



Enhancing Batch Adsorption capacity of Bentonite, Kaolinite and their Organomodified Forms for Phenol removal

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Abstract: In the present work, natural and modified clays were applied as adsorbents for the removal of organic contaminants from wastewater. We were mainly interested in the removal of phenol from the polluted water, by using two types of Algerian clays namely bentonite of Maghnia and kaolinite of Annaba in their pure state and their organically modified state.

The study was achieved by optimizing the equilibrium parameters namely: equilibrium time, initial pollutant concentration, pH, clay concentration and ionic strength of the solution. This kinetic study was performed in static mode for each system adsorbent-adsorbate. The determination of parameters such as adsorption capacity, adsorption constant, distribution constant, are used to develop an equilibrium model. Then, a study of each adsorbent-adsorbate system is conducted in dynamic mode so as to assess the possibilities of application of continuous separation process. These experiments aim to generate open curves for each system in order to determine the useful transfer time by changing the flow rate, the concentration, the height and size.

Key-words: bentonite, kaolinite; adsorption; phenol; equilibrium parameters.

Introduction and Experimental

The fight against pollution of the environment due to the different releases is a major concern worldwide. Awareness of this universal problem is quite related to the dangers it causes to human life. The presence of pollutants in the water such as heavy metals and organic aromatic compounds makes it difficult and sometimes impossible to use. These environmental releases can contaminate surface water and/or groundwater with concentrations exceeding the tolerated threshold values. Thus, treatment of industrial and domestic effluents and becomes paramount.

On average, the human need for water is at least 1,000 m³ per year per person. The United Nations Program for the Environment (UNPE) has identified several focal areas including freshwater resources, areas of water shortage, sources of pollution of soil, water and biological diversity.¹

By 2025, according to data published by the United Nations, two-thirds of people worldwide will experience water shortages. The looming water crisis is mainly due to the problems of distribution and management rather than supply².

In this context, several methods are proposed to protect and treat these waters regardless of their source. Among these techniques there has the adsorption, chemical precipitation, ion exchange, membrane

processes etc. Adsorption is the most widely used, wherein the active carbon or the ion exchange resins are generally used. Activated carbon has the advantage of having a high adsorptive capacity for phenolic compounds, heavy metals and dyes, due to its high surface area. However, because of its relatively high cost, it is preferred to use natural adsorbents that are cheaper and equally effective in the treatment of industrial wastewater discharges.

In recent years there is an increase use of materials made of natural clay used for the removal of toxic metals and some organic pollutants from aqueous solutions³⁻¹⁰. Two types of clay minerals can be cited: kaolinite and bentonite.

The organic modification is seen as a way of increasing the mitigation potential of organic compounds of clay. In this process, organic cations are exchanged by natural metal cations and cations of the intermediate layer of the earth (minerals extracted from clay). This can give rise to two types of materials. The first is a layered arrangement of clay sheets which actually increases the specific surface of the clay and can otherwise limit the adsorption of organic compounds. The other type has a growing affinity for the organic content.

The establishment of a new adsorbent-adsorbate system can contribute and complete the industry of water treatment by removing non-biodegradable pollutants. Hence, our study is intended to develop adsorbents extracted from local clays mainly kaolinite and bentonite. In their natural state, these natural silicates, have a low adsorption rate, therefore, a suitable pre-treatment is necessary or even imperative to improve and increase their adsorption capacity by increasing their surface area. Several methods and techniques can be employed to achieve this goal among which we cite chemical and thermal treatments. The first is an acid-base attack which increases porosity in the structure. As regards the second, under the influence of heat causes the rupture of some "bridges" which promotes the creation of cavities in the structure.

The study of the adsorption equilibrium is achieved by choosing typical molecules (pollutants) with pre-treated clays. This should be preceded by optimizing the equilibrium parameters namely: equilibrium time, initial pollutant concentration, pH, clay concentration and ionic strength of the solution. This kinetic study was performed in static mode for each system adsorbent-adsorbate.

The determination of parameters such as adsorption capacity, adsorption constant, distribution constant, are used to develop an equilibrium model. Then, a study of each adsorbent-adsorbate system is conducted in dynamic mode so as to assess the possibilities of application of continuous separation process. These experiments aim to generate open curves for each system in order to determine the useful transfer time by changing the flow rate (yield), the concentration, the height and size.

In the present work, we are interested in studying the removal of organic compounds (phenol) of the polluted water, by using two types of Algerian clays, i.e. bentonite of Maghnia and kaolinite of Annaba in their pure state and their organically modified states.

Analytical Instruments

UV-visible spectrophotometer

The quantitative analysis of phenol in the aqueous solutions was obtained by using a standard Spectrophotometer UV-Visible type Cary-100 Varian in the range 180-1100 Nm, with a quartz cell 1cm large.

Infra-red spectrophotometry (FTIR):

FT-IR spectra were recorded using a spectrophotometer type thermo nicolef Nexus 670 FT-IR. KBr was dried in a dryer at 200 ° C for 24 h, and then it is homogenized with the clay with a 1/100 ratio in a ball mill. The pellets (1 cm diameter, 0.1 cm thickness) were prepared using a hydraulic press. The infrared spectrum was recorded in the frequency range 400-4000 cm⁻¹.

.X-ray Diffraction (XRD)

The X-ray diffraction is performed using the diffractometer (XRD-6000, Shimadzu) with x-ray

copper radiation filtered by nickel ($\text{CuK}\alpha$, $\lambda = 1.5406 \text{ \AA}$), wherein Cu is the material target which produces primary X-rays with voltage of 30 kV and a current of 30 mA. Scanning is done by the following steps: scanning range 2-80 2θ without interruption with speeds of $2^\circ / \text{min}$ and a receiving slit width of 0.3 mm.

X-ray fluorescence (XRF)

The chemical composition of the bentonite, kaolinite and their modified samples is determined using the X-ray fluorescence spectrometer (XRF-1800, Shimadzu). The microscope of type 3400T Wraymer 40-200 with an optical magnification ratio is used to determine the form of bentonite. The shape and surface morphology of the samples are also made with Shimadzu SSX-Sem Super Scan Series. The concentrations of metal ions were determined using ICP (ICPS-7510, Shimadzu) under the conditions: RF Power = 1.2 kilowatts, the refrigerant gas flow = 14.0 l / min gas flow rate plasma = 1.20 L/min and carrier gas flow rate = 0.70 L/min.

Extraction process of phenol in the aqueous solutions:

Experiments are performed in series by introducing an appropriate amount of the mineral clay in a test tube. A preselected volume of the aqueous solution of the adsorbate of a known initial concentration is added. The tube is closed tightly and sealed with para-film covered with a polythene bag. The tube is then placed on the support of the stirring device in a thermostatically controlled water bath. As part of the phenol extraction, the tube is agitated for two hours to reach equilibrium. A portion of the clear solution was sampled for appropriate quantitative analysis.

Preparation of the solutions

A standard mother solution of phenol is prepared by dissolving 1g of phenol in 1 L of de-ionized water, 0.05% of sodium azide is added to the mother solution as a retarder of bacterial growth. Solutions of 250 ml having phenol concentrations from 10 to 100 ppm are prepared by dilution of the mother solution.

Phenol Analysis

The absorbance of the solutions is measured at $\lambda_{\text{max}} = 270 \text{ Nm}^{11}$. The calibration curve for the phenol solutions (absorbance versus concentration) is illustrated in **figure 1** showing the range of the concentration which obeys the law of Beer-Lambert.

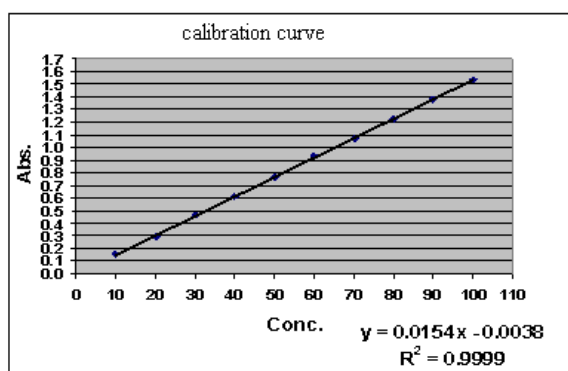


Figure.1: Calibration curve of the phenol solutions

Equilibrium Time

Time required Time for a complete saturation of the surface of the adsorbent to 25°C by phenol is given as follows:

20 ml of volume of an initial concentration, 60 ppm of phenol solution of pH 6.5 are agitated with preselected quantities for each adsorbent made up of particles of diameter of $45 \mu\text{m}$ during a given time. The concentration of phenol remaining in the solution is given according to time (5, 10, 15, 20, 30, 60, 90, 120, 150, 180, 240 and 300 minutes). The time of saturation is given from the curve for each adsorbent

Effect of pH

The adsorption of phenol on each mineral clay sample is studied according to pH (2, 6,5 and 10). The pH of the solution is adjusted by using the hydrochloric acid or the sodium hydroxide.

Organic modification of bentonite and kaolinite

Each of two mineral clays is organically modified with hexadecyltrimethylammonium bromide (HDTMA-Br) and phenyltrimethylammonium bromide (PTMA-Br). Modified clays are used as extractors of phenol aiming to compare them with raw minerals. The modification is carried out as follows^{12,13}:

The mother solutions of HDTMA-Br and PTMA-Br are prepared with a concentration of 50 meq/L, by dissolving 18.5 g and 10.8 g of HDTMA-Br and PTMA-Br, respectively in 1 L de-ionized water. 50 mL of the solution are added to 3.5 g of dry ore of particle size of 45 μm then agitated during one hour.

To the suspension, we add 70 mL of the mother solution then the mixture is stirred during 24 h. the aqueous phase is elutriated and the residue is mixed with 120 mL of de-ionized water then stirred during half an hour. This washing was repeated three times. The modified ores are dried with the air until obtaining a constant mass. The analysis of the modified form is carried out using elementary analysis (microanalysis CHN). Modified bentonite and kaolinite samples will be represented by the symbols B-HDTMA, and B-PTMA; K-HDTMA and K-PTMA respectively.

Characterization of mineral clay

X-rays diffraction (XRD)

The samples to be analyzed are crushed and ground until obtaining particles less than 1 mm in diameter and are placed on a support. These experiments are carried out during the night, in order to reduce the noise/signal ratio. The operating conditions are:

-monochromatic source of x-ray; $\text{CuK}\alpha$ with $\lambda = 1.5418 \text{ \AA}$; tension of 40 KV; intensity 30 mA; Detector of x-ray at 115 KV; range of sweeping of $5\text{-}90^\circ 2\theta$; primary width of slit 3,17 mm; and time of pause is 1 to 5 S under an angle of $0.02^\circ 2\theta$ (interval of stage).

x-ray fluorescence (XRF)

XRF is one of the simple analytical methods used to determine the chemical composition of various types of materials even as traces. XRF has the advantage to be fast, nondestructive, multi-elementary and reliable the methods compared to other methods.

particle sizes Distribution

Multi-channel model type TAIH is used both to measure particle size of particles and to distribute the mineral clay particles according to their dimensions, through various channels

Superficial Surface Measurement.

The superficial surface of powder mineral clays is given using the method of Brunauer, Emmett and Teller (BET) developed in 1938¹⁴.

The method implies the liquid nitrogen physisorption the surface of the sample at 77 K.

Surperficial surface is also determined by the evaluation of the capacity of the monolayer (q_{max}) using adsorption of methylene blue on the solid adsorbents¹⁵⁻¹⁷.

Cation exchange capacity (CEC)

The adsorption of the complex bis(ethylenediaminecuiivre(III)), $[\text{Cu}(\text{en})_2]^{+2}$ is a successful method for the determination of the CEC on mineral clays¹⁸. This method was adopted for the present work.

Results and discussion

Organic Modification of Bentonite and Kaolinite

Two types of organic modifiers were used, namely: hexadecyltrimethylammonium bromide (HDTMA) and phenyltrimethylammonium bromide (PTMA). Both clayey materials were organically modified by adsorption of (HDTMA) and (PTMA) and lead to four organo-modified clays available for further investigation. This process exchanges some of the naturally occurring earth cations for organic cations, which creates a less hydrophilic clay surface. In the case of (HDTMA) modified clays, a hydrophilic surface is created. (HDTMA) was chosen as a representative long chain modifier and (PTMA) was chosen as a representative short chain modifier. Modification was made as described previously. The modified samples of bentonite (B) and kaolinite (K) would be henceforth referred to with the symbol B-HDTMA and B-PTMA; K-HDTM and K-PTMA respectively.

The difference in carbon content between the modified sample C_M , and the unmodified sample C_C , was considered to be entirely due to the exchanged modifier. The modifier loading of the mineral clay can be calculated by using the following formula

$$L_M = \left[\frac{V(C_M - C_C) \cdot 1000}{100M_m - [(C_M - C_C)M_c]} \right] \cdot 100$$

Where

L_M : modifier loading in milliequivalents per 100 g of unmodified clay.

V: valency of the modifying cation, (1 for both HDTMA and PTMA).

C_M : % carbon in modified clay.

C_C : % carbon in unmodified clay.

M_m : M.wt of the carbon atoms in the modifier.

M_c : M.wt of the modifier.

The C H N analytical values of the two clays and their modified forms are given in **Table 1**, and the calculated modifier loadings are given in **Table 2**:

It can be deduced from the data in **Table 2** that in both HDTMA and PTMA modifications, the modifier loading, L_M , is in the order: Bentonite > kaolinite

This order is as well respect for % L_M / L_{av} at the experimental conditions of modification in the present study.

For each mineral clay, the value of L_M is in the order: HDTMA > PTMA

Table 1: C H N analytical results of bentonite and kaolinite and their modified forms

Mineral Clay	%C	%H	%N
Bentonite	0.075	1.012	4.678
B-HDTMA	10.842	2.731	2.264
B-PTMA	8.310	3.731	3.116
Kaolinite	0.130	3.126	5.834
K-HDTMA	7.110	4.955	7.114
K-PTMA	6.849	4.955	6.839

Table 2: Percentage modifier loading of bentonite and kaolinite and their modified forms

Clay Mineral	HDTMA		PTMA	
	L_M	% L_M/L_{av}	L_M	% L_M/L_{av}
Bentonite	76.30	44.51	52.35	30.54
Kaolinite	34.39	20.06	39.91	23.28

L_M in meq/100g

L_{av} : available modifier for loading =171.43 meq/100g clay

The ratio L_M/L_{av} for B-HDTMA, B-PTMA, K-HDTM

and K-PTMA are in the following order:

B-HDTMA > B-PTMA > K-PTMA > K-HDTMA

Mineral Constituents/ XRD Analysis

The mineral constituents of B, K, B-HDTMA, B-PTMA, K-HDTM and K-PTMA as determined by the XRD method are given in **Table.3**.

Table 3. Mineral constituents of bentonite and kaolinite

Clay Minerals	Mineral Constituents		
	Major	Minor	Trace
Bentonite	Montmorillonite*, Quartz	Calcite, Mangetite, Rinneite	Gypsum, Muscovite
Kaolinite	Kaolinite, Quartz	Witherite	Chaoite

*Montmorillonite (Hydrated Sodium Calcium Aluminum Magnesium Silicate Hydroxide), Quartz (Silicon Dioxide), Kaolinite (Aluminum Silicate Hydroxide), Calcite (Calcium Carbonate), Rinneite (Potassium Sodium Iron Chloride), Witherite (Barium Carbonate), Gypsum (Hydrated Calcium Sulfate), Muscovite (Potassium Aluminum Silicate Hydroxide).

Chemical Composition/ XRF Analysis

The chemical elemental composition of the bentonite and kaolinite and their modified forms as determined by the XRF method is given in **Table.4**.

Table 4 Chemical Compositions of B, K, B-HDTMA, B-PTMA, K-HDTMA and K-PTMA

Clays	SiO ₂	Al ₂ O ₃	FeO ₃	TiO ₂	P ₂ O ₅	CaO	MgO	Na ₂ O	K ₂ O	LOI
B	57.94	19.83	1.89	0.17	0.04	0.60	2.18	2.91	1.84	12.60
B-	57.47	19.01	1.08	0.15	0.05	0.25	1.88	2.68	0.83	16.60
B-	57.63	18.91	1.33	0.16	0.05	0.55	1.78	2.71	1.13	15.75
K	46.09	37.76	0.96	0.16	0.12	0.12	0.29	0.18	1.11	13.50
K-	46.11	37.71	0.98	0.14	0.11	0.11	0.27	0.16	1.09	13.32
K-	46.13	37.72	0.98	0.15	0.10	0.07	0.24	0.10	1.06	13.45

FTIR Analysis

The bands at 3621-3698 cm⁻¹ can be assigned to the terminal silanol-OH and to the bridge Si-OH-Si(Al) or to the hydrogen bonded Si(Al)OH. The broad bands at 3432-3470 cm⁻¹ can be assigned to the OH stretching vibrations (ν_{OH}), which may arise from the isomorphous substitution in the tetrahedral and octahedral layers of the clays. Moreover, these bands appear to have shifted to higher wave numbers in the modified in comparison to the unmodified clays. The bands at 2919-3018 cm⁻¹ appearing in the modified species only could be attributed to the symmetric and asymmetric stretching vibrations of the methylene (ν_{CH_2}), belonging to the organic modifier HDTMA cation. The bands at 1629-1642 cm⁻¹ could be attributed to the OH deformation of water molecules β (H₂O) that have shifted to higher wave numbers as compared to molecular water.

The bands at 912-1385 cm⁻¹ that appear as strong bands or as prominent shoulders can be assigned to the symmetric (ν^{sym} Si-O-Si) or asymmetric (ν^{asym} Si-O-Si(Al)) stretching vibrations. The bands at 702-

839 cm⁻¹ are characteristic of quartz and those at 423-523 cm⁻¹ can be attributed to β (Si-O-Si(Al)) or β (Si-O-Si) bending vibrations.

Particle Size Distribution

Table 5 gives the particle size distribution as percentage weight below for the sieved samples of bentonite and kaolinite. It is evident that the particle of the diameters 4.4- 43.4 micrometer constitutes 99.8% of all particles; a result is in an agreement with the experimentally selected portion through sieving of 45 μ m. **Figure 2** gives the particle size distribution curves of the two clayey, showing a smooth distribution over the entire range of diameter.

Table 5. Particle size distribution of bentonite and kaolinite

Particle Diameter (μ m)	Bentonite	Kaolinite
	% Weight, Below	% Weight, Below
2.9	0	0
3.58	0	0
4.4	0.2	0
5.4	1.1	0.5
6.68	3.5	1.8
8.22	9.2	6
10.12	21.8	16.4
12.46	39.8	32.3
15.3	58.6	50.8
18.9	76.7	70.5
23.26	90	87
28.6	97.7	96.6
35.26	99.7	99.4
43.42	100	99.8
53.45	100	100
65.81	100	100

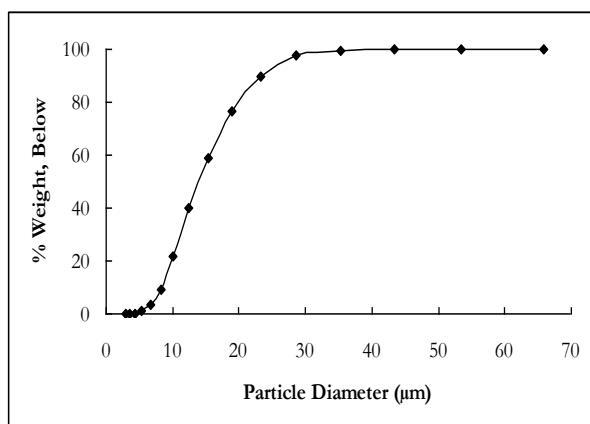


Figure .2a: Particle size distribution curves of bentonite

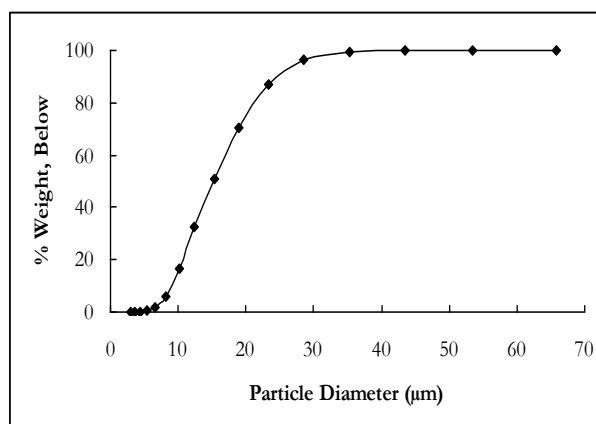


Figure. 2b: Particle size distribution curves of kaolinite

Surface Area

The experimental data obtained by using methylene blue method for the determination of surface area are given in **Table 6**.

For most organic adsorbate materials, the Langmuir equilibrium adsorption isotherm is esteemed, i.e

$$\frac{C_{eq}}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}}C_{eq}$$

Where q_{max} is the saturation capacity for monolayer adsorbate (mg/g).

Table 6 gives the experimentally determined variables of the above equation. Plots of C_{eq}/q_e vs. C_{eq} showing the adsorption isotherm of methylene blue on the bentonite and kaolinite and their organo-modified forms are given. values of q_{max} for each system is determined from the slope. The surface area of each clay and their modified forms can be estimated from the following equation.

$$S = q_{max} \cdot N_A \cdot A_m$$

Where:

S: surface area (m²/g)

N_A : Avogadro's number (molecule/mol)

A_m : molecular cross sectional area (m²/molecule)

The molecular cross sectional area, A_m , of methylene blue is 1.2 nm².

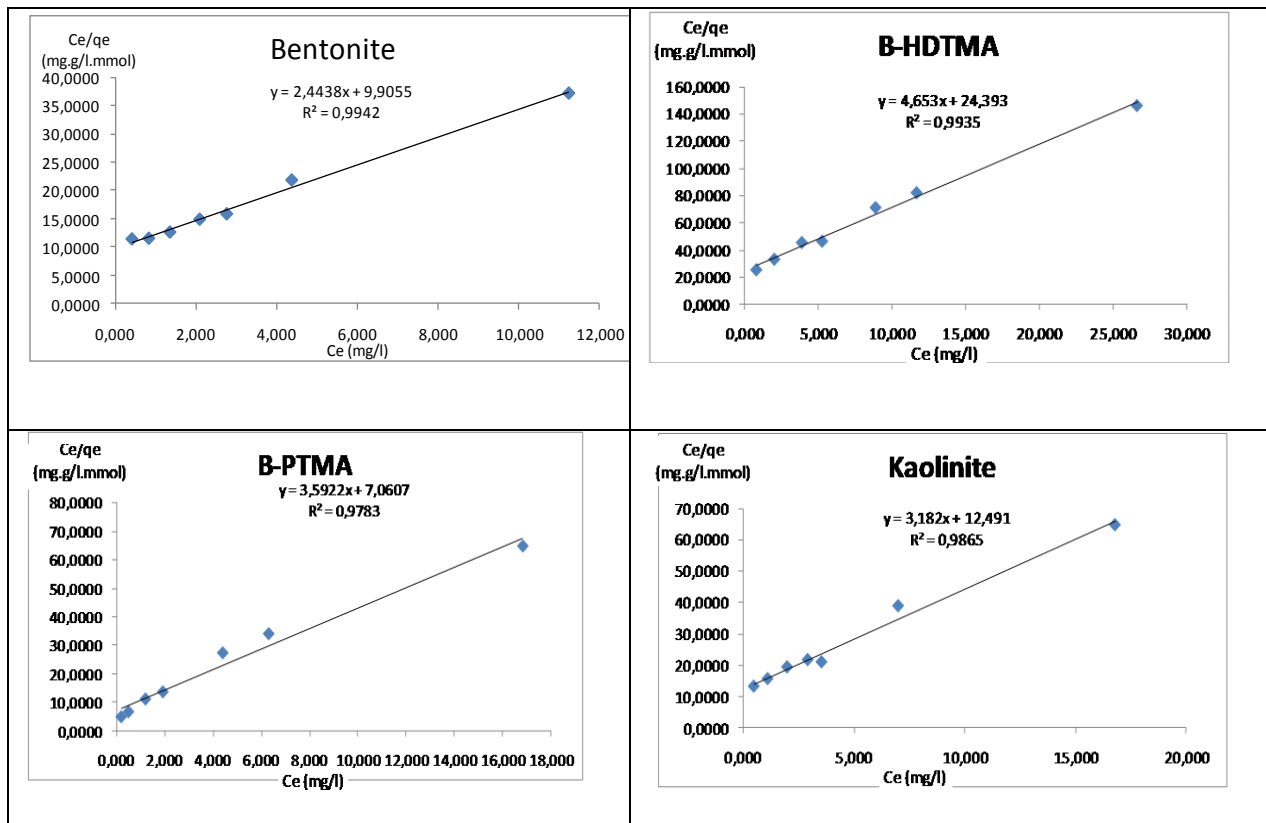
Figure 3 shows the plot of the Langmuir equation for six adsorbents. Linear tits prove a monolayer adsorption of methylene blue on the surface of these adsorbents. The calculated surface areas of these adsorbents determined with methylene blue method together with the values determined by the BET method are given in **Table 7**.

The methylene blue method is the most suited for comparative studies and not for the determination of absolute values. The latter are best obtained by the BET method. This explains why the surface area values obtained by the BET method are not in an agreement with those obtained by the methylene blue method. However, both methods give the same order for these adsorbents i.e. Kaolinite>K-PTMA>Bentonite>B-PTMA>K-HDTMA> B-HDTMA

Table 6: Surface area data of bentonite and kaolinite and their modified species.

Adsorbant	C_o (mg/l)	C_e (mg/l)	$q_e \cdot 10^{+5}$ (mmol/g)	C_e/q_e (mg.g/l.mmol)
Bentonite	5	0.413	0.0359	11.5062
	10	0.833	0.0717	11.6199
	15	1.356	0.1066	12.7131
	20	2.096	0.1399	14.9756
	25	2.767	0.1738	15.9220
	30	4.381	0.2002	21.8801
	50	11.259	0.3028	37.1817
B-HDTMA	5	0.812	0.0327	24.7943
	10	2.028	0.0623	32.5558
	15	3.897	0.0868	44.9044
	20	5.278	0.1151	45.8697
	25	8.900	0.1258	70.7250
	30	11.686	0.1431	81.6411
	50	26.640	0.1826	145.9059
B-PTMA	5	0.176	0.0377	4.6785
	10	0.481	0.0744	6.4695

	15	1.182	0.1080	10.9480
	20	1.904	0.1414	13.4645
	25	4.389	0.1611	27.2423
	30	6.296	0.1853	33.9829
	50	16.836	0.2592	64.9494
Kaolinite	5	0.471	0.0354	13.3011
	10	1.094	0.0696	15.7192
	15	1.979	0.1018	19.4464
	20	2.907	0.1336	21.7622
	25	3.531	0.1678	21.0404
	30	6.997	0.1798	38.9178
	50	16.797	0.2595	64.7237
K-HDTMA	5	0.381	0.0361	10.5585
	10	0.744	0.0723	10.2901
	15	1.441	0.1060	13.5970
	20	2.088	0.1400	14.9159
	25	4.685	0.1588	29.5031
	30	8.034	0.1717	46.7982
	50	21.701	0.2212	98.1138
K-PTMA	5	0.230	0.0373	6.1747
	10	0.812	0.0718	11.3020
	15	1.622	0.1046	15.5105
	20	2.683	0.1353	19.8239
	25	5.367	0.1534	34.9778
	30	7.993	0.1720	46.4658
	50	18.378	0.2472	74.3593



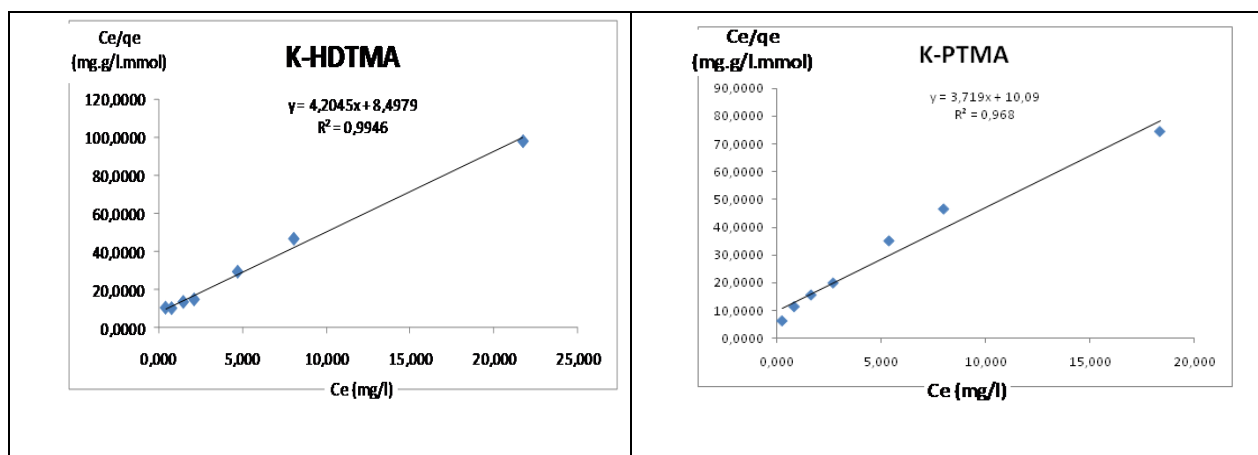


Figure 3: Surface area curves of Bentonite and Kaolinite as representative examples

Table 7: specific Surface area

Adsorbent	Methylene Blue (m ² /g)
Bentonite	296
B-HDTMA	155
B-PTMA	201
Kaolinite	227
K-HDTMA	172
K-PTMA	194

Cation Exchange Capacity (CEC)

The CEC was determined as described previously. The CEC of the samples examined was calculated from the difference between the initial $[Cu(en)_2]^{+2}$ concentration and that remaining in solution after equilibration. The CEC results are given in **Table 8** showing that the order of CEC of these adsorbents together with % CEC exchanged. This is the same order as that of the surface area. The two properties might be directly related to each other, i.e. interdependent.

Table 8: Cation exchange capacity

Adsorbent	CEC (meq/100g)	% CEC exchanged (meq/100g)
Bentonite	77	
B-HDTMA	30	61
B-PTMA	51	34
Kaolinite	60	
K-HDTMA	24	60
K-PTMA	33	45

Bentonite > B-PTMA > K-HDTMA

Equilibration Time

To ascertain the time required for bentonite and kaolinite and their modified species to reach saturation in the removal of phenol from aqueous solution; an initial concentration of (60 ppm) phenol in water was chosen as the mid value between the limits of (10-100 ppm) representing the expected phenol pollution level in surface natural water.

Figure 4 shows plot of % Removal (%R) vs. time of contact for typical cases of Bentonite, B-HDTMA and B-PTMA adsorbents. The shortest time to reach saturation for all systems is deduced from such curves and the results are given in **Table 9** showing that the equilibration time falls in the range 18-100 minutes.

A shaking time of 120 minute was conveniently adopted in all subsequent investigations and for all systems.

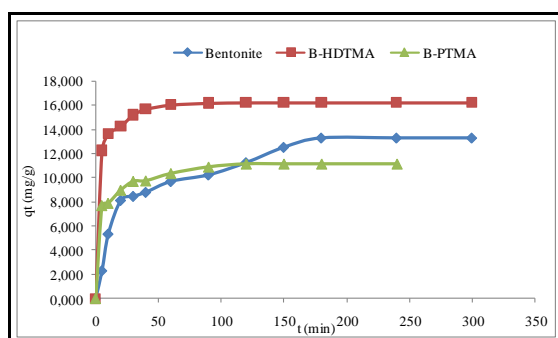


Figure. 4a: Equilibration time of bentonite and modified species

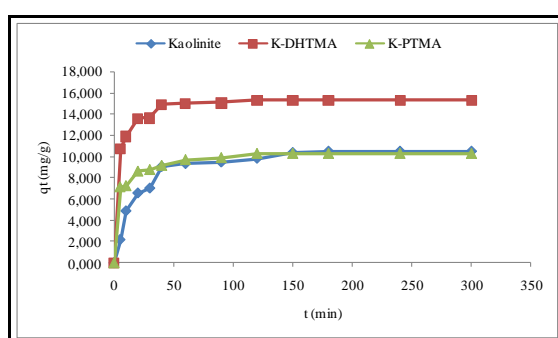


Figure. 4b: Equilibration time of kaolinite and modified species

Table 9: Equilibration time of phenol extraction

Adsorbent	Time (min)
Bentonite	180
B-HDTMA	120
B-PTMA	120
Kaolinite	180
K-HDTMA	120
K-PTMA	120

Effect of pH

A unified preselected weight of 10 g adsorbent per 1 L aqueous solution was chosen for the bentonite and kaolinite and of 5 g adsorbent per 1 L aqueous solution was chosen for the modified species.

For the bentonite and kaolinite, the %R at 25°C was determined as a function of initial phenol concentration in the aqueous solution (10-100 ppm) at three preselected pH values (2.0, 6.5 and 10.0) representing acidic, near neutral and alkaline environment respectively. This selection of pH was made in view of the negatively charged surface of the pure clay minerals and the positively charged adsorbed organic cation on the surface in the case of the modified clay minerals. The pH value was measured before and after reach the equilibrium; the two measurements in each system agreed to within ± 0.3 .

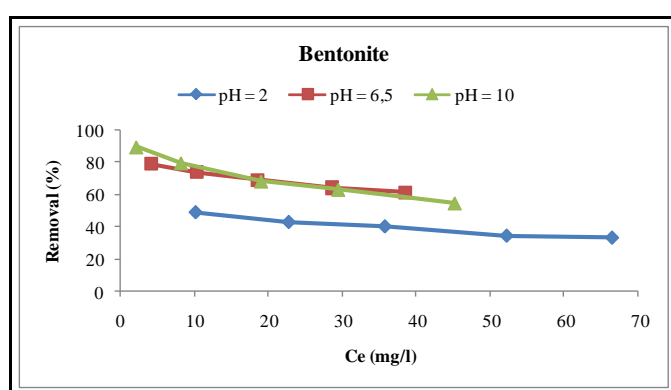
Figure 5 shows plots of %R vs. phenol initial concentration, C_e , at the experimentally adopted pH values for typical systems.

In kaolinite, %R at pH=6.5 is greater than its corresponding value at pH=2.0 for any value of C_e . This can be due to the hydrogen cation competing with the protonated phenol at pH= 2.0 for adsorption on the negatively charged surface of the adsorbent. Hence the lower value of %R at pH=2.0 in comparison to its value at pH=6.5 could be attributed to this competitive action. At pH=10.0, it is interesting to observe the

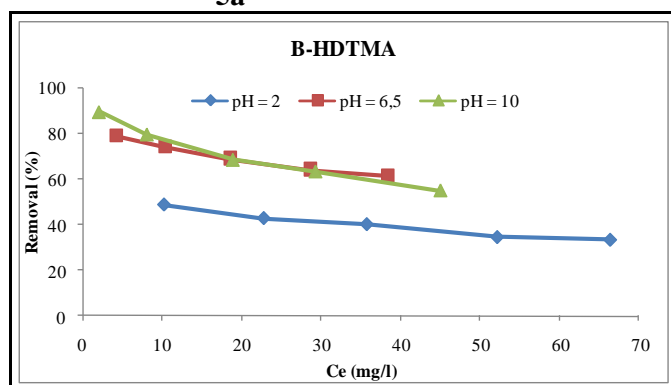
greater adsorption capacity due to the greater attraction of the phenoxide with its very large dipole moment to the adsorbent surface. The phenoxide ion has the highest electrical dipole moment with the positive end located at the tip of the benzene ring.

In the case of the two modified kaolinities, variation of %R with pH is in the order: at pH=2.0 < at pH=6.5 < at pH=10.0 at each C_i . The greater %R at pH=10.0 in comparison to its value at pH=6.5 might possibly be attributed to the greater electrostatic attraction between the positively charged organic modifier and the negatively charged phenoxide (C_6H_5O). The concentration of the phenoxide species at pH=10.0 is greater than at pH=6.5, since phenol is weakly acidic ($pK_a=9.92$); and is not significantly ionised at any pH less than 8.5.

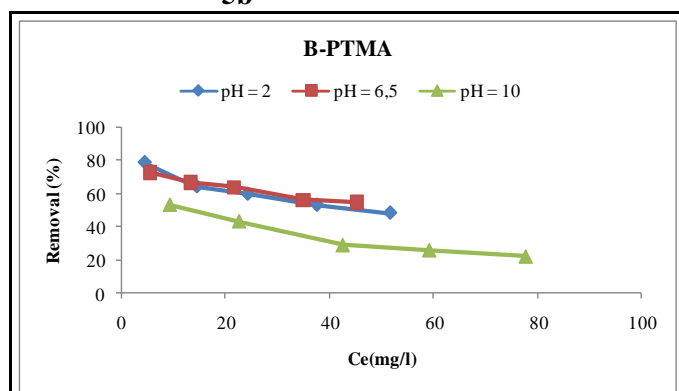
It was decided to conduct the adsorption isotherm investigations at pH= 6.5 so as to avoid both the protonation of phenol at pH= 2.0 and its dissociation at pH= 10.0. Moreover, this pH is within the range of values of Algerian natural water commonly encountered in the environmental applications. Almost the same interpretations can be deduced in the case of bentonite and its derivatives.



5a

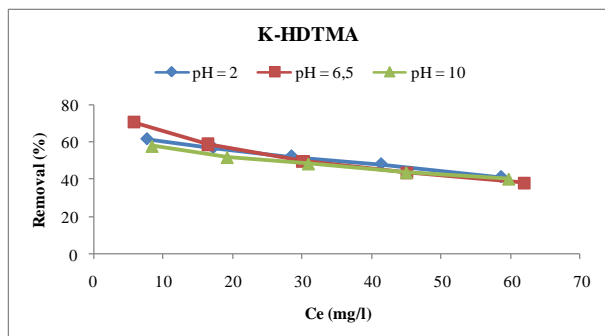


5b

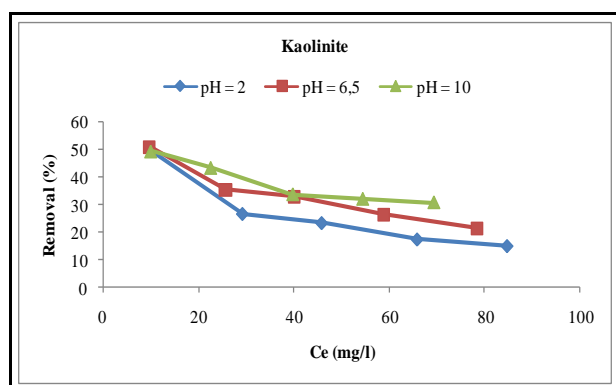


5c

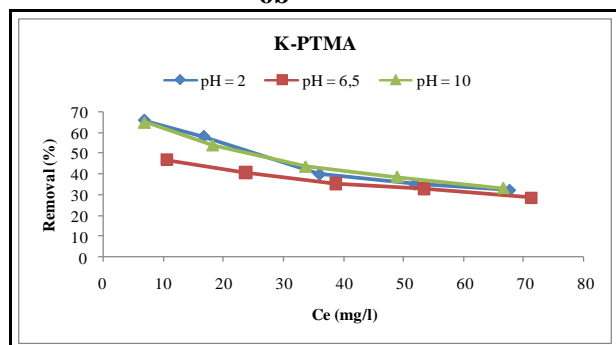
Figure 5. Effect of pH for the phenol removal



6a



6b



6c

Figure 6. Effect of pH for the phenol removal

Conclusion

The present study investigated the use of Bentonite and Kaolinite and their modified forms for environmental applications in terms of removing phenol from aqueous solutions.

It was decided to conduct the adsorption isotherm investigations at pH= 6.5 so as to avoid both the protonation of phenol at pH= 2.0 and its dissociation at pH= 10.0. It was found that the equilibration time falls in the range 18-100 minutes. The CEC results show that the order of CEC of these adsorbents together with % CEC exchanged. This is the same order as that of the surface area. The two properties might be directly related to each other, i.e. interdependent. More investigations might be necessary to assess other parameters.

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