

Modification Technique Influence on the Adsorption Capability of Organobentonites for Reactive and Direct Dyes

Seniha MORSÜMBÜL¹, Emriye Perrin AKÇAKOCA KUMBASAR^{1*},
Saadet YAPAR²



¹Ege University, Engineering Faculty Textile Engineering Department, Bornova, Izmir, Türkiye

²Ege University, Engineering Faculty Chemical Engineering Department, Bornova, Izmir, Türkiye
(ORCID: [0000-0002-4929-0681](https://orcid.org/0000-0002-4929-0681)) (ORCID: [0000-0001-5295-9131](https://orcid.org/0000-0001-5295-9131)) (ORCID: [0000-0003-4237-6869](https://orcid.org/0000-0003-4237-6869))

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Abstract

In this research, the adsorption of reactive and direct dyes from synthetic textile wastewater using organobentonites modified by two different routes was studied. Except for the drying step, the synthesis conditions were the same, and organobentonites were synthesized by employing a cationic surfactant at a level corresponding to the entire cation exchange capacity of bentonite under microwave irradiation. In the final step, the samples were dried using either a freeze dryer or an air dryer. The structural features of the organobentonites were identified via XRD and FTIR analyses. The obtained equilibrium data indicated that the adsorption process fit the Langmuir isotherm model for both dyes. Although the results indicated that both organobentonites adsorbed two of the dyes, the freeze-dried sample could serve as a more effective adsorbent for removing reactive and direct dyes from wastewater.

1. Introduction

The textile sector is known for its substantial water consumption. The various textile finishing processes involved, such as dyeing and washing, result in the discharge of a significant amount of wastewater containing concentrated dyes and chemicals. This discharge poses a major threat to the ecosystem, contributing to elevated levels of chemical and biochemical oxygen demand as well as coloring substances. Consequently, effective treatment of textile wastewater has become an increasingly crucial issue.

It is important for textile companies to develop an economical and environmentally friendly treatment system in order to adapt to today's competitive conditions. In this context, it becomes crucial to research and improve the methods of wastewater treatment. Among these methods, wastewater treatment through the adsorption of pollutants by pristine and/or modified clays has become increasingly notable [1]-[3].

Clay minerals are typically layered aluminum silicates with a large surface area and nanometer-scale size. Moreover, their surfaces are negatively charged and hydrophilic, rendering them unsuitable for the adsorption of organic molecules like textile dyes. The surface properties of clay minerals can be altered by using organic compounds, such as alkyl ammonium ions, to achieve hydrophobic/organophilic surfaces. This modification leads to an enhanced interaction between the organic molecules and the surface [4]-[6]. Therefore, organoclays modified with cationic surfactants exhibit strong interactions with textile dyes, driven by the hydrophobic affinity among the dye molecules and the clay surfaces [7]-[9]. As a result, clays have found widespread use in various environmental applications, such as the removal of pollutants like anionic dyes [10, 11], cationic dyes [12], [13], heavy metals [14]-[16], etc. from wastewater, either alone or in composite form with other materials. However, to our knowledge, the impact of drying conditions on the adsorption of textile dyes by modified bentonites has not been

*Corresponding author: perrin.akcakoca@ege.edu.tr

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investigated, despite previous studies investigating the impact of chemical modifications on the adsorption capability of bentonites for textile dyes. Thus, the purpose of this study is to comparatively examine the effect of drying conditions applied in the modification of bentonite on its adsorption properties for reactive and direct dyes.

In this study, two different types of organobentonites were synthesized under identical conditions, except for the drying step, where either freeze-drying or air-drying was employed. The modified bentonites obtained through air-drying and freeze-drying were labeled Sample I and Sample II, respectively.

2. Material and Method

2.1. Materials

The synthetic textile dyes, Reactive Red 141 (RR141) and Direct Red 81 (DR 81), were supplied from Dystar. The molecular configurations of these dyes are illustrated in Figure 1 for RR141 and Figure 2 for DR 81. The bentonite used in the experiments was sourced from the Tokat Reşadiye region of Türkiye. Its cation exchange capacity (CEC) was assessed to be 0.91 meq/g by Yılmaz and Yapar [17]. The surfactant used for the modification, hexadecyltrimethylammonium bromide (HDTMAB) [$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$], was obtained from Merck.

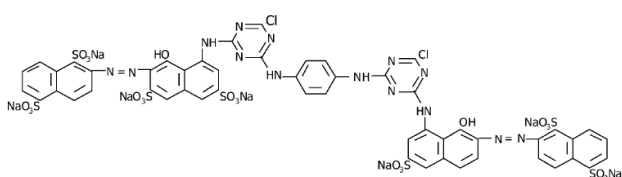


Figure 1. Molecular configuration of C.I. Reactive Red 141 [18].

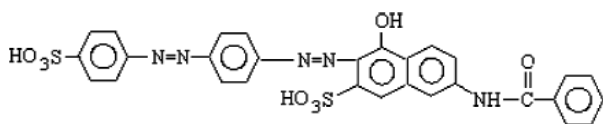


Figure 2. Molecular configuration of C.I. Direct Red 81 [19].

2.2. Organobentonite Production

The organobentonites were prepared using the procedure described in a prior investigation [20], with the exception of drying conditions. In brief, the

sedimentation method was initially used to remove unwanted components such as iron oxide and silica from crude bentonite. Following the sedimentation process, the specimens were subjected to drying in an oven at 60 °C and pulverized using a grinder.

The purified bentonite-water dispersion and HDTMAB solution, prepared following the procedures outlined in the literature [17], were mixed. The mixture was subsequently exposed to microwave irradiation at 360 W for 5 minutes in a microwave oven. This step was followed by multiple washes with purified water until no surfactant particles were detected in the filtered solution. The detection of surfactant presence in the filtered solution was carried out using the methyl orange technique [21]. Following the washing process, the samples were dried using either an air dryer or a freeze dryer. The specifics of the drying parameters can be found in Table 1.

Table 1. Drying parameters.

Sample no	Method of drying	Drying conditions
I	Oven	T=60 °C, time = 2 days
II	Freeze	T = -45 °C, P = 0.060 mbar, time=8h

2.3. Material Characterization

The structural characteristics were examined through X-ray diffraction employing a Philips X'Pert Pro diffractometer within the 2 ° to 40 ° (2θ), and FTIR spectra of bentonites were acquired using a Perkin-Elmer FTIR spectrophotometer.

2.4. Adsorption Studies

The studies were conducted on Samples I and II by agitating dispersions containing 50 mg of adsorbent in 50 mL of dye solution at different concentrations. Agitation took place at 30 °C for 24 hours in a water bath (Nuve, ST 402). At the end of the agitation period, the solid phase was separated from the solution through centrifugation, followed by filtration to eliminate the tiny bentonite particles that could affect the absorbance measurements. The dye content in the supernatant was determined using a UV-Vis spectrophotometer (Perkin-Elmer Lambda 25).

The adsorption capacity, denoted as q_e (mg/g), for the adsorbent was computed utilizing Equation 1. Subsequently, the equilibrium concentration, C_e (mg/L) versus the adsorption capacity was plotted.

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_0 is the initial concentration of dye in the solution (mg/L); V represents the total volume of dye solution used (L); and m is the mass of adsorbent employed (g).

2.4. Adsorption Isotherms

The Langmuir equation is shown in Equation 2 [22]:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{2}$$

Here, q_{max} represents the maximum adsorption capability with full monolayer coverage on the surface (mg/g), and K_L represents the Langmuir constant (L/mg). Equation (2) can be linearized as follows [22]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \tag{3}$$

The constants can be determined by analyzing the intercepts and slopes on the linear graphs of C_e/q_e plotted against C_e .

The dimensionless separation factor, R_L , is a fundamental aspect of the Langmuir equation. Equation 4 presents the formulation for R_L [22]:

$$R_L = \frac{1}{1 + K_L C_H} \tag{4}$$

where C_H is the highest initial solute concentration and K_L is the Langmuir adsorption constant (L/mg). Table 2 shows the parameter R_L indicated the shape of isotherm.

Table 2. The R_L parameters indicate the isotherm type [22].

Value of R_L	Type of isotherm	Value of R_L
$R_L > 1$	Unfavorable	$R_L > 1$
$R_L = 1$	Linear	$R_L = 1$
$0 < R_L < 1$	Favorable	$0 < R_L < 1$
$R_L = 0$	Irreversible	$R_L = 0$

The Freundlich equation characterizes heterogeneous systems and may be expressed through the heterogeneity factor $1/n$. The equation is presented as follows [22]:

$$q_e = K_F C_e^{1/n} \tag{5}$$

where K_F represents the Freundlich constant (mg/g) (L/mg)^{1/n}, and $1/n$ is the heterogeneity factor. The Freundlich model can be linearized by applying the logarithm of Equation (5):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

The constant K_F and the exponent $1/n$ can be derived from analyzing the intercepts and slopes in the linear graphs of $\ln q_e$ plotted against $\ln C_e$ [22].

3. Results and Discussion

3.1. XRD Results

The basal spacings (d_{001}) for raw bentonite, Sample I, and Sample II are shown in Figure 3. A close examination of the figure reveals that the d_{001} values of the samples were increased in comparison to the raw bentonite. This outcome suggested that quaternary ammonium cations are present within the interlayer of the modified bentonites. Besides, the calculated interlayer spacing of Sample I and Sample II was 0.88 nm and 0.915 nm, respectively. These values correspond to a bilayer arrangement in the interlayer spaces [23], [24].

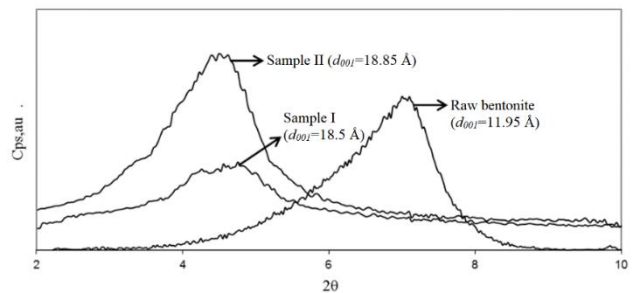


Figure 3. X-ray diffraction spectra of raw bentonite, Sample I, and Sample II.

3.2. FTIR Results

Figure 4 displays the FTIR spectra of the untreated bentonite, Sample I, and Sample II. The strong peaks at 2850 and 2920 cm^{-1} detected in the samples are assigned to the symmetric and asymmetric stretch vibrations of the methyl and methylene units, respectively [25]. The peaks observed between 1465 and 1475 cm^{-1} also represent their bending vibrations [26], [27]. These peaks, identified in

organobentonites, indicate the insertion of surfactant particles between the silica layers of organobentonites. Consequently, this observation can be considered evidence supporting the surface modification of bentonites.

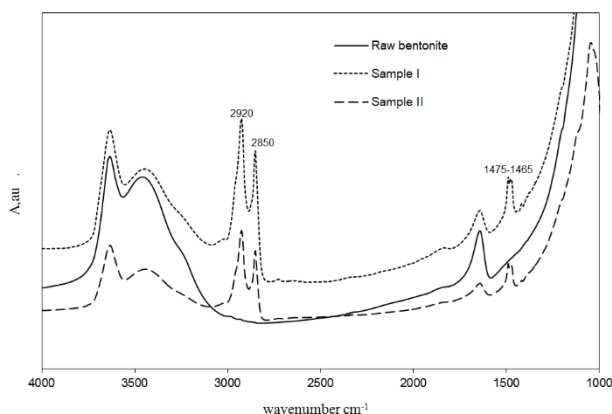


Figure 4. FTIR spectra of the untreated bentonite, Sample I, and Sample II.

3.3. Adsorption Isotherms

The experiments were conducted using raw bentonite for comparison purposes. The approximately equal concentration values before and after adsorption showed that the natural clay adsorbed almost no Reactive Red 141 and Direct Red 81 dyes. Because of the negative surface charge and the hydrophilic nature of the mineral surface, water is preferably adsorbed, and organic compounds cannot compete with water. In other words, Na-clays are less effective adsorbents

for organic molecules. However, the anionic surface property of clay can be altered by using positively charged organic compounds such as alkyl ammonium ions. The modified clay surface (HDTMA-Bentonite) becomes hydrophobic and can strongly interact with organic molecules. Textile dyes are also significantly large organic molecules and can be adsorbed between the dye molecule and HDTMA-Bentonite through hydrophobic interaction.

Studies have been conducted to obtain the adsorption isotherms of HDTMA-bentonite. The Langmuir and Freundlich isotherm equations were employed to model the experimental isotherms. The determination of the r^2 values for these equations was conducted to assess the appropriateness of the isotherms. Normalized deviation values (ΔQ) were additionally examined with respect to every isotherm. The ΔQ values were computed using the following formula:

$$\Delta Q = \frac{1}{N} \sum \left[\frac{(Q_{calc} - Q_{exp})}{Q_{calc}} \right] \quad (7)$$

Here, the subscripts “*exp*” and “*calc*” indicate the experimental and calculated values, respectively, and N represents the quantity of experimental data points [28].

Tables 3 and 4 show the Langmuir and Freundlich constants for the adsorption of RR 141 and DR 81, respectively. Additionally, Table 5 displays the normalized deviation values for the samples.

Table 3. The Langmuir and Freundlich constants for the adsorption of RR 141.

SAMPLE	Langmuir isotherm model				Freundlich isotherm model		
	q_{max} (mg/g)	K_L (L/mg)	r_L^2	R_L	K_F (mg/g)(L/mg) ^{1/n}	n	r_F^2
I	82.9	0.076	0.98	0.062	19.42	3.502	0.83
II	167.97	0.308	0.98	0.016	53.97	3.489	0.72

Table 4. Langmuir and Freundlich constants for the adsorption of DR 81.

SAMPLE	Langmuir isotherm model				Freundlich isotherm model		
	q_{max} (mg/g)	K_L (L/mg)	r_L^2	R_L	K_F (mg/g)(L/mg) ^{1/n}	n	r_F^2
I	84.55	0.07	0.98	0.066	18.94	3.409	0.86
II	173.96	0.27	0.99	0.017	53.87	3.309	0.87

Table 5. The normalized deviation values (ΔQ) for Samples I and II.

Sample	Dye	Langmuir isotherm	Freundlich isotherm
		model	model
I	RR 141	0.0491	0.0797
	DR 81	0.0375	0.0751
II	RR 141	0.1674	0.1797
	DR 81	0.0112	0.1231

Considering the r^2 and ΔQ values, it can be concluded that the equilibrium data for RR 141 and DR 81 on Samples I and II adhere to the Langmuir isotherm. The correlation coefficient values for the Langmuir isotherms of both organobentonites ($r^2 \approx 0.99$) indicate a robust positive relationship. The calculated R_L values, intrinsic to the Langmuir isotherm, were also determined to be within the range of 0 and 1 for both modified bentonites, indicating favorable adsorption of the dyes (Table 2).

The adsorption isotherms of RR 141 and DR 81, plotted using both the experimental and calculated data, are illustrated in Figures 5 and 6, respectively.

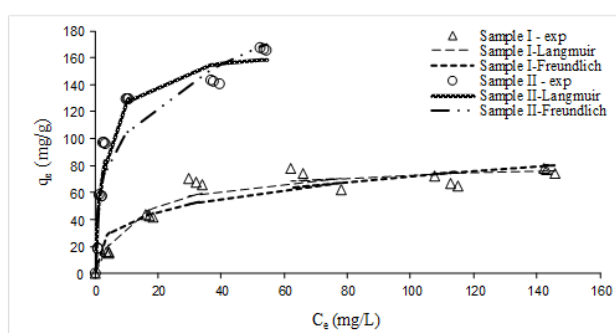


Figure 5. The adsorption of RR 141 on Sample I and Sample II.

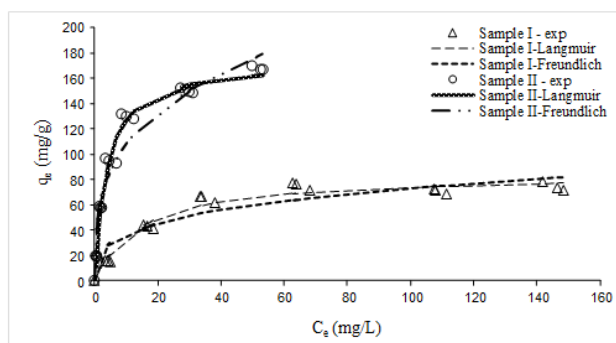


Figure 6. The adsorption of DR 81 on Sample I and Sample II.

The adsorption isotherms of the dyes indicate that the quantity of absorbed dye increases as the initial dye concentration increases until it reaches a state of equilibrium (Figs. 5 and 6). The enhanced adsorption capacity of Sample II, in contrast to Sample I, can be ascribed to the distinct surface morphology formed due to variations in drying conditions. During the freeze-drying process, as water evaporates, the frozen water within the product transitions directly to vapor, thus creating a porous structure in the product. This porous structure can

affect the properties of the product and may assist in achieving desired characteristics in the adsorption process.

4. Conclusion

In the present study, XRD and FTIR analyses demonstrated that HDTMAB was successfully intercalated within the clay. The Langmuir isotherm model, indicating favorable adsorption of both dyes, explained the adsorption behavior of RR141 and RR81. The removal of more than 80% of the dye by freeze-dried organobentonite suggests a relatively more positive impact of freeze-drying than air-drying (which achieved 60% removal) on the removal of reactive and direct dyes from wastewater. The greater adsorption capacity was attributed to the existence of a porous structure formed during the freeze-drying process. In contrast to previous studies that reported the effect of modification on dye adsorption of clay, this study investigates the effect of drying, demonstrating that the applied drying method in the modification process significantly influences the dye adsorption capacity of organobentonite.

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Contributions of the authors

The authors' contributions to the paper are equal.

Conflict of Interest Statement

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The study is complied with research and publication ethics.

Nomenclature

q	Dye concentration on adsorbent, mg/g
C	Dye concentration in aqueous solution, mg/L
V	Total volume of dye solution (L)
M	Mass of adsorbent, g
R^2	Linear regression coefficient
K	Adsorption isotherm constant, L/g
T	Time, min
T	Temperature, C
R_L	Characteristic of the Langmuir equation
N	Heterogeneity factor
RR 141	C.I. Reactive Red 141
DR 81	C.I. Direct Red 81
HDTMAB	Hexadecyltrimethyl ammoniumbromide

CEC	Cation exchange capacity
XRD	X-ray diffraction
FTIR	Fourier transform infrared spectroscopy

Subscripts

cal	Calculated
exp	Experimental
0	Initial condition
e	Equilibrium condition
max	Maximum
L	Langmuir isotherm
F	Freundlich isotherm
t	The condition at time, t

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