

Obtaining adsorbents from acid and acid-thermal activation of bentonite for chlorothalonil pesticide removal

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Abstract

Bentonite samples collected from M'Zila of Mostaganem (Algeria) were treated in first protocol with sulfuric acid at concentrations 1, 3 and 6N. The second protocol concerns the acid attack of bentonite combined with thermal treatment at temperatures of 100 and 200 °C. The obtained adsorbents were characterized by different analyses techniques such as chemical composition, X-ray diffraction (XRD), specific surface area and pH_{PZC} . The modified bentonites were used for removal of Chlorothalonil (Chl) from aqueous solution. The adsorption behavior of the pesticide was studied under different experimental conditions of pH, contact time, concentration of Chl and temperature of solution. The adsorption of Chl followed pseudo-second order kinetics and was described by the Freundlich equation. Thermodynamic study revealed that Chl adsorption was endothermic and physical in nature.

Key words: acid attack, adsorption, bentonite, chlorothalonil, thermal activation

Highlights

- Contribution to environmental protection and treatment of wastewaters.
- The pesticides in nature have a huge impact on the quality of our surface waters and our health.
- To remediate water pollution problems, the adsorption technique is easy to use and efficient for pollutant removal from aqueous solution.
- Using low cost materials such as modified bentonite, the adsorption capacity for pesticide molecules was very high.

INTRODUCTION

Montmorillonite (Mt) is the most widely known and applied clay mineral. It is of type 2:1 of the phyllosilicates family, where each layer has two silica tetrahedral sheets, and between them an alumina octahedral sheet (Mokaya & Jones 1995). Mt is dominant in bentonites and determines their defining properties, such as high surface area, cation exchange capacity, and surface acidity. Bentonites are widely used as catalysts, as geo-environmental barriers and liners (e.g. landfills), for wastewater treatment, and for oil-spill cleanup (Tsai *et al.* 2004).

One of the most common chemical modifications of clay minerals, used for both industrial and scientific purposes, is their acid activation. This consists of the reaction of clay minerals with a mineral acid solution, usually HCl or H₂SO₄. The main task is to obtain partly dissolved material of increased specific surface area, porosity and surface acidity (Vengris *et al.* 2001; Carrado & Komadel 2009; Daou *et al.* 2017). Acid activation reduces or eliminates most of the oxidic minerals, including

calcium, magnesium, and alkali metal oxide, from the clay material relative to SiO₂ (Bergaya & Lagaly 2001; Chaisena & Rangariwatananon 2005). It also generally increases the surface area and adsorption capacity (Rusmin *et al.* 2016; Boudouara *et al.* 2017).

When bentonite is subjected to thermal treatment, its surface properties are also significantly changed. The specific surface area (SSA) of bentonite increases at 100 °C due to the removal of physio-adsorbed water and volatile impurities (Toor *et al.* 2015). However, a further increase of temperature (up to 500 °C) reduces the significant SSA (Bojemueller *et al.* 2001), caused by the dehydroxylation of kaolinitic minerals followed by montmorillonitic minerals (Nones *et al.* 2015; España *et al.* 2019).

The combined application of thermal and acid treatment was also found effective in increasing the surface area of clay minerals (Toor 2010; Rusmin *et al.* 2016; Yaghoobi-Rahni *et al.* 2017). In most of the cases, this would cause a significant difference in the pore size distribution of the adsorbent and impact its interaction with contaminant molecules or ions. For example, kaolinite modified by thermal treatment followed by acid activation showed a slight increase in specific surface area and cation exchange capacity (CEC) (Suraj *et al.* 1998; San Cristóbal *et al.* 2009; Toor 2010). Similarly, acid activated palygorskite displayed increased SSA following thermal treatment due to loss of mesopores and consequent development of micropores (Gonzalez *et al.* 1990).

The massive use of pesticides in recent decades has caused serious damage in nature. Many residues and metabolites of these phytosanitary products are found in most compartments of the environment, especially in surface waters (Gonzalez-Pradas *et al.* 2005). Chlorothalonil is one of the pesticides used in agricultural fields as an inhibitor of spore germination, acting on various enzymes and on the metabolism of fungi. It can seep into the aquatic environment by means of spray and runoff (Fletcher *et al.* 1994). Exposure to chlorothalonil is possible through ingestion of contaminated food or water (Hayward *et al.* 2010). Chlorothalonil has been classified by the U. S. Environmental Protection Agency (EPA) as a probable carcinogen, regardless of the route of exposure, with very high toxicity to fish and aquatic vertebrates (U.S. EPA 1999). Numerous water treatment processes such as membrane separation, photocatalysis, oxidation, and adsorption have been used for pesticide removal (Shen *et al.* 2012; Zuo *et al.* 2012; Mehta *et al.* 2017; Khairy *et al.* 2018; Mohammadi & Sheibani 2019). In general, adsorption is one of the favoured treatment processes because of its simplicity, high efficiency, and low cost (Djebri *et al.* 2017).

The focus of this work is partially structural modification of local bentonite in order to enhance its adsorption capacity for chlorothalonil pesticide. For this, in the first step, the purified bentonite was activated by acid leaching with sulfuric acid at different concentrations. The second step included two successive operations: bentonite activation by sulfuric acid attack was followed by thermal treatment at two temperatures, 100 and 200 °C. The effect of the experimental conditions on the behavior of adsorption was studied. The adsorption data were analyzed by the traditional models and the thermodynamic parameters were also calculated.

MATERIALS AND METHODS

Materials

Bentonite used in this study was purchased from Mostaganem. This material is commercialized as industrial charge bentonite without additives by ENOF Company, Algeria. Before the experiments, the samples were purified and sieved at 80 µm. The cation exchange capacity (CEC) of natural bentonite was determined to be 48 meq/100 g by applying the conductometric titration method (Agouborde & Navia 2009). The point of zero charge (PZC) of purified bentonite, as determined by the solid addition method (Srivastava *et al.* 2006), was equal to 6.8.

Chlorothalonil (Chl) is a fungicide, and was obtained from Syngenta Protection of Plants S.A, Bale, Switzerland. It contains 400 g/L of chlorothalonil in the form of a concentrated suspension with some

impurities. The chemical formula of Chl is $C_8Cl_4N_2$, and its molecular weight is 265.93 g/mol. The IUPAC name of Chl is 2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile and its N° CAS is 1897-45-6. The solubility of chlorothalonil in water is 0.6 mg/L at 20 °C. The structure of the Chl molecule is presented in Figure 1.

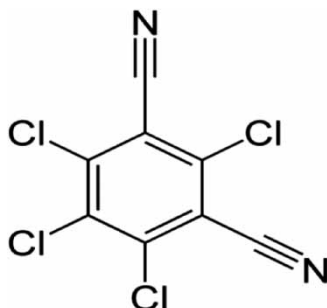


Figure 1 | Chemical structure of Chl.

Acid activation of bentonite

The bentonite samples were treated with different sulfuric acid normalities of 1 N, 3 N and 6 N. A sample amount of 5 g was added to 100 mL of H_2SO_4 solution at a temperature of 70 °C for four hours' contact time (Amari *et al.* 2010; Tomic *et al.* 2011; Khoualdia *et al.* 2017). The solids obtained after drying were designated as BA-1, BA-3 and BA-6.

Combined acid and thermal activation of bentonite

Purified bentonite (5 g) was treated in 100 mL of 1N sulfuric acid solution under reflux condition at 70 °C for 4 h. The acid-activated bentonite was then separated from the liquid by centrifugation followed by thorough washing with distilled water. After drying at 60 °C, BA was subjected to thermal activation by heating in a muffle furnace at 100 and 200 °C for 30 minutes (Toor *et al.* 2015; Rusmin *et al.* 2016). The final product obtained after both the acid and thermal treatments was denoted as BAT-100 and BAT-200.

Material characterization

X-ray diffraction (XRD) patterns of powdered samples were collected by INEL CPS 120 diffractometer using $Co\lambda_{\alpha}$ ($\lambda = 0.178$ nm) radiation operating at 25 mA and 40 kV with fixed slit. Specific surface area tests were determined by BET method via Quantachrome instruments using adsorption nitrogen at -196 °C and by Methylene blue adsorption method (Chen *et al.* 1999; Santamarina *et al.* 2002). The main characteristics of the sorbents obtained, such as PZC and specific surface area, are summarized in Table 1. The absorbance measurements of chlorothalonil were undertaken with a spectrophotometer VIS 7220 G, Biotech Engineering Management at the $\lambda_{max} = 360$ nm.

Adsorption experiments

Adsorption isotherms

The adsorption isotherms were obtained by placing 0.2 g of dry sample of BA and BAT in a series of flasks containing 20 mL of Chl solution at the range of initial concentrations 100–300 mg/L. The pH was adjusted at 3 by addition of HCl or NaOH solutions. The flasks were conditioned for 2 h at the

temperatures of 20, 30 and 40 °C, and then the residual concentration of the pesticide was determined. The amount of Chl retained by the adsorbent was calculated using the following equation:

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

where q_e is the equilibrium adsorption capacity (mg/g), C_0 and C_e are the initial and equilibrium pesticide concentrations (mg/L), respectively. V is the volume of solution (L) and m is the mass of the adsorbent (g).

Adsorption models

The Langmuir sorption isotherm, which is valid for monolayer adsorption onto a surface containing a finite number of identical sites, has been widely used to characterize adsorption phenomena from solution. The Langmuir isotherm can be represented by the following linear equation (Langmuir 1918; Sawalha *et al.* 2006):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{K_L Q_0} \quad (2)$$

where Q_0 is the maximum adsorption capacity (mg/g), and K_L (L/mg) is a constant that relates to the heat of adsorption.

The Freundlich isotherm represents satisfactorily the sorption data at low and intermediate concentrations on heterogeneous surfaces (Freundlich 1906). This model can be expressed in the linear form below:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where K_F (mg/g(L/mg)^{1/n}) and n are the Freundlich constants, indicating the capacity and intensity of adsorption, respectively.

Adsorption kinetics

The data obtained from adsorption experiments of chlorothalonil onto activated bentonite were evaluated by pseudo-first and pseudo-second order models. The linear form of the pseudo-first order rate equation is given by (Lagergren & Svenska 1898; Ho 2004):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where q_t is the amount adsorbed (mg/g) at time t . k_1 is the rate constant (min⁻¹). The value of k_1 was calculated by plots $\ln(q_e - q_t)$ versus t drawn at different concentrations.

The pseudo-second order kinetic model equation may be expressed by the following equation (Ho & McKay 1998; Azizian 2004):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where k_2 is the rate constant of the adsorption process (min⁻¹). Plots of t/q_t against t for the adsorption of Chl onto bentonite are drawn to obtain the rate parameters.

Thermodynamic study

Thermodynamic parameters of the adsorption of Chl onto treated bentonite at 30 and 40 °C were calculated using the following equation (Wang *et al.* 2005; Fan *et al.* 2008):

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)$$

The distribution coefficient K_d (L/g) is calculated from the following equation:

$$K_d = \frac{(C_0 - C_e)}{C_e} \cdot \frac{V}{m} \quad (7)$$

where ΔH^0 , ΔS^0 and T are the adsorption enthalpy (kJ/mol), entropy (J/mol·K) and temperature in Kelvin, respectively and R is the gas constant (8.31 J/mol·K). The slope and intercept of the plot of $\ln K_d$ versus $1/T$ correspond to $\Delta H^0/R$ and $\Delta S^0/R$, respectively.

The Gibbs free energy, ΔG^0 (kJ/mol) of specific adsorption is represented by the following equation (Chion *et al.* 2004):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

RESULTS AND DISCUSSION

Characterization of activated bentonite

The chemical analysis of raw bentonite was performed by X-fluorescence (XRF 9900, Thermo Instruments). The result of this analysis revealed that silica (64.22%), alumina (11.62%) and lime (9.33%) are the main oxides of the bentonite with the existence of other oxides in very small amounts such as Fe_2O_3 (4.88%), TiO_2 (1.06%), Na_2O (3.38%) and P_2O_5 (0.03%). According to the results mentioned in Table 1, the pH_{PZC} values of acid activated bentonite were almost identical at around 4, but this value was below to that of purified bentonite (6.8). The values of pH_{PZC} for BAT-100 and BAT-200 were equal to 3.7 and 3.8, respectively. We can conclude that acid attack and thermal activation considerably reduce the pH_{PZC} value of raw bentonite. However, the activated bentonite samples develop positive electrical charges at their surfaces at pH values below 4 while these charges become negative above pH 4.

The specific surface areas, S_{BET} , of acid activated bentonites are almost identical at around 80 m^2/g , which is higher than that of purified bentonite (59 m^2/g). That means the acid attack enhanced the specific surface area of bentonite and created microporosity. The average value of the S_{MB} (292 m^2/g) of the activated bentonite proves the existence of a mesoporosity at the surface of samples. In the case of thermal activation, the calcination of bentonite at 100 or 200 °C affects the structure of the montmorillonite. The surface area of the BAT increased with the temperature increase up to

Table 1 | Characteristics of raw and treated bentonite

	BP	BA-1	BA-3	BA-6	BA-100	BA-200
pH_{PZC}	6.8	4.53	4.00	3.12	3.7	3.8
S_{MB} (m^2/g)	272.48	294.93	291.41	309.86	–	–
S_{BET} (m^2/g)	59.52	80.08	77.06	81.93	57.98	55.76

100 °C and then gradually decreased beyond 100 °C. Thermal activation under a high temperature can remove water molecules and other impurities. The initial increase in the surface area with temperature is due to the removal of adsorbed and hydrated water molecules, and volatile organic compounds attached on the surface of the raw bentonite, while calcinations at a higher temperature can alter the chemical and physical properties of the bentonite (Purkait *et al.* 2007; Toor *et al.* 2015).

The XRD patterns of purified and activated bentonite are shown in Figures 2 and 3, respectively. The bentonite sample contains some mineral phases such as montmorillonite (M), kaolinite (K), calcite (C), quartz (Q) and dolomite (D). The characteristic peak d_{001} of montmorillonite appears at $2\theta = 5.5^\circ$, kaolinite is observed at $2\theta = 10^\circ$ and the peak of calcite appears at $2\theta = 31^\circ$. The bentonite samples treated by sulfuric acid show no significant change in the mineral composition of the purified bentonite except for a decrease in the intensity of the peak of montmorillonite. The concentrations of acid used contributed to partially attack the structure of the clay by dissolving the octahedral sheets. Similar results were found by activating bentonite with sulfuric acid (D'Amico *et al.* 2014). Tomic *et al.* (2011) observed no significant change in the crystallinity of the main d_{001} peak of Aleksinac bentonite treated with 6M of H_2SO_4 ; at the same time, they found that the indexed peak (001) in Petrovac bentonite was reduced with increased H_2SO_4 concentrations (6M).

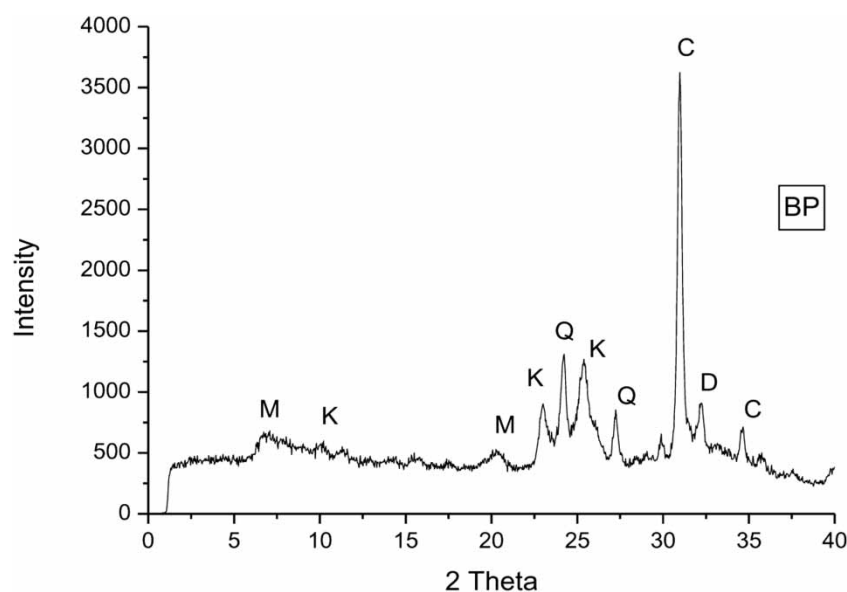


Figure 2 | XRD pattern of raw bentonite.

The XRD patterns of acid-thermal activated bentonite samples are illustrated in Figure 4. The sample treated at 100 °C after acid attack presents no notable modification in the intensity of the main peak d_{001} of the montmorillonite, while in the BAT-200 sample we see clearly the decrease in intensity and crystallinity of the characteristic peak of montmorillonite.

Adsorption of chlorothalonil

Effect of pH

The effect of pH is among the parameters that affect the adsorption capacity; it can change the electric surface charge of adsorbents. In this study the evolution of pH was followed by adsorption of

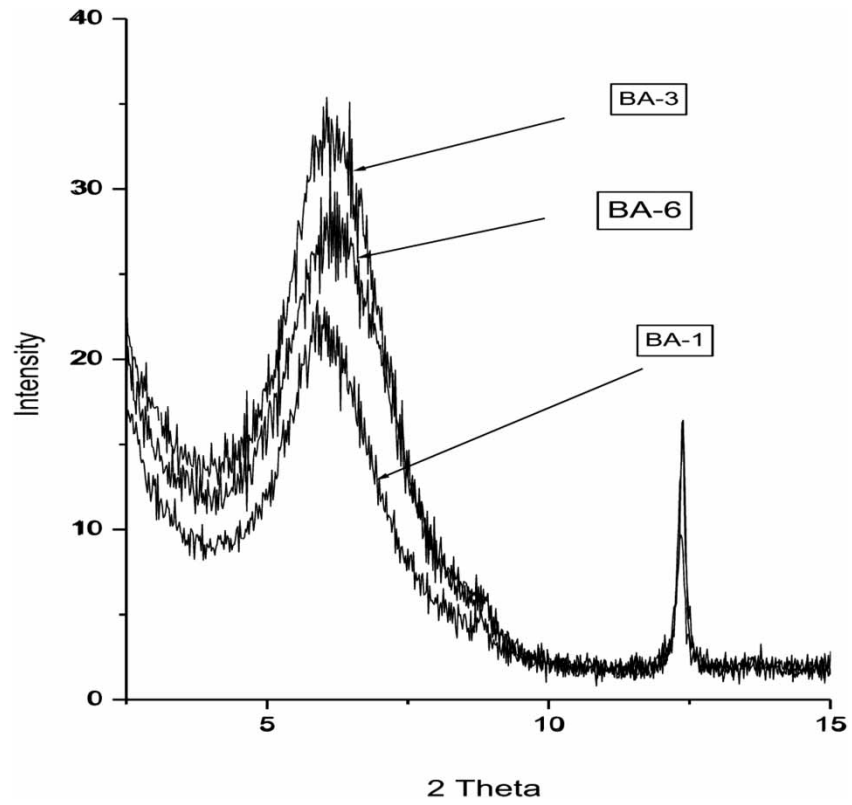


Figure 3 | XRD pattern of acid activated bentonite.

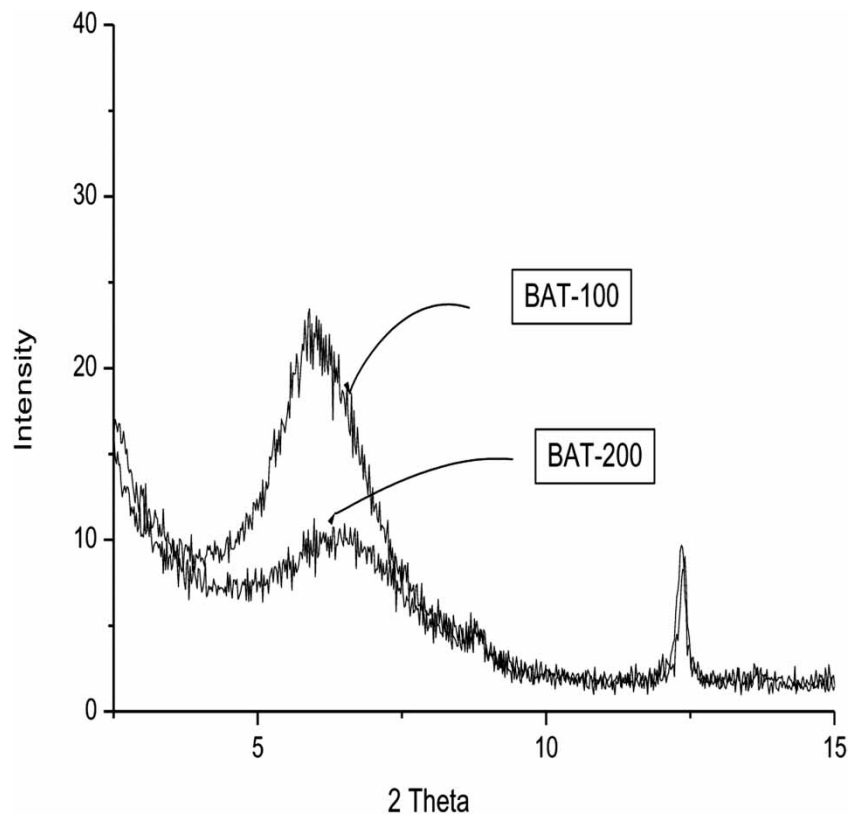


Figure 4 | XRD pattern of thermal-acid activated bentonite.

chlorothalonil onto activated bentonite samples, for an initial concentration of about 30 mg/L at room temperature. Figure 5 shows the adsorbed amount of Chl onto acid activated bentonites related to the change in pH of the solution. The first thing noticed is that the amount of Chl adsorbed by the three adsorbents is maximum at around pH 2 and 3. Then it begins to decrease gradually until pH 5 for BA-3 and BA-6, while for BA-1 the adsorbed amount decreases to pH 7. Above these pH values, there is a slight increase in the adsorbed amount, and then it decreases.

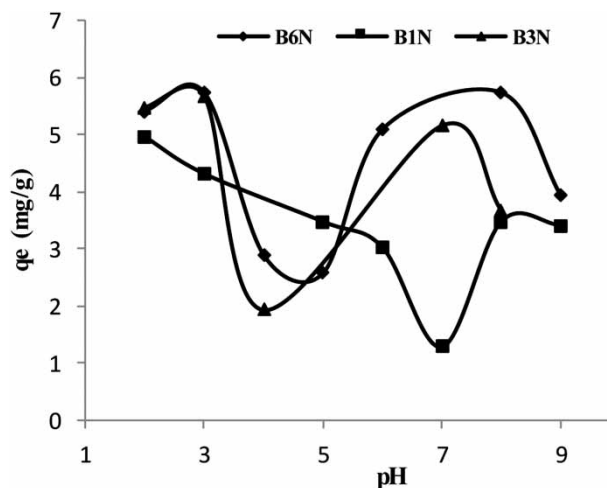


Figure 5 | Effect of pH on adsorption of Chl by acid activated bentonites.

These results can be explained by the fact that chlorothalonil is an anionic pesticide in solution, and in acid medium the number of protons, H^+ , becomes higher, which makes the charge positive on the surface of the material. However, the chlorothalonil molecules will be adsorbed by these same positive sites of treated bentonite. Figure 6 also presents the same behavior of acid-thermal activated bentonite against the evolution of pH; that is, the adsorbed amount of Chl was optimal at pH range 2–3 and decreased continually until pH 9. Previous studies have been conducted by Sahnoun *et al.* (2016) on the adsorption of 2,4,5-trichlorophenol pesticide by clay treated at 2N H_2SO_4 , and they have found that the pH maximum noted was pH = 4.

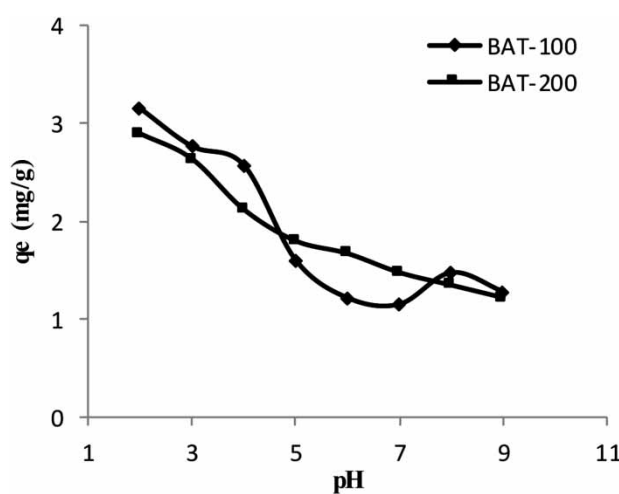


Figure 6 | Effect of pH on adsorption of Chl by acid-thermal activated bentonites.

Effect of contact time

Research into the optimum contact time is the aim of the kinetic adsorption study, and to determine the process mechanism, for this a series of samples were prepared in the time range of 5–180 min. The concentration of Chl was fixed at 60 mg/L in 20 mL volume of solution, into which 0.1 g of adsorbent was added.

The results are registered in Figure 7, and show that the removed amount of chlorothalonil varied with the contact time, a maximum efficiency was obtained after 60 min for all acid activated bentonites and the equilibrium was reached at 45 min for BAT-100 and BAT-200. Note that the kinetics of pesticide adsorption on the clays studied have the same shape from the first minutes of contact, followed by an increase until a state of equilibrium is reached. The first stage is fast and corresponds to the transfer of external mass while the second stage is slow, linked to the phenomenon of diffusion (internal mass transfer).

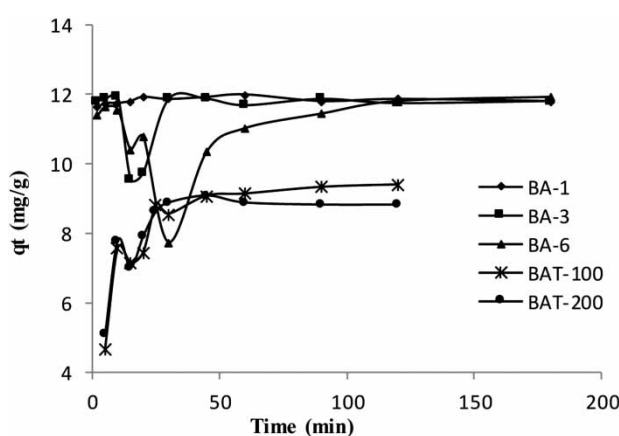


Figure 7 | Effect of contact time on adsorption of Chl by activated bentonites.

Adsorption kinetics

To evaluate the adsorption rate, the adsorption kinetics were examined by both models, pseudo first-order and pseudo second-order. According to the results as listed in Table 2, it is clear that the pseudo second-order model describes very well our experimental data because the correlation coefficients R^2 are near to 1 and the experimental adsorbed amount of Chl for all samples is almost identical to that calculated. On the other hand, the equations of the pseudo first-order are very far from giving good straight lines.

Table 2 | Constants fitting of kinetics models

Kinetic model	Constants	BA-1	BA-3	BA-6	BAT-100	BAT-200
Pseudo first order	K_1 (min^{-1})	0.018	0.001	0.001	0.038	0.018
	q_e (mg/g)	1.415	0.192	0.166	3.145	1.217
	R^2	0.535	0.005	0.017	0.936	0.312
Pseudo second order	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.642	0.0756	0.021	0.0231	0.05
	q_e (mg/g)	11.90	11.89	12.05	9.804	9.09
	R^2	1	0.993	0.992	0.999	0.998
	$q_{e \text{ exp}}$ (mg/g)	12.0	11.95	11.94	9.450	9.150

Adsorption isotherms

The adsorption isotherms were obtained at different initial concentrations (100–300 mg/L) during 2 h at three temperatures of 20, 30 and 40 °C. The isotherms are formed by plotting adsorbed amounts of the pesticide versus equilibrium concentrations. Figure 8 shows the adsorption of Chl by the activated adsorbents at room temperature (20 °C). This figure indicates that the adsorbed amount of Chl onto BA materials increases in parallel with the equilibrium concentrations. Using the classification of Giles *et al.* (1960), the experimental isotherm obtained is of type S. This type of isotherm suggests a cooperative adsorption where the adsorbed molecules promote adsorption from the other molecules. The maximum amount of Chl adsorbed is registered at 56.40 mg/g, attributed to BA-6, but the difference in the adsorbed amount is very small between the three solids chemically treated. The acid-thermally modified adsorbents adsorb less than the adsorbents treated with acid. It was noted that the Chl amounts adsorbed onto BAT-100 and BAT-200 were 52.29 mg/g and 48.34 mg/g, respectively.

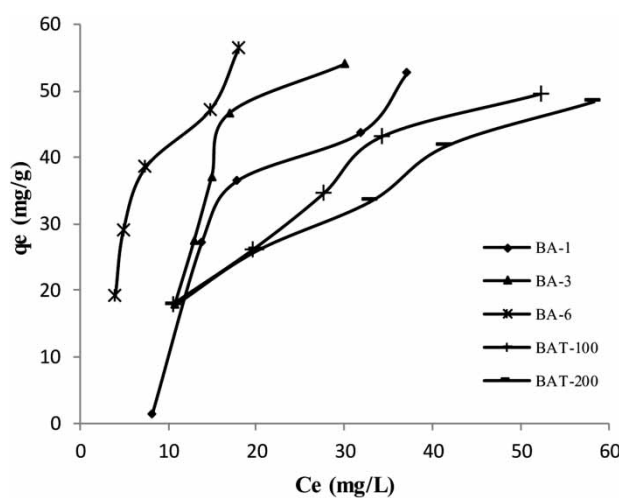


Figure 8 | Adsorption isotherms of Chl onto activated bentonites.

The adsorption of Chl by BA-1, BAT-100 and BAT-200 at temperature 30 and 40 °C was examined (Figure 9). The adsorption capacity slightly decreases with increased temperature only in the case of BA-1, but it increases with increased temperature for BAT-100 and BAT-200. For comparison, the

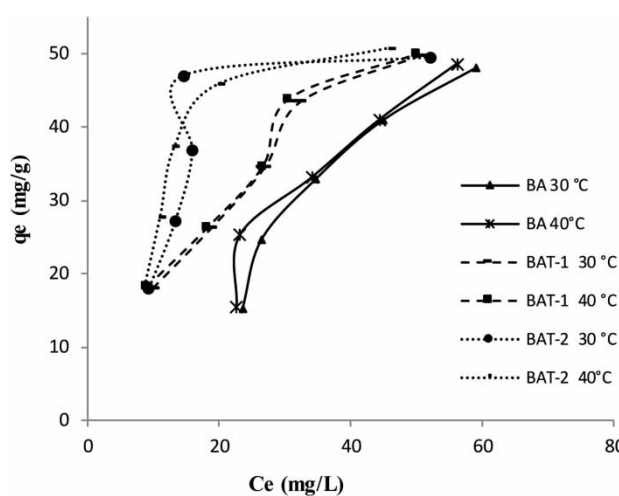


Figure 9 | Adsorption isotherms of Chl onto activated bentonites at 30 and 40 °C.

adsorption capacity of the Chl by the acid-activated bentonite was more than that for acid-thermal activated bentonite at the three temperatures studied.

Models fitting

Two isotherm models are widely used to describe experimental adsorption data. These are the Freundlich equation and the Langmuir equation. As illustrated in Table 3, the correlation coefficients, R^2 , for the Langmuir isotherm model were very low to the unit for acid treated samples, and were above 0.94 for acid-thermal activated samples, but we noted also that the maximum calculated amount of Chl adsorbed was very high compared to that tested. While for the Freundlich model the regression coefficients were greater than 0.91 for all samples. This result revealed that the number of adsorption sites on activated bentonite was unlimited and that the pesticide molecules may form poly-molecular layers on the heterogeneous adsorbent surface. The $1/n$ values observed were all less than unity, which proves the adsorption of Chl was favorable. It should be noted that the plots of the amount of Chl adsorbed against the equilibrium Chl concentration were well fitted by the Freundlich equation.

Table 3 | Fitting constants of Chl adsorption isotherms by Langmuir and Freundlich models

Model	Constants	B1N	B3N	B6N	BAT-100	BAT-200
Langmuir	K_L (L/mg)	0.03	0.003	0.08	0.020	0.023
	q_m (mg/g)	100.0	1,000.0	100.0	100.0	83.33
	R^2	0.88	0.02	0.88	0.940	0.963
Freundlich	K_f (mg/g(L/mg) ^{1/n})	6.32	2.15	9.81	3.751	4.267
	$1/n$	0.57	0.99	0.61	0.665	0.599
	R^2	0.93	0.77	0.91	0.981	0.994

Thermodynamic study

The objective of the thermodynamic study was to calculate the heat adsorption of pesticide onto treated bentonites. For this, we carried out the reaction of adsorption at 20, 30 and 40 °C. The values of the heat adsorption (ΔH° , ΔS° and ΔG°) in the range of initial concentrations of Chl of 100, 200 and 300 mg/L are reported in Table 4. The values of enthalpy and entropy are positive for all samples, proving that we are in physical adsorption and endothermic reaction, and the molecules disorder was located at the solid/liquid interface. It is noted that the BAT-200 adsorbent presents great values of enthalpy and entropy changes compared to the others adsorbents.

Table 4 | Thermodynamic parameters of Chl adsorption on BA-1, BAT-100 and BAT-200

Material	C_0 (mg/L)	ΔH (kJ/mol)	ΔS (J/mol-K)	ΔG (kJ/mol)			R^2
				293 K	303 K	313 K	
BA-1	100	4.2189	10.32	1.195	1.0914	0.9882	0.992
	200	2.8898	9.06	0.235	0.1446	0.054	0.977
	300	4.8508	14.30	0.660	0.517	0.374	0.998
BAT-100	100	6.290	25.87	- 1.289	- 1.548	- 1.807	0.968
	200	1.480	6.924	- 0.548	- 0.617	- 0.684	0.991
	300	1.964	6.276	0.125	0.062	- 0.388	0.972
BAT-200	100	9.514	36.697	- 1.238	- 1.605	- 1.972	0.979
	200	39.457	135.55	- 0.259	- 1.614	- 2.970	0.902
	300	10.971	35.847	0.467	0.109	- 0.249	0.996

The free energy ΔG° values were negative for BAT-100 and BAT-200, which means the adsorption reaction of Chl by acid-thermal activated bentonites was spontaneous and the spontaneity increases with increasing temperature, while the adsorption of Chl on BA-1 is favorable only at room temperature. This fact was confirmed by the lower removal of Chl concentrations from the aqueous phase at 30 and 40 °C (Figure 9). These findings have been reported in the works of Gil *et al.* (2013), which removed methylene blue using acid and thermal activated clay minerals.

CONCLUSIONS

The aim of this work was to study the adsorption of the pesticide chlorothalonil on bentonite treated with acid attack at different concentrations for the first time, then the acid activation was combined with thermal treatment at 100 and 200 °C.

The acid and thermal activation of bentonite affects the structure of clay minerals, especially montmorillonite and kaolinite. Therefore the specific surface area was enhanced with increasing sulfuric acid concentration and decreased when the temperature of treatment increased.

The amount of Chl uptake increased with increasing initial Chl concentration and contact time, and decrease with pH of the solution. Also, the adsorption efficiency of the Chl onto the acid-activated bentonites was greater than that with acid-thermal activated bentonites. The maximum Chl adsorption onto treated clay was rapidly attained within 60 min. Kinetic data tend to fit well with the pseudo-second order rate expression. The adsorption equilibrium Chl/bentonite system is most suitably described by the Freundlich model. The adsorption follows a spontaneous, endothermic and physical adsorption. The study shows that acid activated bentonite or acid-thermal activated bentonite can be used as a cheap and efficient adsorbent for removing pesticide from water and wastewaters.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Agouborde, L. & Navia, R. 2009 Heavy metals retention capacity of a non-conventional sorbent developed from a mixture of industrial and agricultural wastes. *Journal of Hazardous Materials* **167**(1–3), 536–544.
- Amari, A., Chlendi, M., Gannouni, A. & Bellagi, A. 2010 Optimised activation of bentonite for toluene adsorption. *Applied Clay Science* **47**, 457–461.
- Azizian, S. 2004 Kinetic models of sorption: a theoretical analysis. *Journal of Colloid and Interface Science* **276**(1), 47–52.
- Bergaya, F. & Lagaly, G. 2001 Surface modification of clay minerals. *Applied Clay Science* **19**, 1–3.
- Bojemueller, E., Nennemann, A. & Lagaly, G. 2001 Enhanced pesticide adsorption by thermally modified bentonites. *Applied Clay Science* **18**, 277–284.
- Boudouara, N., Marouf, R., Ouadjenia, F. & Schott, J. 2017 Removal of Chlorothalonil from water by a bentonite treated chemically. *Journal of Materials and Environmental Sciences* **8**(12), 4523–4531.
- Carrado, K. A. & Komadel, P. 2009 Acid activation of bentonites and polymer-clay nanocomposites. *Elements* **5**, 111–116.
- Chaisena, A. & Rangariwatananon, K. 2005 Synthesis of sodium zeolites from natural and modified diatomite. *Materials Letters* **59**(12), 1474–1479.
- Chen, G., Pan, J., Han, B. & Yan, H. 1999 Adsorption of methylene blue on montmorillonite. *Journal of Dispersion Science and Technology* **20**(4), 1179–1187.
- Chion, M. S., Ho, P. Y. & Li, H. Y. 2004 Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. *Dye Pigment* **60**, 69–84.
- D'Amico, D. A., Ollier, R. P., Alvarez, V. A., Schroeder, W. F. & Cyras, V. P. 2014 Modification of bentonite by combination of reactions of acid-activation, silylation and ionic exchange. *Applied Clay Science* **99**, 254–260.
- Daou, I., Zegaoui, O. & Amachrouq, A. 2017 Study of the effect of an acid treatment of a natural Moroccan bentonite on its physicochemical and adsorption properties. *Water Science and Technology* **75**(5), 1098–1117.

- Djebri, N., Boutahala, M., Chelali, N., Boukhalfa, N. & Zerroual, L. 2017 Adsorption of bisphenol A and 2, 4, 5-trichlorophenol onto organo-acid-activated bentonite from aqueous solutions in single and binary systems. *Desalination and Water Treatment* **66**, 383–393.
- España, V. A. A., Sarkar, B., Biswas, B., Rusmin, R. & Naidu, R. 2019 Environmental applications of thermally modified and acid activated clay minerals: current status of the art. *Environmental Technology & Innovation* **13**, 383–397.
- Fan, Q. H., Shao, D. D., Hu, J., Wu, W. S. & Wang, X. K. 2008 Comparison of Ni²⁺ sorption to bare and ACT-graft attapulgites: effect of pH, temperature and foreign ions. *Surface Science* **602**, 778–785.
- Fletcher, J. S., Nellessen, J. E. & Pflieger, T. G. 1994 Literature review and evaluation of the EPA food-chain (Kenaga) nomogram, an instrument for estimating pesticide residues on plants. *Environmental Toxicology and Chemistry* **13**(9), 1383–1393.
- Freundlich, H. M. F. 1906 Über die adsorption in lösungen (on the adsorption in solutions). *The Journal of Physical Chemistry* **57**(1), 385–470.
- Gil, A., El Mouzdahir, Y., Elmchaouri, A., Vicente, M. A. & Korili, S. A. 2013 Equilibrium and thermodynamic investigation of methylene blue adsorption on thermal and acid-activated clay minerals. *Desalination and Water Treatment* **51**(13–15), 2881–2888.
- Giles, C. H., Mac Ewan, T. H., Nakhwa, S. N. & Smith, D. 1960 Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *Journal of the Chemical Society* 3973–3993.
- Gonzalez, F., Pesquera, C., Blanco, C., Benito, J., Mendioroz, S. & Pajares, J. A. 1990 Structural and textural evolution under thermal treatment of natural and acid-activated Al-rich and Mg-rich polygorskites. *Applied Clay Science* **5**, 23–36.
- Gonzalez-Pradas, E., Socias-Viciano, M., Urena-Amate, M. D., Cantos-Molina, A. & Villafranca-Sanchez, M. 2005 Adsorption of chloridazon from aqueous solution on heat and acid treated sepiolites. *Water Research* **39**, 1849–1857.
- Hayward, S. J., Gouin, T. & Wania, F. 2010 Levels and seasonal variability of pesticides in the rural atmosphere of Southern Ontario. *Journal of Agriculture and Food Chemistry* **58**, 1077–1084.
- Ho, Y. S. 2004 Citation review of Lagergren kinetic rate equation on adsorption reactions. *Scientometrics* **59**(1), 171–177.
- Ho, Y. S. & McKay, G. 1998 Sorption of dye from aqueous solution by peat. *Chemical Engineering Journal* **70**, 115–124.
- Khairy, M., Ayoub, H. A., Rashwan, F. A. & Abdel-Hafez, H. F. 2018 Chemical modification of commercial kaolin for mitigation of organic pollutants in environment via adsorption and generation of inorganic pesticides. *Applied Clay Science* **153**, 124–133.
- Khoualdia, B., Loungou, M. & Elaloui, E. 2017 Adsorption of organic matter from industrial phosphoric acid (H₃PO₄) onto activated bentonite. *Arabian Journal of Chemistry* **10**, 1073–1080.
- Lagergren, S. & Svenska, B. K. 1898 Zur theorie der sogenannten adsorption gelöster stoffe (The theory of so-called adsorption of dissolved substances). *Handlingar* **24**(4), 1–39.
- Langmuir, I. 1918 The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society* **40**(9), 1361–1403.
- Mehta, R., Brahmabhatt, H., Mukherjee, M. & Bhattacharya, A. 2017 Tuning separation behavior of tailor-made thin film poly(piperazine-amide) composite membranes for pesticides and salts from water. *Desalination* **404**, 280–290.
- Mohammadi, P. & Sheibani, H. 2019 Evaluation of the bimetallic photocatalytic performance of Resin–Au–Pd nanocomposite for degradation of parathion pesticide under visible light. *Polyhedron* **170**, 132–137.
- Mokaya, R. & Jones, W. 1995 Pillared clays and pillared acid-activated clays: a comparative-study of physical, acidic, and catalytic properties. *Journal of Catalysis* **153**(1), 76–85.
- Nones, J., Riella, H. G., Poli, A., Trentin, A. G. & Kuhnen, N. C. 2015 Thermal treatment of bentonite reduces aflatoxin b1 adsorption and affects stem cell death. *Materials Science and Engineering C* **55**, 530–537.
- Purkait, M. K., Maiti, A., DasGupta, S. & De, S. 2007 Removal of Congo red using activated carbon and its regeneration. *Journal of Hazardous Materials* **145**, 287–295.
- Rusmin, R., Sarkar, B., Biswas, B., Churchman, J., Liu, Y. & Naidu, R. 2016 Structural, electrokinetic and surface properties of activated polygorskite for environmental application. *Applied Clay Science* **134**, 95–102.
- Sahnoun, S., Boutahala, M., Zaghoulane-Boudiaf, H. & Zerroual, L. 2016 Trichlorophenol removal from aqueous solutions by modified halloysite: kinetic and equilibrium studies. *Desalination and Water Treatment* **57**, 15941–15951.
- San Cristóbal, A. G., Castelló, R., Luengo, M. A. M. & Vizcayno, C. 2009 Acid activation of mechanically and thermally modified kaolins. *Materials Research Bulletin* **44**(11), 2103–2111.
- Santamarina, J. C., Klein, Y. H. & Prencke, E. 2002 Specific surface: determination and relevance. *Canadian Geotechnical Journal* **39**, 233–241.
- Sawalha, M. F., Peralta-Videa, J. R., Romero-Gonzalez, J. & Gardea-Torresdey, J. L. 2006 Biosorption of Cd(II), Cr(III) and Cr(VI) by saltbush (*Atriplexcanescens*) biomass: thermodynamic and isotherm studies. *Journal of Colloid and Interface Science* **300**(1), 100–104.
- Shen, S., Kentich, S. E. & Stevens, G. W. 2012 Effect of operational conditions on the removal of phenols from wastewater by a hollow-fiber membrane contactor. *Separation and Purification Technology* **95**, 80–88.
- Srivastava, V. C., Mall, I. D. & Mishra, I. M. 2006 Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. *Journal of Hazardous Materials* **134**(1–3), 257–267.
- Suraj, G., Iyer, C. S. P. & Lalithambika, M. 1998 Adsorption of cadmium and copper by modified kaolinites. *Applied Clay Science* **13**, 293–306.

- Tomic, Z. P., Logar, V. P., Babic, B. M., Rogand, J. R. & Makreski, P. 2011 [Comparison of structural, textural and thermal characteristics of pure and acid treated bentonites from Aleksinac and Petrovac \(Serbia\)](#). *Spectrochimica Acta Part A* **82**, 389–395.
- Toor, M. K. 2010 [Enhancing Adsorption Capacity of Bentonite for dye Removal: Physicochemical Modification Characterization](#). Master's Thesis, School of Chemical Engineering, University of Adelaide, Adelaide, Australia.
- Toor, M., Jin, B., Dai, S. & Vimonses, V. 2015 [Activating natural bentonite as a cost-effective adsorbent for removal of Congo-red in wastewater](#). *Journal of Industrial and Engineering Chemistry* **21**, 653–661.
- Tsai, W. T., Hsien, K. J. & Yang, J. M. 2004 [Silica adsorbent prepared from spent diatomaceous earth and its application to removal of dye from aqueous solution](#). *Journal of Colloid and Interface Science* **275**, 428–433.
- U.S. Environmental Protection Agency 1999 *U.S. EPA Office of Prevention, Pesticides, and Toxic Substances Reregistration Eligibility Decision (RED) for Chlorothalonil*.
- Vengris, T., Binkiene, R. & Sveikauskaite, A. 2001 [Nickel, copper and zinc removal from waste water by a modified clay sorbent](#). *Applied Clay Science* **18**, 183–190.
- Wang, X. K., Chen, C. L., Hu, W. P., Ding, A. P., Xu, D. & Zhou, X. 2005 [Sorption of ²⁴³Am\(III\) to multiwall carbon nanotubes](#). *Environmental Science and Technology* **39**, 2856–2860.
- Yaghoobi-Rahni, S., Rezaei, B. & Mirghaffar, N. 2017 [Bentonite surface modification and characterization for high selective phosphate adsorption from aqueous media and its application for wastewater treatments](#). *Journal of Water Reuse and Desalination* **7**(2), 175–186.
- Zuo, S., Liu, F., Zhou, R. & Qi, C. 2012 [Adsorption/desorption and catalytic oxidation of VOCs on montmorillonite and pillared clays](#). *Catalysis Communications* **22**, 1–5.