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Study of the Adsorption of Bright Green by a Natural Clay and Modified

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Abstract

The adsorption of Bright Green (BG), a cationic dye, was studied by clay treatment experiments by modification with an aqueous solution of a cationic surfactant. Hexadecyltrimethylammonium bromide (HDTMA) and Cetylpyridinium chloride (CPC) were used for the modification of the clay. Clay modified HDTMA showed the greatest adsorption capacity compared to the other adsorbents studied. The adsorption of HDTMA on BG depended on the adsorbent dose, the pH of the solution, the contact time and the initial dye concentration studied.

The adsorption data to correspond to the HDTMA experiments have been better described by the Langmuir isotherm model. The isothermal adsorption capacity of BG on HDTMA modified clay was found to be 45.5 mg/g (for an initial BG concentration of 50 mg/L), which is significantly higher than that of other adsorbents. The kinetics of adsorption of BG on clay modified by HDTMA has been described more precisely by the pseudo-second order kinetics model. The adsorbent was characterized by analysis of the Brunauer-Emmett-Teller surface (BET), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The BG adsorption mechanism on the surfactant-modified clay may comprise a hydrophobic interaction or van der Waals interaction or a combination of the two.

Keywords: Adsorption; Cationic dye; Surfactant; HDTMA; CPC; Modified clay

Introduction

Nowadays, wastewater effluents from different industries have become a major environmental concern. The treatment of water contaminated with textile dyes has been the subject of several studies aimed at reducing the intensity of the colors and the quantity of organic matter [1]. There are many methods for removing dyes from wastewater such as flocculation, chemical coagulation, oxidation, precipitation and filtration [2-6]. Among these methods, adsorption is the most effective technique for the treatment of wastewater [5-7]. Many adsorbents have been tested to reduce dye concentrations from aqueous solutions such as activated carbon [8], adsorbents including agricultural waste [9,10], natural phosphate [11], chitosan [12], kaolinite [13], montmorillonite [14]. However, the use of natural materials is a promising alternative because of their relative abundance and low commercial value. The surface properties of the natural clays can be substantially modified with large organic surfactants such as long chain quaternary alkylammonium salts such as HDTMA by ion exchange reaction. The intercalation of the cationic surfactants modifies only the surface properties, from hydrophilic to hydrophobic, but also greatly increases the basal spacing of the layers. The organo-clay becomes a more efficient adsorbent. In particular, the hydrophobic nature of the organo-layer suggests that the material can be used as a filter material to leach water from organic pollutants [15], transport of non-ionic contaminants into groundwater [16].

This work deals with the study of the potentiality of Tunisian natural clay with surfactants, Hexadecyltrimethylammonium bromide (HDTMA) and Cetylpyridinium chloride (CPC) as a low cost adsorbent for the removal of organic textile dye.

Experimental

Materials

Bright Green (BG) was purchased from Sigma–Aldrich. The formula weight of BG is 482.62 and its chemical formula is $C_{27}H_{34}N_2O_4S$. The maximum wavelength (λmax) of BG is 625 nm. The molecular structure of BG is illustrated in Figure 1. Organic surfactants used were Hexadecyltrimethylammonium bromide (HDTMA, formula weight: 364.45, and chemical formula: $C_{19}H_{42}BrN$) and Cetylpyridinium chloride (CPC, formula weight: 339.9, and chemical formula: $C_{21}H_{38}ClN$) were obtained from Sigma–Aldrich. The molecular structure of CPC and

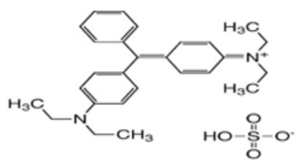
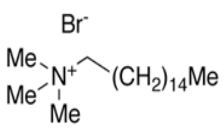
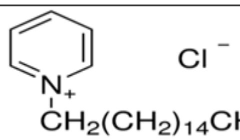
Molecules	Molecular structure
Bright Green (BG) $C_{27}H_{34}N_2O_4S$	
Hexadecyltrimethylammonium bromide HDTMA $C_{19}H_{42}BrN$	
Cetylpyridinium chloride CPC $C_{21}H_{38}ClN$	

Figure 1: Molecular structure of GB, HDTMA, and CPC.

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HDTMA are illustrated in Figure 1. Other chemical reagents, such as NaOH, HCl, and KCl were of analytical grade.

Preparation of the adsorbent

The absorbent clay used in this work which is named Gafsa clay located in the south of Tunisia. The mineralogical composition was determined from the fraction <2 µm with XRD. Clay Gafsa is mainly composed of smectite as shown in Table 1 the techniques of surface area (Ss) and the cation exchange capacity (CEC) and the BET were measured respectively. The point of zero charge (PZNPC) clay of Gafsa was conducted by the potentiometric titration method acid-base (Table 1).

Synthesis of the surfactant modified adsorbent

The exchange capacity of the outer cation (CEC) of the clay, determined by the MANTIN method, is 91 meq/100 g of purified clay [17]. It can be seen that: the value of the CEC decreased due to the application of an organophilic treatment adsorbent. Theoretically, CEC is defined as the number of monovalent cations that can replace compensating cations to compensate for the 100 g mineral electrical charge. Adsorbents modified by the following procedure [18] were prepared: on the one hand, 20 g of the adsorbent (Gafsa Clay) was dispersed in about 500 ml of water in distilled water. Then, a desired amount of surfactants (HDTMA or CPC) was stirred in 100 mL of distilled water until completely dissolved and then added drop wise to the clay solutions. The amounts of each surfactant were calculated on the basis of the CEC of the adsorbent. The reaction mixtures were mechanically stirred at room temperature for 48 hours. The resulting modified adsorbent surfactant was then filtered by filter papers and washed with distilled water until complete disruption of Br^- and Cl^- ($AgNO_3$ test). The products were dried at 80°C. for 12 h. Finally, the adsorbents were ground in an agate mortar and stored in a sealed glass container to be vented and labeled.

Characterization of the modified adsorbents

The prepared organoclays were characterised by X-ray diffraction (XRD), surface area measurement (BET), Fourier transform infrared spectroscopy (FT-IR). XRD for obtaining basal spacing d(001) values was operated and the method was described in the paper by Park et al [19]. The BET specific surface area, pore structure parameters were characterize from N_2 adsorption–desorption isotherms using a Micromeritics Tristar 3000 instrument.

Determination of the point of zero charge

The point of zero charge of the clay adsorbent in aqueous phase was analyzed using the solid addition method [20]. For this purpose, 0.1M KNO_3 solutions were applied and its pH was adjusted in the range of 2-12 by adding either 0.1 N HCl or NaOH and measured by a pH meter (Selecta Lab, PHW 100 Model, China). And then 0.2 g of the clay adsorbent was taken to each solution. The solutions were agitated for 48 h and the final pH values of the solution were measured.

Parameter	Unit	Gafsa clay < 2 µm fraction
Specific surface	m^2/g	83
CEC	meq/100 g	91
PZNPC		9.9
SiO_2	%(weight)	54.3
Al_2O_3	%(weight)	16.4
Fe_2O_3	%(weight)	8.2
MgO	%(weight)	4.7
CaO	%(weight)	4.6
SO_3	%(weight)	2.2
K_2O	%(weight)	1.3

Table 1: Physico-chemical characteristics of Gafsa clay.

Adsorption experiments

To study the adsorption isotherms of dyes by the raw and modified clays, volumes of 0.05 L of different concentrations of dye from (10 to 500 mg/L) are brought into contact with a mass of 0.1 g of the adsorbent. The experimental conditions are analogous to those of adsorption kinetics.

Modelling of the adsorption isotherm: The last stage of the study is to model isothermal curve, or more specifically, to report by a mathematical equation of the entire curve. Conventional models of Langmuir and Freundlich characterizing the formation of a monolayer are used for their simplicity of artwork. The model Langmuir [21] is based on the following hypotheses. Forming a single layer of adsorbate on the surface of the adsorbent, the existence of adsorption sites defined, the surface is uniform with no interaction between the adsorbed molecules.

The Langmuir equation is as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$

With:

q_m(mg/g): Adsorptive capacity at saturation (characteristic of the formation of the monolayer of adsorbed molecules), and b (L/mg): Constant characteristic of adsorbent equilibrium temperature dependent and experimental conditions.

The model Freundlich [22] is based on an empirical equation reflects a change in energy with the amount adsorbed. This distribution of energy interaction is explained by heterogeneity of the adsorption sites. Unlike the model of Langmuir, Freundlich equation does not plan to limit higher than adsorption which restricts its application to dilute media. However, this model admits the existence of interactions between the adsorbed molecules [23]. It is of the following form:

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

Where K: adsorbent's capacity (L/g) and n: heterogeneity factor.

Results and Discussions

The study of the point of zero charge

The PZNPC or pH zero corresponds to the pH value for which the net charge of the adsorbing surface is zero [24]. This parameter is very important in the adsorption phenomena, especially when electrostatic forces are involved in the mechanisms. A quick and easy way to determine the PZNPC is to place 50 mL of distilled water in closed bottles and adjust the pH of each (values between 2 and 12) by addition of NaOH solution or HCl (0.1M). Then added to each flask, 50 mg of sample material to be characterized. The suspensions should be kept in agitation at room temperature for 24 h, and the final pH is then determined. It relates to a graph pH=f (pH_i) where pH=(pH_f-pH_i), the intersection of the curve with the axis that passes through the zero gives the isoelectric point (Figure 2).

Initial considerations

To determine the best adsorbent for the removal of Bright Green, several adsorption experiments were carried out using 0.1 g of adsorbent prepared. Each adsorbent was added to 50 mL of 100 mg/L BG dye to 30°C and the solution was stirred at a speed of 200 rpm for 12 h. The results are illustrated in Figure 3. It can be seen that the modified surfactants adsorbents have a capacity significantly higher for the adsorption of BG with respect to the clay. Indeed, adsorbents produced by intercalation by Cationic surfactants improved the adsorption capacity of the adsorbents. This is consistent with the results of other researchers [25-28]. According Figure 3, the surfactant is a modified adsorption capacity slightly higher compared to the surfactant that can be attributed to the higher value of CEC clay. The CEC is a value characterizing parameter representing the adsorbent with a higher amount of the CEC is more likely to be able to exchange cations with the cationic surfactants [29]. We continue the rest of experiences with the organophilic clay with HDTMA due to its high adsorption capacity compared to other adsorbents.

The adsorption mechanism

Technically, the adsorption of cationic surfactant onto the surface of adsorbent may follow two approaches. The first approach: the surfactant molecules interact with clay through their non-polar (alkyl) groups; hence the positive head of the surfactants points toward the bulk of the solution. The second approach [26]: in this approach, the adsorption of the cationic surfactant onto the negatively charged surface of the adsorbent can be considered to be controlled by two steps; (1) the formation of surfactant monolayer through the ion exchange and electrostatic attraction and (2) the formation of surfactant bilayer via hydrophobic interactions [30-32]. As a matter of fact, firstly, the positive head of the surfactants are exchanged with the interlayer exchangeable cations within the clay, thereby forming a surfactant monolayer with outward pointing head groups. Secondly, the bilayer is organized by the attachment of the surfactant alkyl chains to the outer surface of the monolayer by means of the hydrophobic–hydrophobic interactions. Therefore, the external surface of the modified adsorbent has become positive and accordingly, more appropriate for the adsorption of the cationic adsorbantes like the BG molecules. The first stage is more probable to occur at low surfactant concentrations (at about 100% CEC or below) and the second stage takes place at higher concentrations hemimicelles or micelles (more than 100% CEC) [33,34]. In the present research, the amount of the surfactant is provided at about 200% of CEC; hence it can be assured that the bilayer is formed. Figure 4 best schematizes the modification procedure of clay using cationic surfactant. Owing to the different configurations of the CPC and HDTMA surfactants on clay, various interactions may be involved in the adsorption of the BG from aqueous solution. On the one hand, the positive head of the surfactants covering the exterior surface of the adsorbent may be the main responsible for the increase of BG sorption in the case of organically modified adsorbents. In fact, the electrostatic attraction between the anionic $SO_4^{-}H$ group of BG molecules and positively charged adsorbent is the dominant phenomenon for the adsorption of BG. On the other hand, as reported in the literature, the hydrophobic portion of the adsorbent surface has more preference for dissociated species of BG in aqueous solution. Furthermore, the van der Waals interaction between the phenyl ring of BG and CH_2 group of the modified adsorbent can be considered as one of the driving forces through the adsorption process [28]. It should be pointed out that in the case of the CPC modified adsorbent, the phenyl ring of BG can be bound to the pyridine ring of CPC molecules via the π stacking interaction. But then, it can be questioned that why the HDTMA modified adsorbent is superior to the CPC modified adsorbent in the adsorption of BG if the latter adsorbent take advantage of the π stacking interaction. This can be justified by the spatial hindrance arising from the pyridine ring around the CPC head (Figure 4).

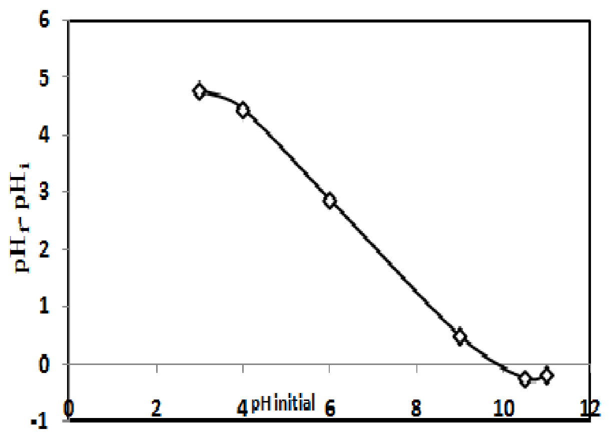

Figure 2: The inv estigation of the point of zero charge of clay.

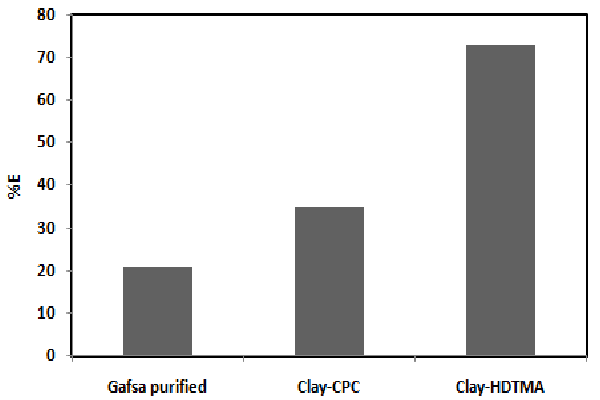

Figure 3: The effect of the adsorbent type on the removal of the GB.

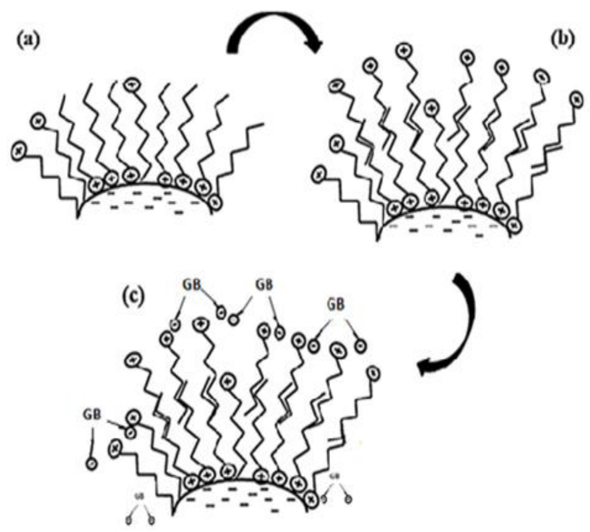

Figure 4: (a) Surfactant monolayer formation on the adsorbent surface, (b) surfactant bilayer formation on the adsorbent surface and (c) schematic representation of the interactions of GB molecules with the surfactant modified adsorbent.

The study of the adsorbent dosage on the sorption of BG

Figure 5 shows the effect of the adsorbent dose on the removal of BG from aqueous solution. It can be seen that the adsorption of BG has rapidly increased with the increase of the adsorbent dose. The optimum amount of the adsorbent is 0.7, 0.4 and 0.2 for clay, clay-CPC, and clay-HDTMA, respectively, and after the optimum amount of each adsorbent, the increase of the adsorbent do not effect on the removal of BG and the adsorption is nearly constant. The sharper adsorption curve was observed in the case of the modified adsorbent with the cationic surfactants. It is revealed that the implementation of the surfactant has an influential effect on the adsorption of BG and the optimum amount of the adsorbent has decreased.

The study of the initial pH of the solution on the sorption of GB

pH is an important factor in any adsorption study, because it can influence the adsorbent and adsorbate structure as well as the adsorption mechanism. In this article, we studied the adsorption efficiency of a bright green dye by varying the pH from 4 to 11 using a solution of hydrochloric acid HCl (0.1M) or soda NaOH (0.1 M) according to the desired pH. Under these pH conditions, a mass of 100 mg of the adsorbent was stirred in 100 mL of the colored solution at 20 mg/L. The results obtained in these tests are shown in Figure 6.

The results obtained show that the variation of the residual dye concentrations is relatively low. Discoloration is therefore little influenced by the variation in pH. In the light of these results, all the discoloration tests on the fly ash and bottom ash were carried out at the natural pH of the colored solution (between 6 and 7) for the bright green.

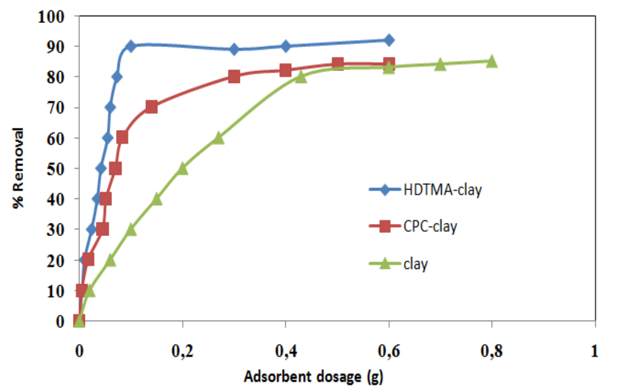

Figure 5: The effect of the adsorbent dosage on the adsorption of GB on three different adsorbent.

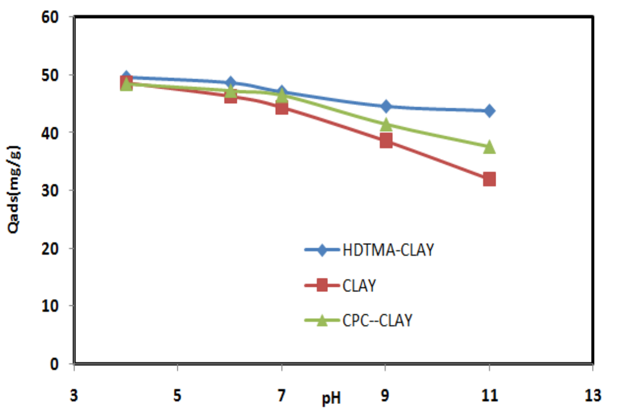

Figure 6: The effect of pH on the adsorption of GB on three different adsorbent.

Kinetics of adsorption of dyes by different clays (natural and modified by HDTMA)

Figure 7 shows the evolution of the adsorbed amount as a function of time. The kinetics of dye adsorption on the clays used shows a strong adsorption from the first minutes of dye-clay contact, followed by a slow increase until reaching an equilibrium state.

The kinetics of adsorption rapid during the first minutes of reaction can be interpreted by the fact that at the beginning of the adsorption the number of active sites available on the surface of the adsorbent material is much higher than that of the sites remaining after a certain time

Adsorption isotherms

The adsorption isotherm is an important technique providing precious information to predict the adsorbent efficiency for the removal of a specific adsorbate. It is reported in several studies that non-linear analysis should be considered as a better approach to obtain the isotherm parameters as sometimes linearization of non-linear experimental data may distort the error distribution structure of isotherm [36-38]. Hence, the non-linear procedure was carried out for describing the adsorption isotherms and predicting the overall sorption behavior for the removal of BG using clay-HDTMA adsorbent. In this section two-parameter isotherm models (Freundlich and Langmuir) were examined to find out the best fit for the experimental data. The experimental adsorption isotherm of BG on clay and clay-HDTMA are illustrated in Figure 8. It is apparent from Figure 8 that clay-HDTMA has higher adsorption capacity compared to clay for the removal of BG from aqueous solution. It is important to be noted that the shape of the isotherm can be used for the interpretation of the adsorption process. According to classification of Giles [39], the adsorption isotherms are classified into four groups: L, S, H, and C. According to the aforementioned classification, the adsorption of BG onto clay and clay-HDTMA followed the L curve pattern which indicates that there is no strong competition between solvent and the adsorbate to occupy the adsorbent surface sites.

The isotherm model parameters and the statistical results are presented in Table 2. Figure 8 shows the experimental data as well

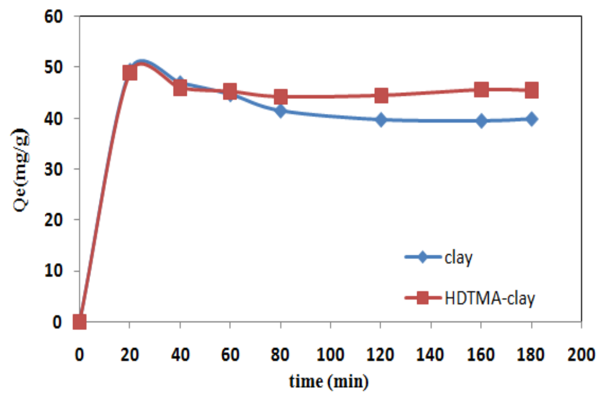

Figure 7: Kinetics of adsorption of Brilliant Green on the clays used.

as the isothermal models for the adsorption of BG on the HDTMA-clay. According to Table 1, all isothermal models correctly describe the adsorption of BG on the adsorbent; However, the R^2 statistical parameter amounts are related to the Langmuir model (R^2=0.9997) higher than those of the other isothermal models that are closer to the unit.

The quantity of the dye increases more or less rapidly for low concentrations in solution and then equilibrates to reach a plateau, corresponding to saturation of the adsorption sites and reflecting an adsorption in monolayer. The isotherm obtained is of type L according to the classification of Giles [39].

It is clear that the maximum adsorption capacity of the surfactant-modified adsorbent (clay-HDTMA; 45.5 mg/g) was significantly higher than that of the clay (30.26 mg/g). Furthermore, it is found that the BG adsorption capacity of the HDTMA-clay is relatively high compared to the other adsorbents reported in the literature which indicates that the HDTMA clay is a promising adsorbent for the removal of BG.

Adsorption kinetics

The modeling of the adsorption kinetics of the removal of BG on clay-HDTMA was studied by the two most common models, namely pseudo-first-order model and pseudo-second-order model. The pseudo-first-order model is represented by the following equation:

$$\text{Log}\ (q_e - q_t) = \log\ (q_e) - \left(\frac{k1}{2{,}303}\right)t$$

Where k_1 (1/min) is the rate constant of pseudo-first-order adsorption. A linear plot of log (q_e – q_t) versus t was used to determine

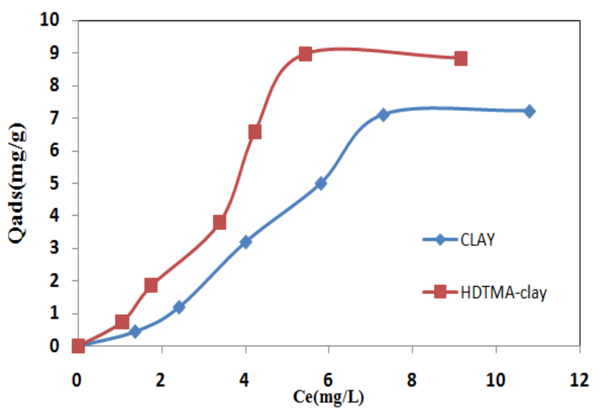

Figure 8: Isotherms models for the adsorption of GB onto clay-HDTMA.

Model	Model parameter	R^2
Frendlich	K_F=5.11, n=1.498	0.998
Langmuir	q_m=45.5, b=0.029	0.9997

Table 2: The isotherm constants and coefficients for the adsorption of GB on HDTMA-clay.

the values of k_1 and the equilibrium adsorption capacity (q_e). The model parameters used to evaluate the experimental data and the corresponding correlation coefficient are presented in Table 3. A comparison between the resulted correlation coefficients (Table 3) implies that the pseudo-first-order model cannot provide a suitable description for the adsorption of GB on clay-HDTMA adsorbent. Besides, the calculated q_e resulted from the pseudo-first-order model were obviously different from that of the experimental values. The pseudo-second-order model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where k_2 (g/mg min) relates to the constant of pseudo-second-order adsorption. The straight line plots of t/qt versus t permits the calculation of k_2 and q_e (Figure 9). The results are shown in Table 3. According to Figure 9, the pseudo-second-order model was found to be most appropriate and accommodate with the experimental results. It can also be observed from the correlation coefficient values from Table 3 that R^2 values were tending to ward unity. In addition, the calculated q_e values from the pseudo-second-order model fairly agree the experimental ones better than the pseudo-first-order. All in all, this can be concluded that the adsorption of BG on clay-HDTMA obeys the pseudo-second-order kinetic model.

Structural characteristics

BET analysis of clay and surfactant modified HDTMA and CPC: Table 4 shows the BET surface area (m^2/g), the total pore volume (cm^3/g) and the average pore diameter (nm) and the basal distance (d_{001}) of the clay, clay-CPC adsorbent and Clay-HDTMA. The BET surface area decreased from 54 to 1.28 m^2/g for CPC-modified clay and to 2.19 m^2/g for HDTMA clay modification, which can be attributed to blockage and pore screening of clay by surfactant alkyl chains [40]. It should be noted that, despite our hypothesis, the average pore diameter decreases slightly from 4.0 to 3.3 nm from clay to HDTMA clay, which is likely due to the complete removal of Micro-pores of the adsorbent structure [40].

S_{BET}: specific surface area.

VP: pore volume determined by BJH method from N2 desorption isotherm.

APD: average pore diameter determined by the curve of BJH desorption dV/dD pore volume. d_{001}: Basal distance

The results of XRD of the untreated natural clays and those modified with the cationic surfactant HDTMA are given in Figure 10. The purified natural clay (from GAFSA) shows a position of the basal distance (001) of reflection (d = 12.72 Å) characteristic of a smectite exchanged with sodium. The modified clay model (HDTMA-GAFSA clay) compared to the others shows a spacing of (d=26 Å), indicating the intercalation of the HDTMA molecules. The spacing d is in agreement with that obtained by Slade and Gates [41] for various smectites.

Initial concentration (mg/L)	q_e, exp (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		K_1(g/mg min) 10^3	q_e, cal (mg/g)	R^2	K_2(g/mg min) 10^3	q_e, cal (mg/g)	R^2
50	4.20	11.52	0.69	0.91	53.99	11.63	0.999
100	9.08	0.02	0.88	0.071	16.13	22.73	0.999
150	16.19	13.82	25.27	0.994	1.2	40.00	0.999
200	24.04	29.94	570.15	0.563	0.68	47.62	0.997
250	35.09	9.21	54.2	0.826	0.35	58.58	0.999

Table 3: Kinetic parameters of pseudo-first and pseudo-second order models for the adsorption of GB on clay.

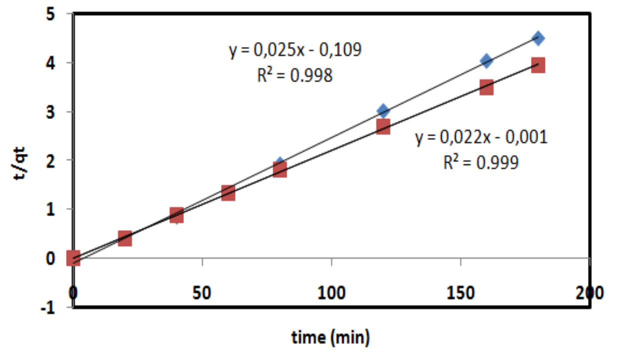

Figure 9: Pseudo-second-order model for adsorption of GB onto clay-HDTMA.

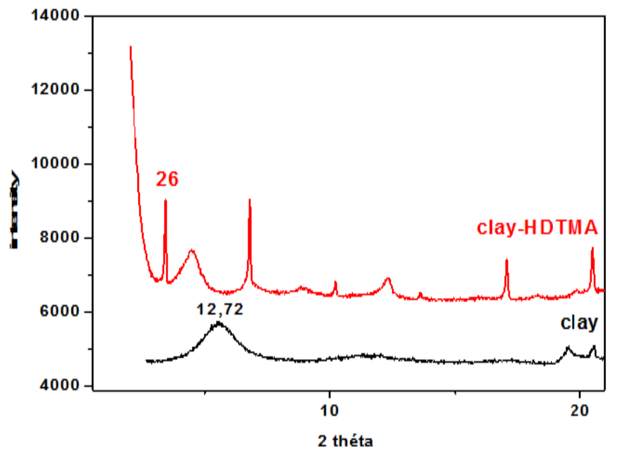

Figure 10: RX diffractogram of purified clay (0 CEC) and organophilic clays by HDTMA (3CEC).

Adsorbent samples	S_{BET} (m²/g)	VP (cm²/g)	APD (nm)	d_{001} (nm)
Clay	54	0.107	4.0	1.27
HDTMA-clay	2.19	0.011	3.3	2.6
CPC-clay	1.28	0.007	2.7	2.1

Table 4: The BET surface area, total pore volume, and average pore diameter for clay, and HDTMA-clay.

X-ray diffraction analysis of clay and surfactant modified clay-HDTMA: The results of XRD of the untreated natural clays and those modified by the cationic surfactant HDTMA are given in Figure 11. The potted Na-stah gafsa clay shows a position of the basal distance (001) of reflection (d = 12,72 Å) characteristic of a smectite exchanged with sodium. The modified clay model (HDTMA-stah gafsa) with respect to the others shows a spacing of (d = 26 Å), indicating the intercalation of the HDTMA molecules. The value of the spacing d is in agreement with those obtained by the slats and the grids for various smectites.

FTIR analysis of clay and surfactant modified clay: Based on the results of XRD, it is possible to confirm that the exchange of HDTMA polycations with Na^+ alkalin cations in the interlayer space is successful (Figure 11).

The main peaks are:

- A peak at 1480 cm^{-1} indicating the presence of the functional group N-C, corresponding to the tertiary amine.

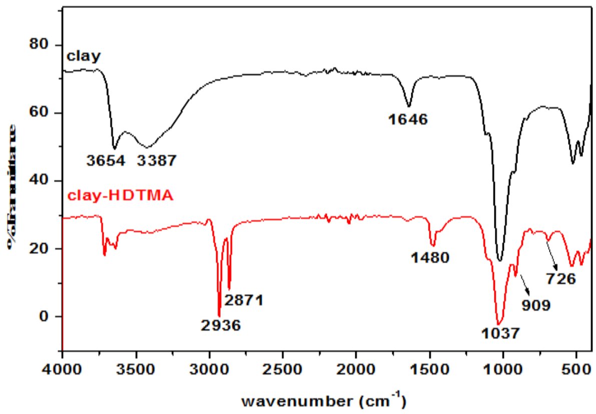

Figure 11: FTIR analysis of clay and surfactant modified clay.

- Two absorption peaks at 726-780 cm^{-1} corresponding to the deformation vibration mode outside the plane of the CH_2 group.

- Two strong peaks at 2871 and 2936 cm^{-1}, corresponding to the symmetrical stretch vibration mode and incline the methyl amine.

Conclusions

The equilibrium and dynamics of Bright Green (BG) adsorption on the surfactant-modified adsorbent were studied in this study. It has been found that the value of the zero charge point of the clay is about 9.9 and above that the surface of the adsorbent is negative. Several adsorbents such as clay, HDTMA clay and clay-CPC have been used for the adsorption of BG from aqueous solutions. The modified HDTMA clay remarkably has the highest adsorption capacity compared to the other adsorbents prepared. It was observed that the BG adsorption capacity for the clay increased with the contact time and the initial dye concentration.

The equilibrium data have been well described by the Langmuir model. Kinetic studies of BG adsorption on clay indicate that the pseudo-second order kinetic model agrees very well with experimental adsorption data (Qe=45.5 mg/g).

The clay studied in the GAFSA region (south of Tunisia) has a very high adsorption capacity because of their specific properties (CEC=91 meq/100 g…Surfac Specific=54 m²/g). Several characterizations analyzes, including BET, FTIR and XRD, confirmed the modification of the surfactants of the adsorbent. The results revealed that the modified HDTMA clay could be applied as a low cost material for the adsorption of the BG dye from aqueous solutions.

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