equilibrium sorption of MG onto Moroccan clay although the Langmuir equation also provides a reasonable fit. Evaluation of the adsorption results obtained on the basis of different kinetic models showed that dye / clay system was best described by the pseudo second order model. The kinetic study revealed that approximately 25 minutes of agitation are sufficient to reach a complete equilibrium for the MG Raw clay system.

The results from the column test indicate the possibility of using fixed bed of mixed sand-clay in separation of dyes from water; it revealed that the continuous adsorption system represented by the breakthrough curves was dependent on the initial dye concentration and adsorbent bed height.

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