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Improvement of phenol removal from aqueous medium by adsorption on organically functionalized Moroccan stevensite

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Abstract

Keywords

- ✓ Phenol;
- ✓ Rhassoul;
- ✓ Surfactant;✓ Hydrophobic
- *interactions;*
- ✓ Kinetic modeling;✓ Adsorption
- isotherm.

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1. Introduction

In this work, the adsorption of phenol on natural and organically modified Moroccan clay named Rhassoul was investigated using the batch equilibrium method. Several techniques, such as, X-ray fluorescence analysis (XRF), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermal analysis (TGA/DTG) were used for clays characterization. Adsorption experiments were carried out varying initial phenol concentration, pH and contact equilibrium time. The adsorption isotherms of phenol on Rhassoul and modified Rhassoul by the HDTMA surfactant molecules were determined and modeled by Langmuir equation. The experimental results indicate that the adsorption was improved by increasing pH and initial concentration of phenol in the solution. Experimental and calculated kinetic data for equilibrium are well fitted with the pseudo second order kinetic model. The adsorption isotherm was described satisfactorily using the mathematical model of Langmuir with a maximum monolayer adsorption capacity of 25 mg.g⁻¹ for organically-Rhassoul. The results indicate that raw and organically modified Rhassoul could be used as a low cost adsorbent in wastewater treatment for the elimination of phenolic compounds.

The industrial emissions cause serious degradation of the environment and damage to human health. Pollution of the environment is directly related to the economic development of civilization. It is a threat that is increasing and may affect both the natural balance and the human health. Phenolic compounds are among the most dangerous pollutants for human health and the environment. They have been classified as high-priority contaminants by the USA EPA (Environmental Protection Agency) [1]. Phenol is mainly used as an intermediate in various industries (Refining petroleum, pharmaceuticals, plastics industry, production of dyes and pesticides...). The toxic and hazardous nature of phenols and their derivatives have been well documented [2-5] and can cause several health problems [6]. The treatment of water contaminated with phenolic compounds remains a major challenge, especially for developing countries that have not yet all opportunities to integrate the concepts of sustainable development. The complexity of their chemical structure and the presence of aromatic rings, mean that the corresponding aqueous effluents require treatment in several steps. One of the most important steps is the adsorption process permitting the concentration of the compound in a solid phase. Some adsorbents commonly used on the removal of phenolic compounds by adsorption techniques are activated carbon, clays, zeolites, polymeric adsorbents, and some other low-cost materials [7-9]. These materials are very promising in this area. These adsorbents generally require subsequent specific treatment for the degradation of these molecules and regeneration of adsorbents [10-11]. The present investigation aims to study a simple and economic process for phenol removal from aqueous solution using low cost abundantly available adsorbent (natural or modified Rhassoul). The Rhassoul clay is characterized by a large cation exchange capacity CEC [12]. This parameter is responsible for hydration of these mineral materials and subsequently for their hydrophilic properties. The intercalation of cationic surfactants in the clay galleries improves drastically the hydrophobic properties which play a key role in the retention of non-ionic organic pollutants. We used for this study the natural and modified Rhassoul by hexadecyltrimethylammonium bromide HDTMA: [N(CH₃)₃(C₁₆H₃₃)]Br. Batch experiments were carried out involving experimental parameters such as initial phenol concentration, pH and contact equilibrium time. Equilibrium and kinetic analysis were conducted to determine the factors controlling the rate of phenol adsorption. The optimization of the experimental parameters was achieved to find out the possibility of using this abundant material as low-cost adsorbent for phenolic compounds removal.

2. Materials and methods

2.1. Materials

The clay sample studied in this work was sampled from deposits in the careers of Tamdalet in East side of the Middle Atlas Mountains, Fez-Boulemane area, Morocco. The Moroccan natural clay, called locally Rhassoul, is a mineral product composed mostly of stevensite mineral [13-14]. This clay was modified by hexadecyltrimethylammonium bromide (HDTMA) as previously described [3, 15]. All chemicals used for analyses were reagent grade obtained from Sigma-Aldrich (Sigma-Aldrich Chimie S.a.r.l., Lyon, France). They were used without further purification.

2.2. Preparation of phenol solutions and organically modified Rhassoul by HDTMA

Phenols solutions were prepared by dissolving the phenol in distilled water. The modified clay used in the experiments of the phenol adsorption, was prepared as follows: in a beaker using 200 ml of distilled water with 5g of natural Rhassoul and 0.375 g HDTMA for CEC reached saturation. After 2 h stirring at temperature of 60 $^{\circ}$ C, the suspensions were then centrifuged and intensively washed with distilled water until the total elimination of bromide ions as confirmed by AgNO₃ test. The product obtained was filtered and dried at 50 $^{\circ}$ C in an oven for 24 hours.

2.3. Characterizations.

2.3.1 X-ray fluorescence (XRF).

Elemental composition of the Rhassoul sample was determined by X-ray fluorescence (XRF) using a Bruker S4 Pioneer spectrometer. Total organic matter contained in the clay was analyzed by measurements of loss on ignition.

2.3.2 X-ray diffraction.

Mineralogical composition of raw and modified clay was identified by powder X-ray diffraction analysis (XRD) using powder diffractometer model D8 Bruker, Bragg-Brentano geometry theta-theta, with a Lynxeye detector, autosampler nine positions for performing measurements to conventional angles (2θ >4) but also at small angles ($0.5^{\circ} < \theta < 4$) and equipped with CuK α radiation (λ = 1.5406 Å). Mineral phases were identified by database of the International Centre for Diffraction Data (ICDD). The measured angle is associated with the lattice spacing (between the two planes) by law Bragg

$$2d_{hkl}\sin\theta_{hkl} = n\,\lambda \tag{1}$$

 d_{hkl} : interplanar distance, that is to say distance between two planes crystallographic of the same family, θ_{hkl} : deflection half angle (half the angle between the incident beam and the direction of the detector), n=1 order of reflection on diffractometers we use and λ is wavelength of X-rays (we use a copper anti-cathode and using the K α line of copper and therefore). The sample holder disk comprises a cavity 20 nm in diameter and 0.2 mm deep. Powdered samples were packed into the cavity and leveled with a glass slide to obtain a flat surface in the plans of the sample holder. The acquisition results are computerized and governed by Diffrac software. Graphic EVA evaluation program resulted in the identification of compounds by graphic comparison with the JCPDS cards.

2.3.3 Infrared spectroscopy in transmission mode (FTIR).

The apparatus used is a Vertex 70 spectrometer (resolution 4 cm⁻¹) equipped with KBr windows. The field of wave numbers is between 400 and 4000 cm⁻¹. The spectra were recorded in transmission mode on self-supported or diluted in KBr pellets. These are obtained by milling a small amount of the analyte with powdered potassium bromide. The mixture is then subjected to a pressure of about 10 ton/cm² into a cylindrical mold of 13 mm in diameter.

2.3.4 Thermal analysis (TGA/DTG).

Thermogravimetric analysis studies were performed to determine the mass loss of the sample relative to an inert reference for a temperature rise in the gas stream. The experiments were performed on a Q600 SDT TA Instruments under industrial air flow (100 mL / min) with a temperature rise of 5 °C/min between 25 and 800 °C. We trace the mass loss rate depending on the temperature (°C) to clearly observe the thermal phenomena. This method has enabled us to quantify the organic species present in the samples by integrating DTG peaks.

2.4 Adsorption experiments

Bath adsorption was performed in glass flasks of 50 mL containing 0.08 g of adsorbent mass and 20 mL of phenol solutions with an initial phenol concentrations ranging between 0 to 200 mg L^{-1} . The mixture was shaken (~200 rpm) until the equilibrium was reached using a water shaker bath. Then, the solid phase was recuperated from the liquid phase by centrifugation (2000 rpm for 10 min) and the concentrations of phenol remaining were

determined by a UV-vis spectrophotometer by measuring the absorbance at λ_{max} = 270 nm (Jasco 630 spectrophotometer).

The amount of adsorbed phenol at the equilibrium time, $q_e (mg g^{-1})$, and the adsorbed amount of phenol at time t onto adsorbent, q_t (mg g⁻¹), were determined by Eq. (2), where C_0 , C_e and C_t (mg L⁻¹) are the initial concentrations of phenol, at the equilibrium and at the time t respectively. V (L) is the volume of the solution, and m (g) is the mass of the adsorbent used. The amount of adsorbed phenol per gram of adsorbent (q_e , mg g⁻¹), was determined from a mass balance, as follows:

$$q_{t,e} = \frac{(C_0 - C_{t,e})V}{m}$$
(2)

The influence of operating conditions such as initial concentration, contact equilibrium time and pH on the adsorption of phenol onto raw and modified Rhassoul were studied in a batch system. The effect of pH conditions on phenol adsorption was conducted by varying the pH of the phenol solution from 2 to 10.6 at 25°C. The initial pH was adjusted by adding HCl (0.1 mol L^{-1}) or NaOH (0.1 mol L^{-1}). In this work, adsorption isotherms data were modelled using one well known Langmuir equation model [16-18].

Langmuir model

The Langmuir isotherm is one of the most used adsorption models to describe adsorption equilibrium. This model has been used successfully in many adsorption processes for aqueous medium [20-21]. The Langmuir isotherm model explains adsorption assuming the following hypotheses: (a) the surface of solid is homogeneous and the total of number of available active single type of sites remains constant, (b) absence of interactions between adjacent sites and (c) the coverage of the surface by the molecules is limited to the assembly of one molecular layer. Adsorption isotherm models correspond to the variation of adsorbed quantity of phenol per mass of adsorbent, $q_e (mg g^{-1})$, as a function of phenol amount at the equilibrium, $C_e (mg L^{-1})$. The Langmuir equation is given in Eq. 3:

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

Where $q_{\rm m}$, expressed in mg g⁻¹, is the maximum adsorption capacity of adsorbent that is reported to the monolayer adsorption capacity and K_L (L mg⁻¹) is the Langmuir adsorption equilibrium constant expressing the affinity and the energy of the binding sites $(L \text{ mg}^{-1})$. The separation factor, R_L , is the essential parameter to identify the existing affinity between the stevensite

surface and phenol molecules [22]. It can be determined from the Langmuir isotherm model given by the equation (4):

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

 C_0 (mg. L⁻¹): the initial concentration of phenol

K_L (L mg): the Langmuir constant related to the energy of adsorption.

 $R_{\rm L}$ >1: adsorption process is unfavourable.

R = 1: linear adsorption

R_L value ranged between 0 and 1 show that the adsorption is linear and favourable.

 $R_L = 0$: irreversible adsorption.

3. Results and discussion

3.1. Characterization of the solids

3.1.1 X-ray fluorescence analysis

The characterization of the Rhassoul clay by X-ray fluorescence indicate that the sample is mainly composed of SiO₂ and MgO constituting 83.36 wt.% of the total weight. Al₂O₃ concentration in the fine clay is about 2.47 %. The presence of CaO (2.34 %) may be ascribed to the dolomite and gypsum. Other associated oxides such Fe₂O₃, FeO, TiO₂, Na₂O, K₂O, MnO, P₂O₅ are present with very low percentages (Table. 1).

Table 1: Chemical composition of raw Knassoul clay (wt %).												
Chemical composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	MnO	P ₂ O ₅	L.O.I *
wt. (%)	58.16	2.47	0.64	0.36	0.18	2.34	25.20	0.34	0.69	< 0.01	0.003	9.52

Table 1. Chemical composition of raw Rhassoul clay (wt %)

3.1.2 XRD analysis powder.

The XRD patterns of raw and functionalized Rhassoul are presented in Figure 1. This figure gives the mineralogical composition of raw and modified natural Rhassoul. Results indicate that the structure of raw clay

* L.O.I: loss on ignition.

is complex and heterogeneous. A typical smectite d_{001} basal spacing is observed at 15.32 Å, corresponding to stevensite mineral. Therefore, the mineral clay is considered as magnesian smectite. The reflection of quartz and dolomite are also detected as associated minerals. The data of the XRD patterns for the studied clays are compared in Table 2. The diffraction pattern shows a shift of the d_{001} peak after HDTMA intercalation. The Modification of Rhassoul by HDTMA gives rise to a pronounced change in the clay structure. The organo-clay shows an important increasing of interlamellar spacing distance from 15.32 to 17.9 Å, which confirms the intercalation of the cationic surfactant HDTMA in the clay gallery.

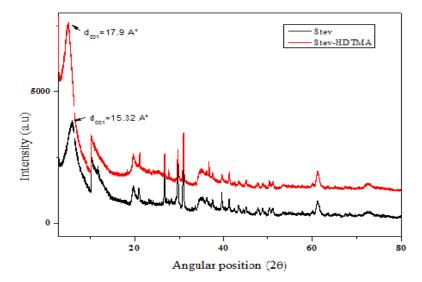


Figure 1: X-ray diffraction of raw and modified stevensite

Therefore, XRD study (Table 2) reveal that the d(001) basal spacing of the organo-clay increase about 2.58 Å with respect to basal spacing of unmodified Rhassoul . These data confirm an important difference of the structure between the two clays.

Sample	2θ (°)	d ₀₀₁ (Å)	Intensity (a.u.)
Stevensite	5.76	15.32	4851
Stevensite-HDTMA	4.93	17.9	876

Table 2: The XRD analysis data of stevensite and modified stevensite

3.1.3 Fourier transforms infrared spectroscopy (FTIR)

The Fourier Transform Infrared Spectroscopy for (FT-IR) for natural and modified Rhassoul are shown in Figure 2. It can be observed the presence of the bands at 464 and 452 cm⁻¹, for Rhassoul and modified Rhassoul respectively, which can be mainly attributed to the deformation of the vibration of Si-O bond of the quartz. The intense peaks observed at 1000 and 1010 cm⁻¹ are ascribed to Si-O stretching. The FTIR bands at 790 and 800 cm⁻¹ are assigned to the quartz valence band. The bands at 3430 to 3650 cm⁻¹ correspond to the vibration of the hydroxyl groups.

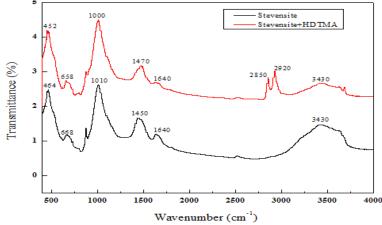


Figure 2: FTIR spectra of stevensite and stevensite-HDTMA at room temperature.

These bands are attributed to Al-OH vibrations and those of water molecules in the interlamellar space. The bands at 1450 and 1470 cm⁻¹ correspond to the dolomite. After the clay modification, a significant change was observed. An appearance of the bands at 2850 and 2920 cm⁻¹ was observed corresponding to the absorption bands of vibration bonds C-H of methyl group. The bands around 2930 and 2850 cm⁻¹ are assigned also to methylene group, antisymmetric stretching vibration v_{as} (CH₂) and symmetric stretching vibration v_s (CH₂), respectively. These bands are sensitive to the interactions changes in the gauche/trans conformer ratio and the chain–chain introduced by the intercalation of HDTMA in the clay matrix.

3.1.4 Thermal analysis (TGA and DTG)

The thermogravimetric analysis of the raw and modified Rhassoul clays is presented in Figure 3. Curve TG presents several losses of mass according to the temperature. In the temperature range from 25 to 120 °C, a first weight loss is around 13 %, that correspond to the phase change of adsorbed water. Then, between 100 °C and 200 °C, the mass loss less than 2% is assigned to the interlayer water's phase change, followed by an important mass loss more than 10% for the temperature ranged from 600 to 800 °C corresponding to calcite decomposition and dehydroxylation of clay. For the stevensite-HDTMA, an important mass loss of is observed between 200 and 400°C. The intense DTG peak is visible to 290 °C.

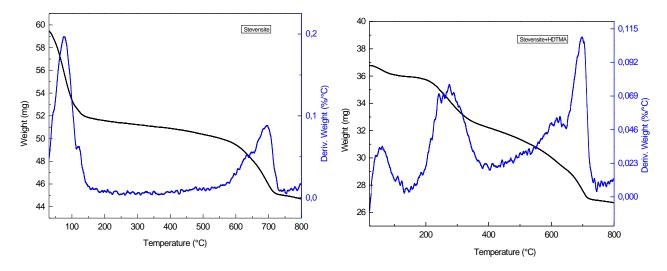


Figure 3: Thermogravimetric analysis of stevensite and stevensite-HDTMA

In this range of temperature, the TG curves show that the mass loss after modification of Rhassoul reached 10.15%. It is greater than that of unmodified raw clay (1.6%) that confirms clearly the incorporation of the surfactant in the clay space gallery.

3.2. Adsorption kinetics

Adsorption kinetic is important from the point of view to determine the time necessary for reaching equilibrium and provide useful data regarding the efficiency of adsorption process. Therefore, Phenol adsorption kinetics onto modified and unmodified Rhassoul was followed for a fixed initial concentration of 100 mg L⁻¹ and mass of adsorbent per liter of aqueous solution ($R=4 \text{ g L}^{-1}$). The adsorption data for the adsorption of phenol molecules versus contact time at constant initial concentration is given in Figures 4 and 5. Results showed that the adsorption amount of phenol by modified and unmodified clays increases rapidly initially. Then, the adsorption rate slows down with the time, and the adsorption processus reaches equilibrium state after 180 min for both samples. After the equilibrium time, the amount of adsorbed phenol remaine almost inchanged. This behavior result from that the adsorption sites are weidly available at the beginning of contact time and reduces with the progress of the reaction. For the organo-clay, HDTMA covered the stevensite negative surface and improve the molecular interaction between phenol molecules and the clay particles. The presence of the surfactant changes the properties of the surface from hydrophilic to hydrophobic after modification [15,23]. Therefore, the adsorption capacities increased from 8.85 mg.g⁻¹ on the raw clay to 13.24 mg.g⁻¹ on the organically-modified clay. The modeling of adsorption kinetics is useful for the elucidation of the removal mechanism of phenol from the aqueous solution. For the kinetic models, it is well know that the rate of adsorption is essentially governed by the adsorption of the solute and the intraparticle diffusion to the available surface active sites of the adsorbent.

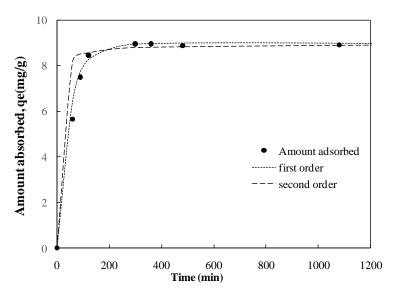


Figure 4: Effect of contact equilibrium time on the adsorption of phenol onto unmodified clay. (Experimental conditions: initial phenol concentration: 100 mg L^{-1} , modified clay ratio: 4 g L^{-1} , temperature: 25 °C).

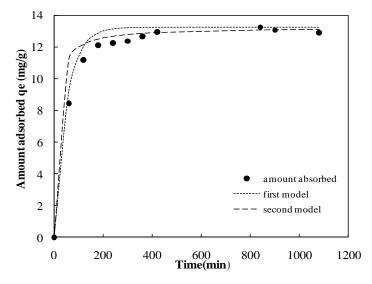


Figure 5: *Effect of contact equilibrium time on the adsorption of phenol onto modified clay. (Experimental conditions: initial phenol concentration: 100 mg* L^{-1} , *modified clay ratio: 4 g* L^{-1} , *temperature: 25 °C).*

Generally, the external mass transport is negligible and is not taken into account .Moreover; it is considered that the adsorption rate of a solute is practically the same as the rate of a chemical reaction on the surface. Therefore, in this study, the pseudo-first-order [24-25] and pseudo-second-order adsorption kinetics models [26], was used to determine the adsorption kinetics of phenol on the natural and modified Rhassoul. The pseudo-first-order kinetic equation [27] is expressed by:

$$q_t = q_e (1 - exp \ (-k_1 t)) \tag{5}$$

Where q_t and q_e (mg g⁻¹) are the adsorption capacity at time t and equilibrium time, respectively and k_1 (min⁻¹) is the pseudo-first order model rate constant. Pseudo-first order constants of the kinetic model are obtained by plotting q_t versus t.

The pseudo-second-order kinetic equation is given as follows [28]:

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \tag{6}$$

 K_2 (g mg⁻¹min⁻¹) is the adsorption rate constant.

The non linear forms of equations (5) and (6) were applied to model the kinetic parameters and mechanism of adsorption process. The coefficient of determination (R^2) and kinetic parameters are given in Table 3.The regression coefficients ($R^2 \sim 0.999$) showed that the pseudo second order model fitted better the experimental data than the Pseudo-first-order kinetic model for both clay and modified clay.

Table 3: Kinetic parameters for the adsorption of phenol onto modified and unmodified clay

Kinetic model	Parameters $q_{exp} (mg g^{-1})$	Stev 8.96	Stev-HDTMA 13.20
Pseudo-first-order	$\begin{array}{c} q_e \ (mg \ g^{-1}) \\ K_1 \ (min^{-1}) \\ R^2 \end{array}$	7.89 0.021 0.89	13.24 0.020 0.94
Pseudo-second-order	$\begin{array}{c} q_{e} \ (mg \ g^{-1}) \\ K_{2}(g \ mg \ ^{-1}min^{-1} \) \\ R^{2} \end{array}$	8.85 0.02 0.99	13.24 0.007 0.99

Furthermore, q_{exp} experimental is closeness to q_e , theoretical value. The applicability of the pseudo-second order model suggests that chemical interactions can be the rate-limiting step in adsorption of phenol on unmodified and modified clay.

3.3. Effect of pH

The value of pH is considered as one of the most critical parameters that can affect the adsorption behaviour of phenol at water- adsorbent interfaces. The solution pH influences directly the adsorbent surface charge and the ratio of ionization of the adsorbate. The adsorption experiments to evaluate the pH effect were carried out at using 120 mg L^{-1} as initial concentration of phenol, 4 g L^{-1} of unmodified and modified clay suspension at 25 °C and in a pH range from 2.0 to 10.6. Results of the pH effect on the adsorption of phenol onto unmodified and modified clay are shown in Figure 6.

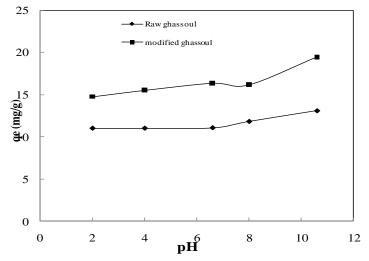


Figure 6: Effect of pH on the adsorption of phenol onto raw and modified Rhassoul. (Experimental conditions: initial phenol conc.: 120 mg L^{-1} , stevensite and stevensite-HDTMA dose: 0.08 mg L^{-1} , contact time: 24 h, temperature: 25 °C)

It can be seen that the amount of phenol removal by unmodified and modified stevensite was practically constant between pH 2 and 8, and then slightly increased in the range of pH 8-10.6. This increase was more important for the modified Rhassoul. The amount of adsorbed phenol reached the maximum of 13.06 mg g⁻¹ and 19.43 mg g⁻¹ at pH=10.6 respectively. Adsorption capacity of clays at higher pH is more important for the organically clay. This increasing of phenol adsorption can be attributed to the presence of HDTMA covering the clay surface with positive charges and to the improvement of the electrostatic interaction between the modified clay and phenol [29]. It is well known that the phenol ionization depend on the pH value. The phenol molecules will be dissociated to the anionic form at pH > pKa (phenol is a weak acid, pK = 9.92). Consequently, the negatively charged, species in solution should be attracted to the positively charged surface sites (Interlamellar cation-exchange or cationic HDTMA), due to the attractive forces predominant at the higher pH. Contrary, on the low pH value, the excess of protons increase the electrostatic repulsions between the positively charged (excess hydrogen ions (H⁺)) of clays surface and phenol molecules. The protonation of silanol groups of the clays by hydrogen bonding make some active sites inaccessible to reactant molecules, leading to the decrease in phenol adsorption at acidic pH.

3.4. Adsorption isotherms

The phenol adsorption isotherms were investigated using different initial concentrations. The equilibrium data in aqueous solutions were modeled using Langmuir isotherm model. The experimental data obtained for

phenol adsorption on the natural and modified Rhassoul are given in Figure 7. A contact time of 4h was allowed to ensure equilibrium condition. The values of q_{max} , K_L , and the correlation coefficients for Langmuir model (R^2) are given in Table 4. According to the R^2 values (Table 4) and also to the fitting curves (Figure 7), it can be concluded that Langmuir model is suitable to evaluate the adsorption isotherms of phenol onto the studied adsorbents.

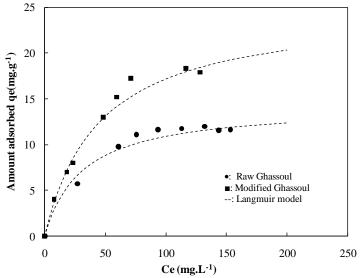


Figure 7: Equilibrium data of phenol adsorption onto raw and modified Rhassoul (Experimental conditions: phenol amount: 0.08g, contact time: 4h, agitation speed: 200 rpm, temperature: 25°C)

The affinity between clays and phenol was evaluated based on the separation factor, given by dimensionless constant named equilibrium parameter R_L . This parameter is expressed and calculated by using the equation (4) determined from the Langmuir adsorption isotherm model [30-31].

Table 4 lists the calculated parameters and coefficient of determination of the Langmuir model using a nonlinear regressive method. The K_L values for unmodified and modified clay are 0.032 and 0.022, respectively indicating that the adsorption process of phenol onto the clays is favourable in this concentration range.

Model	Isotherms parametres	Raw Rhassoul	Modified Rhassoul	
	$q_m (mg/g)$	14.3	25	
Langmuir	K _L (L/mg)	0.032	0.022	
	\mathbf{R}^2	0.98	0.96	

Table 4: Langmuir fitting parameters for the adsorption of phenol by Raw Rhassoul and modified Rhassoul

q_m: maximum adsorption capacity, K_L: adsorption equilibrium constant

The maximum adsorption capacity qm of adsorbed phenol per gram for considered stevensite is less than that measured for the stev-HDTMA. The maximum amount adsorbed q_{max} was 14.3 and 25 mg/g for clay and organoclay respectively. These values are in agreement with experimental data as seen in Figure 7. Results obtained clearly improve those reported in the literature using other raw and modified adsorbents such as Kaolinite (0.468 mg/g), HDTMA-Kaolinite (2.35 mg/g), Bentonite (0.247mg/g) and HDTMA-Bentonite (8.435 mg/g) [15]. The use of modified and unmodified Moroccan Rhassoul is very efficient for phenol removal from wastewater. Furthermore, this clay-mineral resource is an inexpensive and easy to produce and can be used easily in the treatment of phenolic pollutants.

Conclusion

In this study, adsorption experiments for the elimination of phenol from aqueous medium have been investigated using raw and modified Moroccan Rhassoul (stevensite mineral) as low-cost adsorbent. Organo-Rhassoul characterization shows successful intercalation of the cationic surfactant in the interlayer spaces. The adsorption was dependent on the pH of the aqueous solution. Indeed a high phenol removal was observed at high pH. The adsorption was rapid and could be considered to fit pseudo-second order kinetics model. The amount of phenol uptake at the equilibrium was improved with increasing the initial concentration of solution.

The adsorption isotherms could be well modeled by the Langmuir equation. The maximum value of adsorption capacity is of 14.3 and 25 mg.g⁻¹ for Rhassoul and modified Rhassoul respectively. The intercalation of cationic surfactant improved clearly the adsorption properties of raw Rhassoul. These modified clays provide an hydrophobic environment promoting the adsorption of organic molecules having low polarity. Finally, the results obtained in this work show clearly that magnesian Moroccan clay (Rhassoul), in natural form or modified with cationic surfactant can be used for the removal of organic compounds from wastewater as no costly equipment is required.

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