



Sorption of Pentachlorophenol from Aqueous Solution by Acid Activated

Bentonite: A comparative study

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Abstract

Batch measurements were conducted to assess the adsorption performance of raw and acid-activated bentonite with various operating conditions, including pH (3-11), initial PCP concentration (30-1000 mg/l), contact time (10-180 min), and temperature (25-65 °C). Fourier Transform Infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and scanning electron microscopy were used to study the structure and morphology of bentonite. The adsorption isotherms in the system were described using the Langmuir and Freundlich models. The system's thermodynamic characteristics were also examined; including Gibbs free energy, enthalpy, and entropy of the adsorption processes. According to the thermodynamic analysis, the adsorption is exothermic. The kinetic of adsorption is best described by a pseudo-second-order expression than a first order model. The experiment results are compatible with the Freundlich equation

Keywords: Adsorption; Bentonite; Kinetics; Isotherms; Pentachlorophenol.

1. Introduction

Chlorophenols are a class of pollutants that are hazardous to human health and the environment, they're commonly utilized as bactericides, insecticides, herbicides, fungicides, or wood preservatives, as well as dye and pharmaceutical intermediates [1-5]. In addition, natural microbial degradation of herbicides and pesticides results in a worldwide release of highly toxic derivatives in the environment. Although chlorophenols can be decomposed by aerobic and anaerobic microorganisms, their persistence and the toxicity of degradation products inspired the novel techniques for removing these compounds from the environment faster and efficiently [6]. The elimination of organic pollutants is particularly difficult, because they are persistent in the environment. During this research study, we will focus our study on the compound of pentachlorophenol (PCP), which has a high chemical stability. As a polar, hydrophobic and ionizable weak acid organic compound, PCP was once used worldwide as an herbicide, insecticide, wood preservative, disinfectant and ingredient in antifouling paints [7-9].

Several ways for removing organic contaminants from water have been developed during the last few

decades, including adsorption, membrane separation, biological treatment, ion exchange, photo-catalysis, and advanced oxidation processes (AOPs) [10-13]. Adsorption is a potential approach for treating wastewater because of its simplicity, effectiveness, low cost, and easy operation under various conditions [14-15]. One of the benefits of adsorption is that it may be scaled up without releasing any by-products into the environment during treatment. Bentonite clay, a natural mineral, has already been used to remove heavy metals and toxic compounds from wastewater at a low cost. It's also a reasonable solution for recycling water resources [16-18]. Clays have recently become very popular due to their catalytic, adsorptive, and ion-exchange characteristics, their widespread availability and excellent adsorption properties [19]. Because of its exchangeable ability without modifying the clay mineral structure, bentonite clay has been used as an adsorbent to treat dangerous organic and inorganic substances. Furthermore, new research reveals that natural bentonite can absorb pollutants from aqueous solutions [20-22]. PCP adsorption on clays is affected by the clay's chemical and physical properties, as well as the chemical species present in the aqueous phase and the PCP molecules' affinity for the surface.

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The present study was conducted to investigate the adsorption of PCP on bentonite in raw and modified form, phosphoric acid (H_3PO_4) was used as a modifying agent to improve the performance of bentonite, to compare the adsorption capacities of the two forms, and to evaluate the effect of contact time, initial concentration, pH and temperature of the solution on the adsorption capacity of bentonite. The interactions between the bentonite surface and pentachlorophenolate anions in solution are also studied in order to elucidate the adsorption mechanism of PCP on bentonite.

2. Materials and Methods

2.1. Materials

The bentonite used in this study comes from the Nador region (North-East of Morocco). Before the trials, it was rinsed multiple times with distilled water, filtered, and dried in a 60°C oven for 24 hours. Pentachlorophenol, Phosphoric acid was purchased from Sigma Aldrich.

2.2. Preparation of adsorbent

Preparation of a solution of phosphoric acid (34% of 85% purity, by adding 40 ml of the acid to 60 ml of distilled water (total volume 100 ml). The bentonite was activated by phosphoric acid by adding 20 g of bentonite to 20 ml of water, after which the acid was added to the bentonite drop-wise under stirring for 24 hours. The adsorbent was then filtered on filter paper. The pH of the filtered adsorbent was then decreased to 6-7 by washing it multiple times with distilled water. The adsorbent was dried in an oven at 60 °C for 24 hours. The acid-activated bentonite was stored for further use.

2.3. Pentachlorophenol (PCP)

PCP is a monoclinic crystalline solid with a white color. It has a molecular weight of 266.35 g/mol, a melting point of 190 °C, and a boiling point of 310 °C. At 20 °C, its vapor pressure is 1.1.10⁻⁴ mm. Temperature and pH affect the solubility of PCP in aqueous solutions. Increasing temperature or pH causes a significant rise in solubility [23-24].

2.4. Preparation of adsorbent

In a quart cuvette, 10 mL of waste water was collected and analyzed using a UV-VIS spectrophotometer. To calculate the PCP concentration after each experiment, a PCP calibration curve was first prepared. Six different concentrations of pure PCP were prepared and the absorbance was recorded using a UV-Vis spectrometer at $\lambda_{max}=320$ nm. Then, the maximum absorbance at $\lambda_{max}=320$ nm was plotted against each concentration of PCP. From this plot, the concentration of the pollutant was calculated.

2.5. Analysis and concentration measurements of waste water

Batch studies were used to evaluate the adsorption capacity of raw and acid activated bentonite; the PCP solution was prepared by dissolving a quantity of solid PCP with deionized water (1 g/L). Adsorption experiments were performed by adding a fixed amount of 0.25 g of adsorbent to a series of 100 mL Erlenmeyer flasks filled with 50 mL PCP solutions. The Erlenmeyer flasks were then stirred until they reached equilibrium. Samples (10 ml) were taken at specified time intervals and filtered to remove any residual adsorbent in the solution. The UV spectrophotometer (Rayleigh, UV-1800) was then used to determine the concentrations of the liquid samples, at the maximum wavelength of 320 nm for Pentachlorophenol. Different parameters were highlighted in order to study their effect on the adsorption capacity, which are: contact time (10-180 min), initial concentration of the PCP solution (100-1000 mg/L), pH (3-11) and temperature (25-65 °C). Batch adsorption studies were carried out to determine the adsorption capability of modified bentonite for PCP. UV spectrophotometer was used to determine the concentration of PCP. Equations (1) and (2) were used to compute the removal efficiency and adsorption capacity of PCP on modified bentonite:

$$\text{PCP Removal (\%)} = (C_i - C_e) \times 100 / C_i \quad (1)$$

$$q_e = V \times ((C_i - C_f) / w) \quad (2)$$

where R (%) represents removal efficiency of PCP on raw and modified bentonite, C_i and C_f are the initial and equilibrium concentration in PCP solution (mg/L), q_e is the equilibrium adsorption capacity of raw and modified bentonite for the PCP solution (mg/g), m is the mass of raw and modified bentonite (g) and V (L) is the volume of the PCP solution.

3. Results and discussion

3.1. Characterization

3.1.1. Fourier transform infra-red analysis

The diffractogram of raw and activated bentonite is shown in Figure 1. Raw bentonite is often composed of montmorillonite and quartz, as can be seen in the figure. Other than montmorillonite, all components are present as impurities. In the diffractogram of phosphoric acid activated bentonite, which corresponds to quartz, the intensity of the peak at 22° is increased. However, as shown in Figure 1, the strength of the montmorillonite peaks decreases at 20°. Preliminary examination of the diffractogram of bentonite highlights the predominance of silica (SiO_2) in the crystalline form of quartz indicated by an intense peak. This decrease in intensity is produced to aluminum leaching during acid activation, which results in a drop in intensity. External research using X-ray diffraction, infrared spectroscopy, and thermal

analysis reveal that the raw Nador bentonite is really a montmorillonite [25-26].

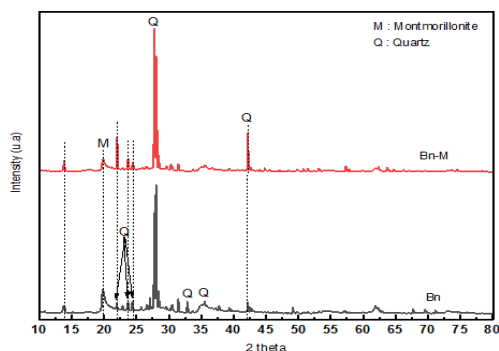


Figure 1. X-Ray diffraction patterns of the raw and modified bentonite.

Table 1. Mass and atomic percentages of elements of raw bentonite and modified.

System		O	Na	Si	Mg	Al	Fe
Bn	Mass%	47.63	1.50	28.87	3.55	11.14	7.31
	Atom%	62.54	1.37	21.60	3.07	8.67	2.75
Bn-M	Mass%	52.18	----	30.91	3.71	12.09	----
	Atom%	65.35	----	22.05	3.05	8.98	----

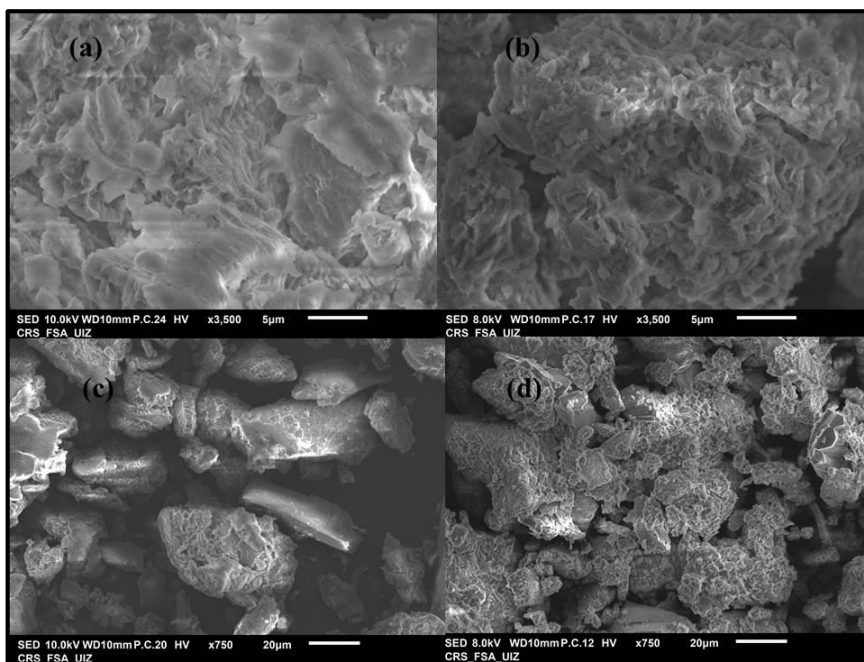


Figure 2. SEM micrographs analyses of bentonite raw (a) 5 μm; (c) 20 μm, bentonite modified (b) 5 μm; (d) 20 μm.

3.2. Batch adsorption studies

3.2.1. Effect of contact time on the PCP adsorption

In the process of adsorption, the contact time is quite important to understand the reaction mechanism. Experiments were performed with an adsorbent dosage of 0.25 g/50 mL PCP solution at 298 K for different contact times. PCP removal (Figure 3) increases with time and reaches saturation in about 100 min, in the work by Seyedi et al [27] on the removal of PCP using Montmorillonite modified by Silane and Imidazole, the amount of adsorption in the initial minutes is considerable, then steadily declines with time until equilibrium is reached after 2 hours [27], in another study by Ahari et al [28],

3.1.2. Scanning electron microscope analysis

Figure 2 depicts the surface morphology of bentonite and bentonite modified as determined by SEM, and Table 1 lists the results of the elemental composition. Figures 2(b) and (d) show the structure of closely packed silicate layers in bentonite aggregate particles, which are smooth and heterogeneous. Figures 2 (a) and (c) show that bentonite modified with sulfuric acid (H_3PO_4) has larger aggregate sizes and a block form after acid modification of the clay.

equilibrium sorption of chlorophenols onto the geotextile of geosynthetic clay liners was achieved after 72 hours [28]. During the first 30 minutes, adsorption was rapid, but after 120 minutes, it was nearly fixed. Adsorption was rapid due to the diffusion of the solution onto the adsorbent surface; it slows down after the first 30 min due to the change in the adsorption mechanism and can also be ascribed to the fact that as reaction time increases, the number of adsorption sites occupied by PCP decreases, and finally reaches a plateau indicating the achievement of equilibrium [29]. In particular, complexation phenomena or ionic exchanges on the surface could

extend competitively to the diffusion phase of the organic compound between the clay sheets [30].

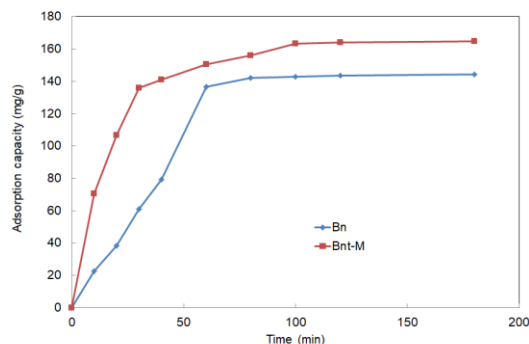


Figure 3. Effect of contact time on the adsorption of PCP.

3.2.2. Effect of initial concentration

At 25 °C and pH 7, Figure 4 illustrates the influence of different initial PCP concentrations range from 30 to 1000 mg/L on PCP adsorption capacity on raw and modified bentonite. It can be seen that as the initial PCP concentrations increase, the amount of PCP adsorbed increases though too. Indeed, the amount of adsorbed PCP increases from 3.5 to 151.79 mg/g for raw bentonite and from 5.6 to 166.13 mg/g for modified bentonite, when the initial PCP concentration increases from 30 to 1000 mg/L. The presence of a higher mass transfer driving force with increasing initial concentration can explain this result that leads to an increase in the diffusion of PCP molecules from the solution to the bentonite surface [29]. According to the findings, the highest amount of PCP absorbed (q_{max}) is 151 mg/g for raw bentonite and 166.13 mg/g for modified bentonite; on comparing this result with the study of Zhang et al [31].

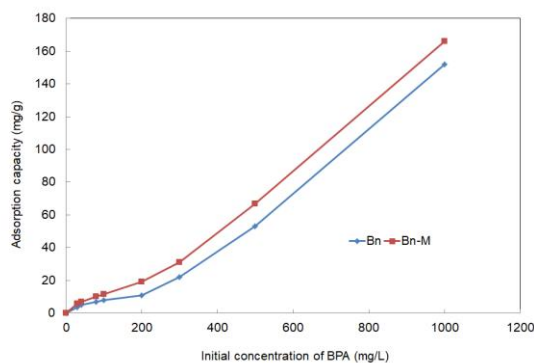


Figure 4. Effect of initial concentration of PCP.

3.2.3. Effect of pH

Because of its effect on the solution chemistry and the degree of ionization of the adsorbent surface, the initial pH of the solution plays a specific role in adsorption. The elimination of PCP was investigated by changing the pH of the aqueous solution from 3 to 11 at 25 °C with a constant PCP concentration of 1000 mg/L and an adsorbent mass of 0.25 mg. As

shown in Figure 5, the adsorption capacity was high in the low pH range (1 to 4), the adsorption capacity and removal efficiency of raw and modified bentonite decrease from 144.27 to 97.13 mg/g and 163.40 to 116.26 mg/g, respectively, when the pH of the aqueous phase increases from 3 to 11. The strong PCP adsorption observed at pH (3-4) is due to the partial contribution of electrostatic interaction between some of the positively charged surface functional groups and negatively charged chlorophenolate ions for PCP adsorption. As the pH shifts to a more basic range, PCP adsorption gradually decreases and then abruptly at pH above 9 [32]. This may be because the quantity of negative charges increased with increasing pH, mostly because of the anionic structure of phenol, the electrostatic force of attraction between sorbent and pollutant reduced, decreasing the efficacy of adsorption [33-34].

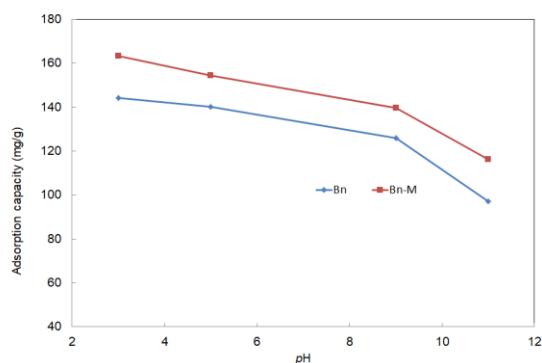


Figure 5. Effect of pH on the adsorption of PCP.

3.2.4. Effect of temperature

As shown in Figure 6, the adsorption capacity of PCP decreases with increasing temperature in the range of 298-338 K. As a result, PCP has a high adsorption capacity at low temperatures. The adsorption capacity of PCP decreases at increasing temperatures, from 157.47 to 37.05 mg/g for raw and from 163.9 to 45.25 mg/g for modified. This behavior, which is consistent with Arrhenius' law, suggests that the PCP adsorption reaction on the bentonite surface is exothermic, and that the adsorption of PCP by the adsorbent becomes increasingly unfavorable as the temperature increases. This behavior can be explained by the intermolecular forces that occur between the active sites of the adsorbent and the PCP. Furthermore, these forces are stronger at low temperatures than those between the bentonite and the solvent molecules [29].

3.3. Adsorption Kinetics Studies

Grasp the mechanism of PCP adsorption onto the adsorbent surface requires an understanding of adsorption kinetics. Batch adsorption versus time data using a fixed dose of adsorbent 0.25 g at 298 K

were used for kinetic modeling of PCP with an initial concentration of 1000 mg/L.

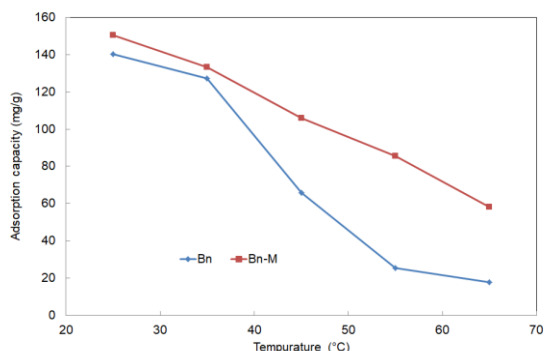


Figure 6. Effect of temperature on the adsorption of PCP.

Experimental data was analyzed further in this study using two kinetic models: pseudo-first-order and pseudo-second-order models. Equations (3) and (4) define the linear forms of the pseudo first order and pseudo second order models, respectively [35]:

$$\ln(q_e - q_t) = \ln q_e - k_1 * t \quad (3)$$

$$\frac{t}{q_e} = \frac{1}{k_2 * q_e^2} + \frac{1}{q_e} * t \quad (4)$$

For starting PCP concentrations of 1000 mg/L in both types of bentonite, the plot of t/q_t versus t of the pseudo-second-order model is more linear with $0.84 < R^2 < 0.99$ than the plot of $\ln(q_e - q_t)$ versus t of the pseudo-first-order model with $0.71 < R^2 < 0.90$, as shown in Figure 7 and Table 2.

Table 2 illustrates the second-order kinetic model's suitability for describing PCP adsorption on bentonite. When comparing the pseudo-second-order model to the first order, the R^2 value for PCP on raw and modified bentonite was also high (0.843 and 0.998, respectively). Furthermore, the value of the theoretical adsorbed quantity (q_{cal}) provided by the pseudo-second-order model is closer to and more comparable with the measured adsorption capacity than the pseudo-first-order model ($q_{e,exp}$).

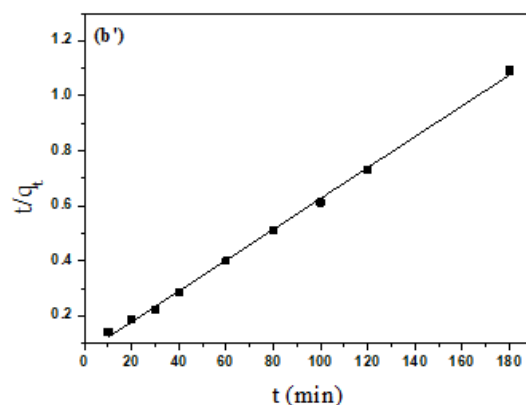
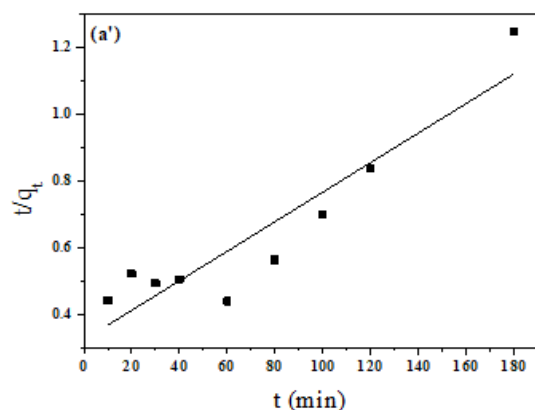
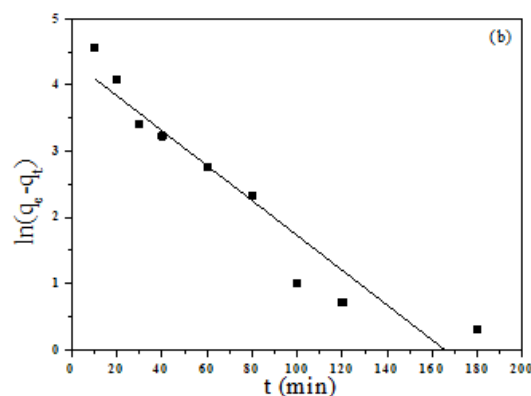
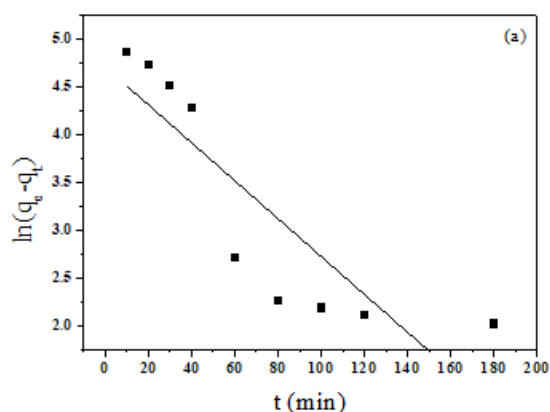


Figure 7. Kinetic models for adsorption of PCP by bentonite raw, (a) Pseudo-first-order model, (a') Pseudo-second-order model, and bentonite modified, (b) Pseudo-first-order model, (b') Pseudo-second-order model (adsorbent dosage = 1 g/L, pH = 7, Temperature=25 °C)

Table 2. Kinetic Model Parameters for the Adsorption Process.

System	Pseudo-first-order				Pseudo-second-order			
	$q_{e, exp}$ (mg/g)	$q_{e, cal}$ (mg/g)	k_1 (min ⁻¹)	R^2	q_e (mg/g)	cal	k_2 (g/mg/min)	R^2
Bn	151.7923	110.6298	0.0001	0.72	155.5209	0.0001	0.84	
Bn-M	166.1397	78.3550	0.0001	0.90	178.2531	0.0004	0.99	

3.4. Adsorption Isotherms

Batch studies were carried out with 0.25 g of the adsorbent and various initial concentrations of PCP (30-1000 mg/L) for a contact time of 100 minutes at pH = 7. The experimental adsorption isotherms were compared to Langmuir and Freundlich's theoretical models. The following are the linear equations for the Langmuir (5) and Freundlich models (6) [29]:

$$\frac{1}{q_e} = \frac{1}{k_L q_{max}} * \frac{1}{C_e} + \frac{1}{q_{max}} \quad (5)$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (6)$$

One of the most common adsorption models is the Langmuir isotherm model. It presupposes that the adsorbate is monolayer covered on a homogeneous

adsorbent surface; at equilibrium, a saturation point is reached at which no further adsorption can take place. The Langmuir isotherm's key properties and practicality are explained using a dimensionless constant separation factor (R_L), which is defined as follows [34]:

$$R_L = \frac{1}{1 + C_i * K_L} \quad (7)$$

The adsorption data obtained at 298 K represent favorable PCP adsorption for raw and modified bentonite as the R_L value is found to be 0.0663, and 0.0057, respectively. An attempt was also made to interpret the data using the Langmuir equation (Table 3).

Table 3. Isotherms parameters for the adsorption of PCP.

Isotherm model	System	Parameters	
Langmuir	Bn	q_m (mg/g)	24.449
		K_L (L/mg)	0.0140
		R_L	0.0663
		R^2	0.85
	Bn-M	q_m (mg/g)	20.554
		K_L (L/mg)	0.1721
		R_L	0.0057
		R^2	0.64
Freundlich	Bn	K_F (mg/g)	0.2894
		n	1.1020
		R^2	0.69
		Bn-M	K_F (mg/g)
	n		1.4369
	R^2		0.63

The determined coefficient values, as well as the correlation coefficients, R^2 , are reported in Table 3. The Langmuir equation matches the experimental data better than the Freundlich model, with R^2 values of 0.85 and 0.64 for raw and modified bentonite, respectively.

This result means that PCP can be homogeneously adsorbed by the active receptor sites on the surface of the bentonite adsorbent and a saturated adsorption capacity is expected due to the limited number of adsorbent sites on the surface. Furthermore, it can be deduced that the value of the dimensionless factor R_L is between 0 and 1, indicating that adsorption is a favorable process.

3.5. Thermodynamic Studies

The following equations were used to determine the thermodynamic parameters for adsorption, such

as the free energy change ΔG° , the enthalpy change ΔH° and the entropy change ΔS° [36]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

$$\Delta G^\circ = -RT \ln K_d^\circ \quad (9)$$

$$K_d^\circ = \frac{q_e}{C_e} \quad (10)$$

The plot of $\ln K_d^\circ$ versus $1/T$ is presented in Figure 8 (a) and (b) for raw and modified bentonite, respectively. Furthermore, the thermodynamic parameters of PCP adsorption on bentonite are presented in Table 4. The entropy change ΔS° and enthalpy change ΔH° were determined from the intercept and slope, respectively [37-38], these values were used to calculate ΔG° using eq 8.

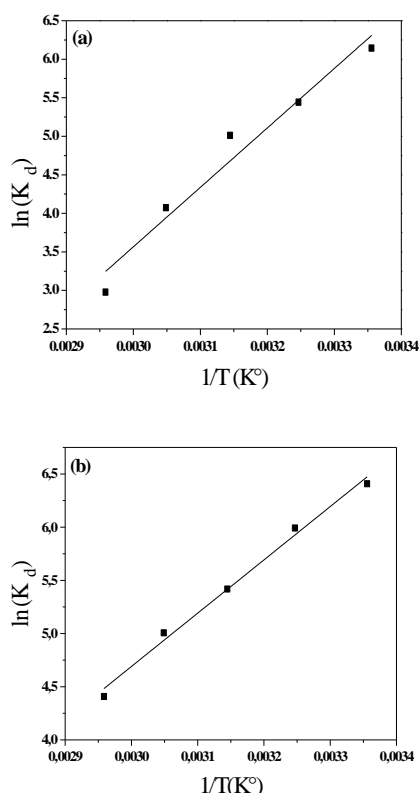


Figure 8. The thermodynamic analysis of the PCP adsorption in the temperature range of T=298–338 K, bentonite raw (a) and bentonite modified (b).

The negative values of ΔG° obtained show the feasibility and thermodynamically spontaneous adsorption process over the temperature range of T=298–338 K. However, the negative values of ΔG° changes from (-15.648) to (-9.140) and (-16.043) to (12.603) KJ.mol⁻¹ for bentonite raw and modified, respectively, with increasing temperature, indicate that the adsorption of PCP on bentonite is more spontaneous at low temperature. The value of ΔG° is approximately equal to -20 kJ/mol and indicates that the adsorption reaction is due to physisorption. In addition, the negative value of ΔH° (-64.133) and (-41.671) kJ/mol for bentonite raw and modified, respectively, indicates that PCP is adsorbed with an exothermic reaction and the negative value of ΔS° shows a decrease in the randomness of the system. Therefore, there were no significant changes in the internal structure of bentonite during the adsorption process [29,32].

The Gibbs energy change values for acid active bentonite are also negative, indicating that PCP adsorption was spontaneous and thermodynamically favorable. ΔG° Values which are more negative indicate that the adsorption process needs higher driving force. The negative values of ΔS° suggest that the adsorbed molecules have a strong affinity for the bentonite surface. Table 5 shows the comparison of PCP removal capacity on bentonite against other adsorbents.

Table 4. Thermodynamic parameters for adsorption of PCP.

T (K)	System	ΔG° (KJ.mol ⁻¹)	ΔH° (KJ.mol ⁻¹ . K ⁻¹)	ΔS° (KJ.mol ⁻¹ .K ⁻¹)
298	Bn	-15.6488	-64.1334	-0.1627
	Bn-M	-16.0431		
308	Bn	-14.0218	-41.6711	-0.08601
	Bn-M	-15.1831		
318	Bn	-12.3948	-41.6711	-0.08601
	Bn-M	-14.3231		
328	Bn	-10.7678	-41.6711	-0.08601
	Bn-M	-13.4631		
338	Bn	-9.1408	-41.6711	-0.08601
	Bn-M	-12.6031		

Table 5. The maximum removal capacity of various adsorbents for PCP.

Adsorbent	q_{max} (mg/g)	Refs.
Amt-Cl-Im	2.846	[28]
FeNi3/SiO2/ZnO magnetic nanocomposite	721	[39]
modified chitosan	24.4-39.1	[40]
Hydrophobically modified thermo-sensitive hydrogels	5.051-7.411	[41]

4. Conclusions

The adsorption of pentachlorophenol by bentonite was studied as a function of several parameters to determine the optimal conditions and then choose the best adsorbent. This approach aims to the valorization of an available and economically profitable mineral resource. PCP adsorption kinetics by bentonite was

determined to be quite rapid. Batch adsorption studies show that bentonite has a significant adsorption capacity for PCP removal from wastewater using pseudo-second-order kinetics, which was shown to be the best model for the equilibrium kinetics. Furthermore, as the temperature increases, the adsorption capacity decreases, indicating that the adsorption process is exothermic. The Gibbs energy change values are negative, suggesting spontaneous and thermodynamically favorable adsorption. The more negative values of enthalpy imply that a greater driving force is required for the adsorption process. The negative values of entropy indicate a high affinity of the molecules adsorbed by the bentonite surface.

5. Notations

Basic SI units are given in parentheses

- C_0 (mg/l) initial concentration
 C_{eq} (ml) equilibrium concentration
 K_F (mg/g) constant of Freundlich model
 K_L (L/mg) constant of Langmuir model
 K_d° is the thermodynamic equilibrium constant
 k_1 (min^{-1}) rate constant of the pseudo-first order
 k_2 (g/mg/min) rate constant of the pseudo-second-order
 q_e (mg/g) amount of PCP adsorbed at equilibrium
 q_m (mg/g) maximum amount of adsorbate retained on the adsorbent
 q_t (mg/g) amount of PCP adsorbed at time t (min)
 R is the universal gas constant ($8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$)
 T is the absolute temperature (K)
 $1/n$ Adsorption intensity

6. Conflicts of Interest

The authors declare no conflict of interest.

7. Formatting of funding sources

This research received no external funding

8. References

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