

Characterization of Two Natural Clays and Their Application as Adsorbents for Treatment Process of Dye Effluents

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Abstract: The aim of the present work is to explore and compare the adsorption capacity of two different clays for removal of textile dye from aqueous solutions. For this purpose, the adsorption of Green Remazole 6B; a reactive dye used in textile industry, was studied in batch mode. The clays used were provided from two different deposits in west of Algeria, one located in Ain-Témouchent (C46) and the other in the region of El Bayadh (C32). Before investigating the adsorption of textile dye, the clays were characterized by various techniques of analysis in order to study all the relevant features. The techniques used are: X-ray diffraction, infrared spectroscopy (IR) and Chemical analysis. Chemical analysis and infrared spectroscopy (IR) show that clays are mainly constituted of alumina and silica in major quantities and other elements in minor quantities. XRD analysis shows that C46 is illite clay, containing kaolinite, smectite and quartz. On the other hand, C32 is kaolinite clay with presence of illite, smectite, chlorite and quartz. To investigate the adsorption of the textile dye, clays have been previously modified by acid treatment with H₂SO₄ and they were tested in their natural state and in their acid-activated form. Different adsorption tests concerning the contact time, the initial dye concentration and the pH were investigated by conducting a series of batch adsorption experiments at room temperature. The adsorption equilibrium data were analyzed by using Langmuir and Freundlich adsorption isotherms models. The results show that Acidic pH was favorable for adsorption of the dye and the Freundlich model agrees very well with experimental data. (C32) clay has the best removal power.

Keywords: Clay, Textile Dye Effluents, Characterization, Adsorption, Reactive Dye

1. Introduction

Water is one of the most important renewable natural resources for supporting life, at the same time invaluable, fragile and limited, which must be the object of coherent and rational management. But through its various uses, water is often polluted. For most industries, water is an important factor of production. Among these industries, the sector of textile represents one of the most consumers of water. Approximately 200 Liters of water are consumed for each kilogramme of textile [1]. In many countries where water resources are decreasing, this high water consumption became intolerable.

In addition, textile industry produces highly polluted

discharge water in large amounts from different steps in the dyeing and finishing processes and which are often rich in color which is not easily removed in treatment systems. The presence of dyes in wastewater is very harmful to aquatic life in rivers where they are discharged. Since, dye can reduce light penetration into the water thereby decreasing the efficiency of photosynthesis in aquatic plants and hence having adverse impact on their growth [2]. Dyes also can cause severe damage to human beings, such as dysfunction of kidney, reproductive systems, liver, brain and central nervous system [3].

Due to the complex chemical structure of these dyes, they are resistant to breakdown by chemical, physical and biological treatments. Furthermore, any degradation by

physical, chemical or biological treatments may produce small amount of toxic and carcinogenic products. Adsorption is known to be a promising technique, which has great importance due to the ease of operation and comparable low cost of application in the discoloration process [4].

Activated carbon is the most commonly used adsorbent to remove the dyes in wastewater due to its excellent adsorption capacity [5]. However, it is very expensive and in addition requires regeneration; this limits its use in the developing countries.

The use of natural materials is a promising alternative due to their relative abundance and their low commercial value. In this context, the objective of this study is to investigate the adsorption capacity of two Algerian natural clays for removal of reactive dye from aqueous solution as an ideal alternative to the current expensive methods of removing dyes from wastewater. Before adsorption tests, the clays were analyzed and examined by different techniques of characterization in order to define their mineralogy.

The adsorption data were fitted to various equations to obtain certain constants related to the adsorption phenomena.

2. Materials and Methods

2.1. Materials

Two clays representative of two different deposits from the west of Algeria were used in the study: A brownish clay symbolized by C46 which come from a deposit located at 03 km south from the city of Beni-Saf and a red clay symbolized by C32, coming from a deposit located in the region of Ain Orack at about 50 km south of the wilaya of El Bayadh.

The raw clays as well as the clay fraction (particle size less than $2\mu\text{m}$) were characterized by X-ray diffraction using a diffractometer Philips PW1830, on powder and on oriented aggregates onto glass slides. The data was collected over a range of $5-50^\circ 2\theta$. Chemical analysis of major elements was performed in the laboratory of Cement Plant of Tlemcen (SCIBS).

The infrared spectra of the natural clays were examined between 4000 cm^{-1} and 400 cm^{-1} using a dispersive spectrometer Perkin-Elmer 180 (coherent self pellets in KBr). The samples were prepared using KBr pellets at sample concentration of about 1%.

Preparation of acid-activated clays was undertaken according to the procedure described by Espanataleon et al. [6]: 10 g of each clay was refluxed for 1h with 100 ml of sulphuric acid 1N. The resulting activated clays were washed until pH 5 and dried at 105°C until constant weight. The materials obtained are named AC46 and AC32.

The dye used for adsorption tests is a reactive dye named Green Remazole 6B. This dye was provided from textile factory "SOITEX" of Tlemcen and used as such. The dye is used for dyeing polyamide fibers in an acidic medium of acetic acid. Its solubility is 70gr /l at 20°C . The formula and the complete structure diagram are not available.

2.2. Adsorption Studies

Adsorption experiments were evaluated in batch equilibrium mode for natural clays and their acid-activated form (C46, C32, AC46 and AC32). A 10 mg of each clay with 10 ml aqueous solution of a 100mg /L dye solution at various pH (2–11) reacted for 2 hours was used for the pH studies. Experiments were carried out at room temperature. The solution pH was adjusted by adding a small amount of HCl (0.1N) or NaOH (0.1). The optimum pH was determined and used through all adsorption processes.

The mixture was then centrifuged and the supernatant liquid was subjected to quantitative analyses. The equilibrium concentration of each solution was determined at the wavelengths of UV-maximum (λ_{max}) at 656 nm of Green Remazole 6B, through the use of a UV-visible spectrophotometer (Agilent model 8543).

Experiments were conducted for various time intervals to determine when adsorption equilibrium was reached and the maximum removal of dye was attained. For that, the effect of contact time on the amount of reactive dye adsorbed onto clays was investigated at two different concentrations of dye (50 and 100 mg/L). The maximum adsorption of the dye onto clays and their acid-activated form was almost the same and was observed at 50 min, beyond which there is almost no further increase in the adsorption, and it is thus fixed as the optimum contact time. This time was maintained for different sets of Adsorption experiments to obtain isotherms. In this group of experiments 10 ml of dye solution was used at different concentrations from 40 to 700 mg/l for 50 min to allow attainment of equilibrium at room temperature.

3. Results and Discussion

3.1. Characterization of Clays

3.1.1. X-ray Diffraction (XRD)

The XRD patterns of the natural clays are presented in Figs.1-2. As shown, we can observe a prevalence of quartz (SiO_2) in both C46 and C32. Indeed, the characteristic peak of Quartz ($d = 3.35\text{ \AA}$) is the most intense in the diffractograms of both clays. We note also, the Presence of the characteristic peaks of calcite at 3.05 \AA for C32 clay and 3.04 \AA for C46.

The clays used was purified by sedimentation based on the law of Stokes to obtain lower size granulometric fraction $<2\text{ }\mu\text{m}$ and prepared for XRD measurement by orienting the clays in a glass slide following standard procedure. Examination of the XRD patterns of the samples show that [7]:

A reflection (001) at $d = 10\text{ \AA}$ (Fig. 3) is clearly visible on the clay pattern of C32 attributed to a substantial illite phase. The asymmetrical shape of the reflection is characteristic of inter-bedded phase of illite / smectite [8]. We also observed two other secondary peaks typical of illite at 5.01 \AA and 3.33 \AA . C32 also has the characteristic peaks of kaolinite at 7.2 \AA and 3.57 \AA .

For the C46 clay, we identified the following mineral

species (Fig. 4):

Kaolinite is the dominant phase; its characteristic peak reflection (001) appears at 7.09 Å and another secondary peak at 3.54 Å. The peaks at 5.03 and 3.34 Å indicate the

presence of illite phase of low crystallinity. Furthermore, a peak appears at 12.36 Å, which can be attributed to smectite, and two other peaks at 14.16 Å and 4.74 Å, probably attributed to chlorite.

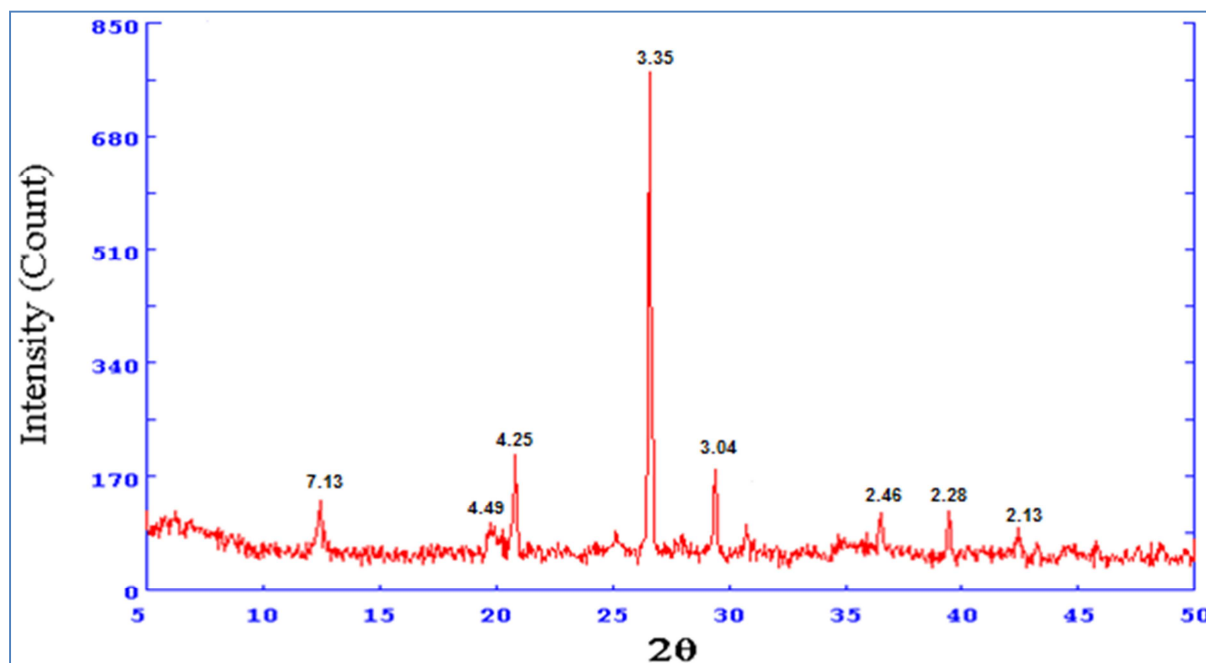


Fig. 1. XRD patterns of natural C46.

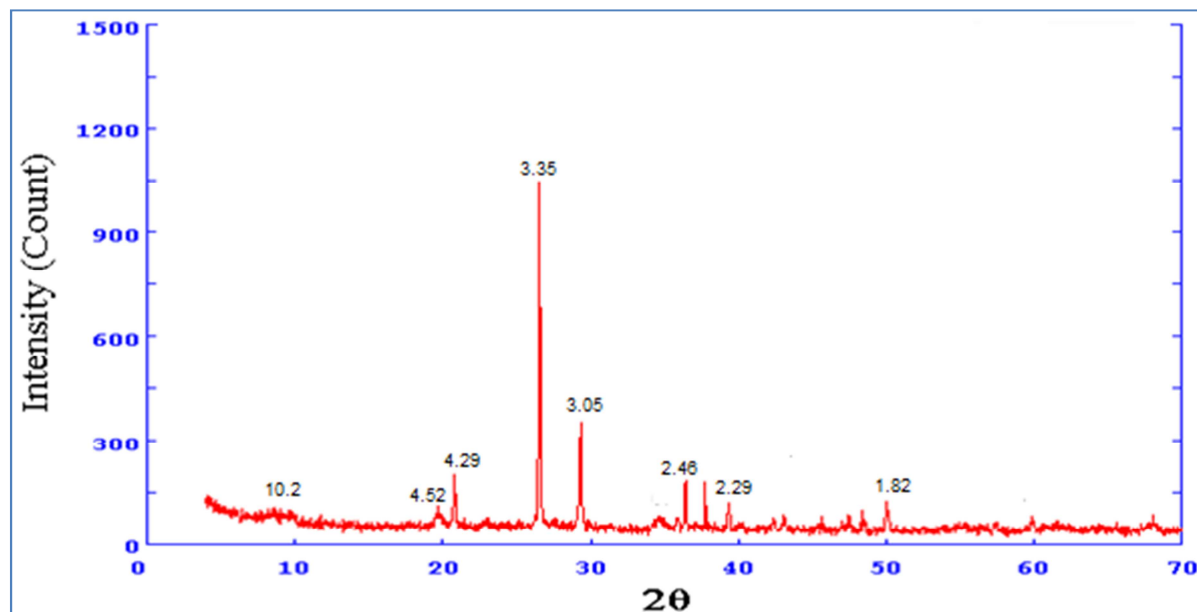


Fig. 2. XRD patterns of natural C32.

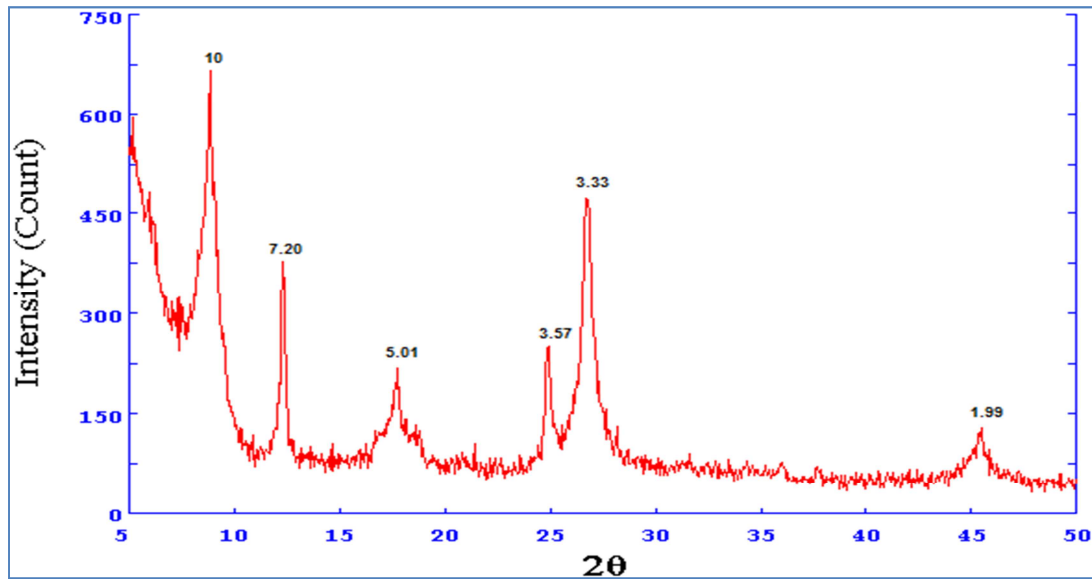


Fig. 3. XRD patterns of C32 (fraction <2 μm).

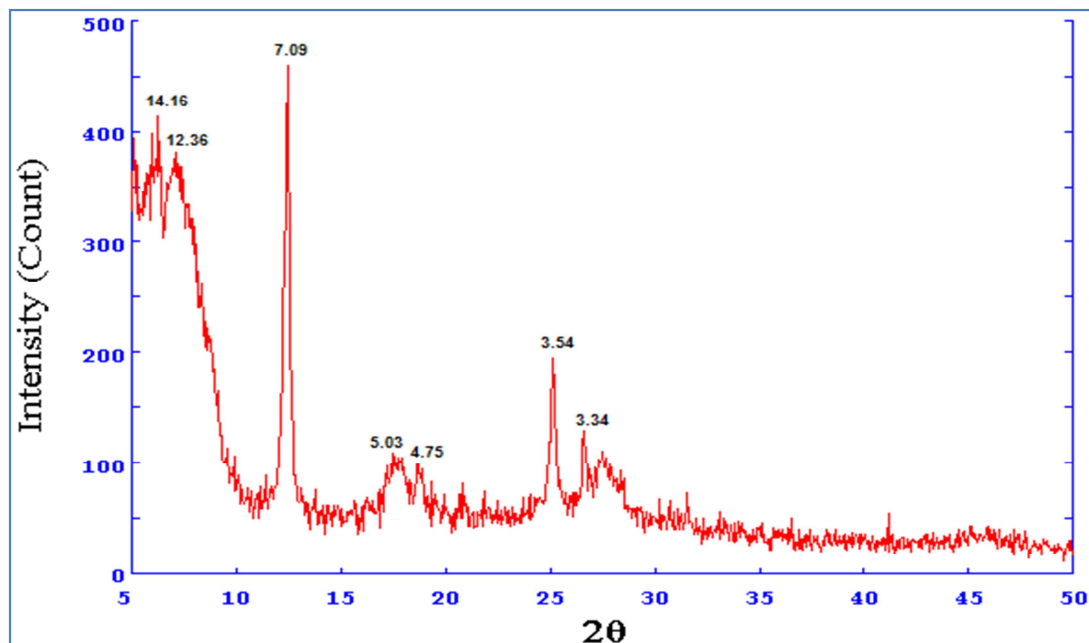


Fig. 4. XRD patterns of C46 (fraction <2 μm).

On the basis of this result, XRD patterns indicates that illite is the predominant clay mineral in C32 with presence of kaolinite phase and an inter-bedded phase (illite / smectite). Against, C46 is essentially a mixture of kaolinite, illite and two minor phases of smectite and chlorite.

3.1.2. Infrared Spectroscopy (IR)

Examination of the IR spectra of the clays shows a set of bands typical of a clay mineral.

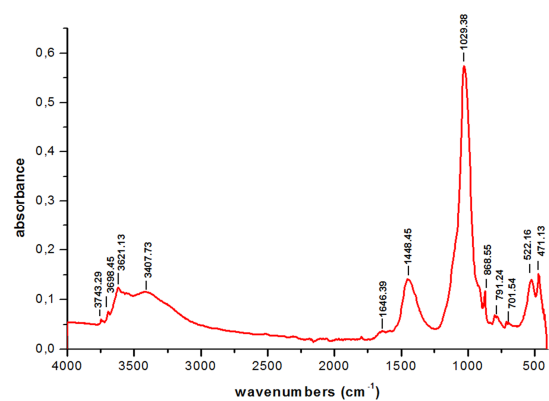


Fig. 5. FTIR spectra of natural C32.

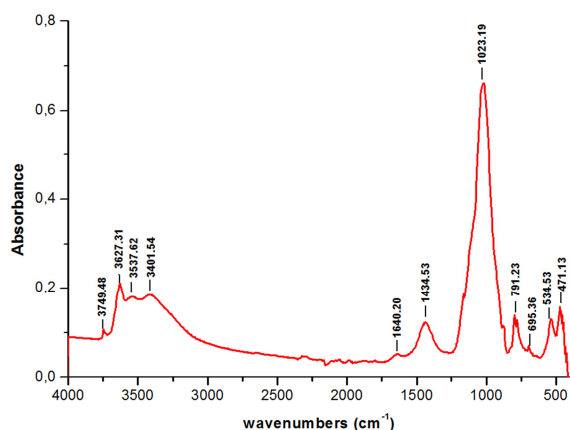


Fig. 6. FTIR spectra of natural C46.

The presence of carbonates and other organic impurities in both clays is confirmed by the absorption bands located at 1448 cm^{-1} for C32 (Fig. 5) and 1434 cm^{-1} for the C46 (Fig. 6), characteristics of elongation CO [9]. Presence of quartz which is confirmed by the appearance of its characteristic bands of vibration located at 695 , 701 , 868 cm^{-1} [10, 11]. Absorption bands at 3621 , 3627 , 3743 and 3749 cm^{-1} are attributed to illite [12, 13].

Kaolinite is identified in both clays by the bands at 3698 and 791 cm^{-1} [13, 14] and a third band observed on the IR spectrum of the C46 clay at 3537 cm^{-1} , which correspond to the absorbance associated to ferric ions of kaolinite [9]. Stretching vibration of OH groups at 3401 cm^{-1} for C46 and at 3407 cm^{-1} for C32 are characteristic of the vibration of the hydroxyl function of the hydration of clay water [9]. The bands at 1646 cm^{-1} for C32 and at 1640 cm^{-1} for C46 are assigned to the vibration of angular deformation of adsorbed water molecules between the layers.

The intense band between $900\text{--}1200\text{ cm}^{-1}$, centered at

1029 cm^{-1} for C32 and at 1023 cm^{-1} for C46 corresponds to stretching vibrations of the Si-O.

3.1.3. Chemical Analysis

The chemical composition of both clay (C32 and C46) is given in Table 1. The results show silica and alumina as major constituents in both of clay samples 51% of SiO_2 for C32 and 61% for C46. Between 12 and 17% of Al_2O_3 in both samples.

The clays are relatively rich in Fe_2O_3 (over 4%). This is attributed probably to the presence of iron oxy / hydroxides in both clays. This high content of iron oxides, explains partly the red color to the C32 and brown color of C46. C32 has high percentage of K_2O (3.422%) compared to the C46 (1.907%), indicating that C32 is rich in illite, this confirms the results obtained by XRD analysis. The results show also the presence of substantial amount of calcium oxide CaO (from 7 to 10.5%) which was confirmed by XRD patterns.

3.2. Adsorption Tests

3.2.1. Effect of pH on the Adsorption of Green Remazole 6B

The pH value of the solution was an important controlling parameter in the adsorption process, as can be seen from Fig. 7. It shows that the adsorption capacity onto natural clays as well as acid-activated clays decreases significantly with increasing pH. The maximum removals of green remazole 6B were carried out at pH 2.

As summarized in Table 2, it is observed the natural clays are more effective than their acid-activated state. A similar result was observed in the study of adsorption of Reactive Red MF-3B onto attapulgite; a fibrous clay conducted by Huang et al. [15]. The results of this study indicate that adsorption of Reactive Red MF-3B on attapulgite in its acid-activated state is very low compared to natural attapulgite.

Table 1. Chemical composition (in weight %) of C32 and C46.

Clay	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	TiO_2	K_2O	Na_2O
C32	51.109	15.571	4.455	10.571	0.868	0.032	0.133	3.422	0.179
C46	61.475	9.565	7.843	6.917	0.748	0.096	0.176	1.970	0.191

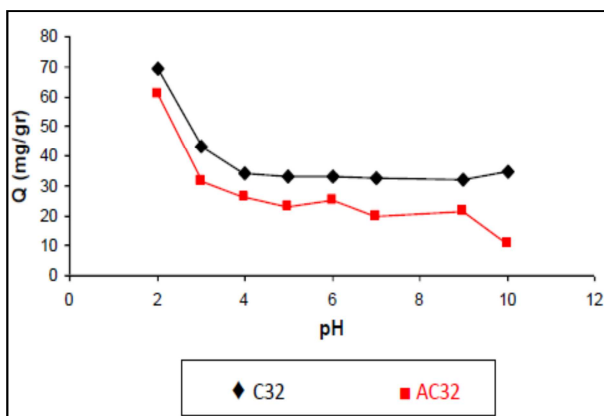
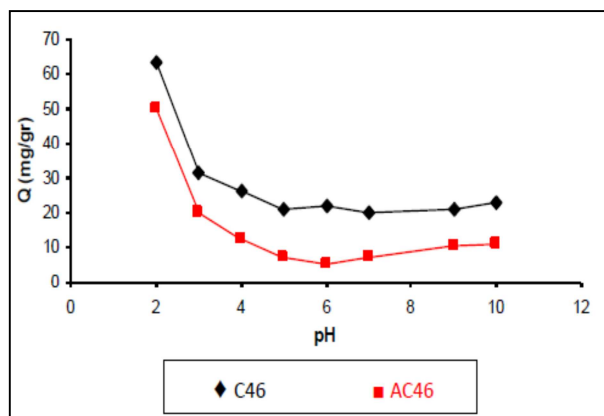


Fig. 7. Effect of pH on the removal of reactive Green Remazole 6B by natural clays (C32, C46) and acid-activated clays (AC32, AC46), $C_0 = 100\text{ (mg/l)}$, contact time = 50 min.

Table 2. Maximal Adsorption of Green Remazole 6B at pH = 2, $C_0 = 100$ (mg/l)

Clay	Maximal Adsorption (%) of Green Remazole 6B at pH = 2, $C_0 = 100$ (mg/l)
C32	69.07 %
C46	63.10 %
AC32	60.60 %
AC46	49.89 %

3.2.2. Adsorption Isotherms

In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlation for the equilibrium data for each system. Two isotherm equations have been tested in the present study: Freundlich and the Langmuir models. The applicability of the isotherm equations is compared by judging the correlation coefficients, R^2 . In this respect, the equilibrium experimental data for Green Remazole 6B on natural and acid-activated clays were compared using the Langmuir and Freundlich isotherms given [16] respectively by:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (1)$$

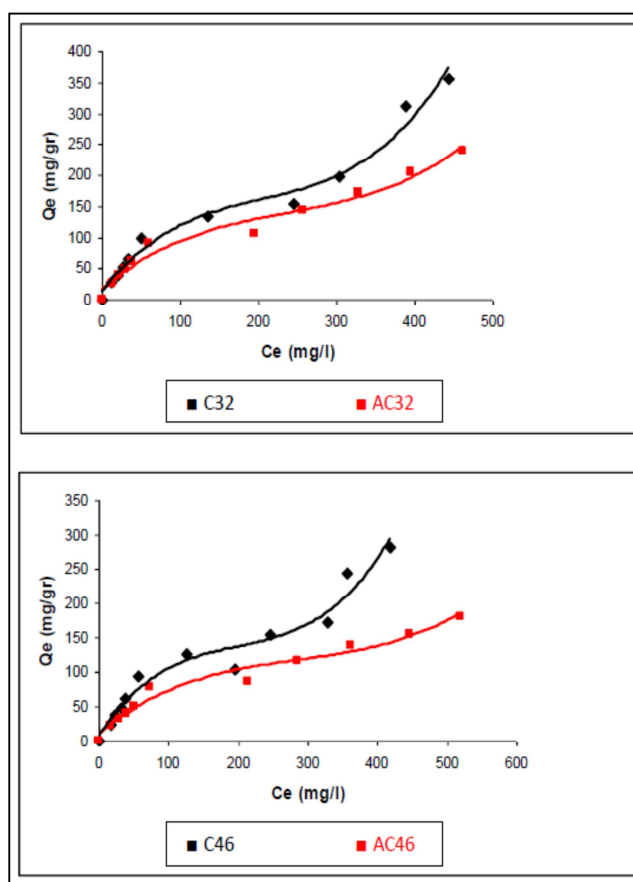
$$\frac{1}{Q_e} = \frac{1}{Q_m K_L} \left(\frac{1}{C_e} \right) + \frac{1}{Q_m} \quad (2)$$

where Q_e is the equilibrium dye concentration on adsorbent ($\text{mg} \cdot \text{g}^{-1}$), C_e is the equilibrium dye concentration in solution ($\text{mg} \cdot \text{L}^{-1}$), and Q_m ($\text{mg} \cdot \text{g}^{-1}$) and K_L are the Langmuir constants related to maximum monolayer capacity and energy of adsorption, respectively, K_F and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity.

The Langmuir adsorption, which is the monolayer adsorption, depends on the assumption that the intermolecular forces decrease rapidly with distance, and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can occur [23].

As shown in Fig.8 the plots does not show the Langmuir monolayer adsorption in the range of studied concentrations which mean that adsorption data of Green Remazole 6B cannot be represented by the Langmuir model.

Fig. 9 shows a linear relationship of $\ln Q_e$ versus $\ln C_e$ using experimental data. The parameters K_F and $1/n$ for the Green Remazole 6B have been calculated from experimental data using the least squares method and the results obtained are given in Table 3. The results indicate that correlation coefficients are very acceptable ($0.9338 < R^2 < 0.9646$) for Freundlich isotherm. This result suggests that Freundlich isotherm represent the ;most appropriate correlation for the equilibrium data for adsorption batch system of Green Remazole 6B.

**Fig. 8.** Langmuir adsorption isotherms of Green Remazole 6B at pH 2

The magnitude of the exponent $1/n$ gives an indication of favorability and capacity of the adsorbent/adsorbate system reflecting the favorability and the capacity of the adsorbent/adsorbate system [23]. The results shows that the values of $1/n$ are lower than 1, suggesting that natural as well as acid-activated clays have a very strong adsorption capacity for reactive Green Remazole 6B in the solution.

Table 3. Freundlich isotherm constants for the adsorption of Green Remazole 6B at pH 2.

Clay	Parameters de Freundlich		
	$1/n$	R^2	K_F
C32	0,624	0,9607	6,639
C46	0,628	0,9338	5,402
AC32	0,547	0,9646	7,432
AC46	0,557	0,9629	5,241

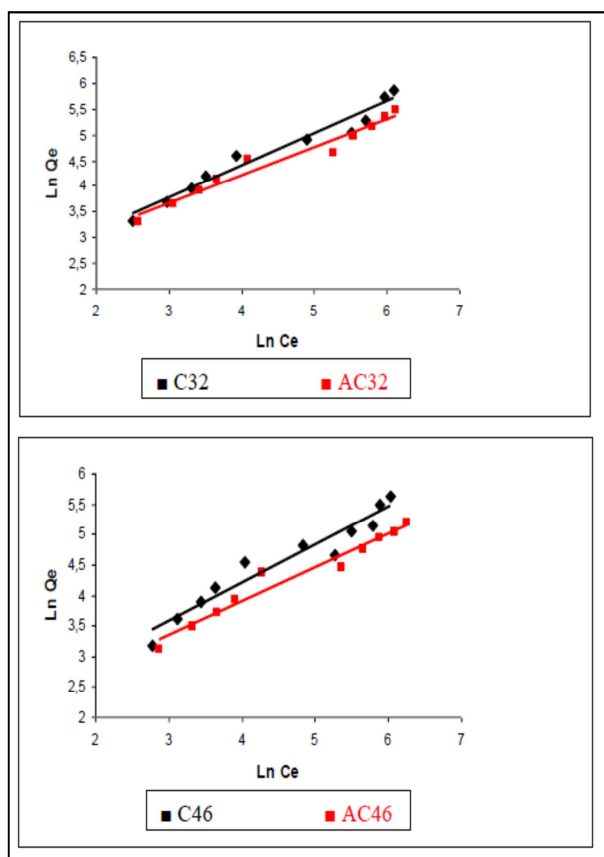


Fig. 9. Freundlich adsorption isotherms of Green Remazole 6B at pH 2

4. Conclusion

Two natural clays from two different deposits symbolized by C32 and C46 were used to remove a reactive dye named Green Remazole 6B from aqueous phase. The clays were tested in their natural state and in their acid-activated form.

Characterization of the two samples shows that each clay is a mixture of different clay minerals. Thus C32 is essentially an illite clay with presence of kaolinite phase and an interbedded phase (illite / smectite). kaolinite is the main phase of the C46 clay mixed with illite and two minority phases that can be attributed to chlorite and smectite.

The adsorption capacity of natural clays of Green Remazole 6B was found to be higher than acid-activated clays. The dye adsorption was influenced by solution pH and concentration. Lower pH will generally result in higher adsorption of the reactive dye. Maximum adsorption capacity is occurred at the pH 2. C32 is more efficient than C46. The best fit of experimental data was obtained by Freundlich isotherm.

Both clays have proven to be a promising material for the removal of textile dyes from wastewater. Not only clays are abundant, but also they are efficient and economic natural adsorbents which could be successfully applied to clean the wastewaters of the dyeing industry.

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