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Adsorption of organochlorine pesticides on modified porous Al_{30}/bentonite: Kinetic and thermodynamic studies

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Abstract Adsorption of pesticides (heptachlor epoxide, dieldrin and endrin) onto modified bentonite by Keggin cation $[Al_{30}O_8(OH)_{56}(H_2O)_{24}]^{18+}$ denoted Al_{30} cation to form composite (Al_{30}/B), has been investigated as a possible alternative method for their removal from aqueous solutions. The study was aimed to use a low-cost material as a step towards cleaner environment. Interestingly, these chemical modifications altered the physicochemical characteristics of bentonite in term of morphology, surface area and functionality which has been confirmed by using nitrogen adsorption–desorption isotherm, scanning electronic microscopy (SEM) and X-ray diffraction (XRD). Gas chromatography coupled to mass spectrometry (GC–MS) was used to identify and analyze the pesticides. Different physicochemical parameters were analyzed: contact time, adsorbent dose, pH, and temperature. The results showed that the removal percentage of pesticides on Al_{30}/B was the highest at contact time of 5 h, adsorbent dosage of 25 mg, at pH 7.5, and at optimum temperature of 45 °C. Furthermore, the Kinetic study indicated that the adsorption of pesticides on Al_{30}/B was well adapted to the pseudo-first order kinetic with a correlation coefficient near unity. The results of adsorption were fitted to the Langmuir and Freundlich isotherms. The Freundlich model represented the adsorption process better than Langmuir model, with correlation coefficients (R^2) values range from 0.986 to 0.989. The Thermodynamic study suggested that the adsorption of pesticides was chemisorption, spontaneous and endothermic process. Therefore, Al_{30}/B composite can be utilized effectively for removal of pesticides with efficiency up to 98%.
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1. Introduction

Among the organic pollutants, the cyclodienes such as endo-sulfan, endrin, dieldrin and heptachlor are usually used as insecticides. They have been established to be highly toxic to

aquatic life, as they exhibit carcinogenic activity, low biodegradability, and highly bio-concentrate in organisms at various trophic levels (Bandala et al., 2006; Kapustka et al., 1996). Indeed, serious environmental problems have been arisen from the release of organic pollutants into wastewaters (Kalnay & Cai, 2003; Ouyang et al., 2006). Therefore, the removal of organic pollutants from the aqueous phase is of a great interest. Among several chemical and physical methods, adsorption is one of the most useful techniques that has been successfully employed for organic pollutants removal from wastewater because of simplicity of design, ease of operation and convenience (Bhatnagar et al., 2015; De Gisi et al., 2016). Activated carbon, as commercial adsorbent, is very effective but expensive due to their high costs of manufacturing and regeneration (Amin et al., 2015). Accordingly, research interest is focused on natural materials that remove dyes from wastewater as they are affordable eco-friendly materials (F. Allouche & Yassaa, 2018).

Bentonite is a clay mineral of phyllosilicate groups, occurs as a silicate layers in a three-phase crystalline structure that promotes intrinsic characteristics. The clay mineral surface poses a negative charge owning to the edge hydroxyls groups, giving raises to intermolecular hydrogen bonds with hydrophilic medium. Furthermore, the presence of inorganic cations can stabilize its silicate layers by Van der Waals forces formation (Motawie et al., 2014). Additionally, the surface Brønsted, Lewis acid sites and ion exchange sites are the main reasons for bentonite clay excellent absorptivity. It is well known, bentonite as a natural mineral, is eco-friendly, inexpensive, and accessible (Issaabadi et al., 2017).

Actually, introducing intercalating long chains and/or grafting with different functional groups, interlayer spacing of clay will have influenced results in enhancing its mechanical and physical properties especially adsorption ability (Mockovčiaková & Orolínová, 2009). Nowadays, the modification of clay by several chemical and physical methods shows extensive attention. Magnetic modification in which, e.g., bentonite coated with iron can be obtained (Oliveira et al., 2003), the use of catalyst support as surfactant or nanomaterials (Bhorodwaj & Dutta, 2010), and the addition of ceramic materials with their refractory nature, good chemical stability, high-temperature strength, low thermal conductivity and expansion coefficient will influence clay properties. Lately, inorganic polycationic species has been widely studied, as these materials converted into a firm metal oxide pillars after calcination. The pillars got inserted between the sheets of the clay mineral and kept them separated from each other, which prevents the collapse of the structure on high temperature application use (Gil et al., 2000). The most commonly used polycation in the pillaring process is the Keggin polycation, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ denoted Al_{13}, due to its big size (0.9 nm), high charge (+7), so after using as a pillaring agent it yields large surface area and thermally stable composite (Johansson, 1960).

The aim of this work is improving the specific surface area and pore size and in turn adsorption property of bentonite by combining with aluminum Keggin polycation. The recently discovered Al_{30} Keggin cation was used in pillaring bentonite because this cation is promising due to its bigger size (1.0 nm) and even higher charge (+18) than Al_{13} (Zhu et al., 2017). The preparation of Al_{30}/B composite and possible mechanisms of pesticides adsorption were presented. In the present work, the structure and morphology of the modified

bentonite were confirmed by different techniques. The effect of the adsorption conditions on adsorption capacity of pesticides onto the modified bentonite was extensively investigated. Finally, the experimental data were described using kinetic and adsorption isotherm models. Simultaneously, the heats of adsorption and the Gibbs free adsorption energy were predicted from the thermodynamic study at equilibrium adsorption isotherms.

2. Experimental

2.1. Method and material

Commercial bentonite as starting material was purchased from (CMB Co., Egypt) and its cation exchange capacity CEC value was measured by $[Co(NH_3)_6]^{3+}$ adsorption method and found to be 0.56 meq/g (Aran et al., 2008). Pesticides standard set including heptachlor epoxide, dieldrin and endrin were purchased from (AccuStandard, Inc., USA). The other materials that used in this study including anhydrous Na_2SO_4, $AlCl_3$·$6H_2O$, $Ba(NO_3)_2$, o-phenanthroline, Ferron, hydroxylamine, $AgNO_3$ were obtained from (SIGMA-ALDRICH Co., Germany) and all are of analytical grade.

2.2. Synthesis of Al$_{30}$-modified bentonite

Al_{30}-modified bentonite (Al_{30}/B) was prepared similar to the methods described in previous studies (Aouad et al., 2006; Chen et al., 2007). A 0.154 g of Al_{30} nitrate was grinded with 1.0 g bentonite till homogeneity and stirred in a water bath shaker for one hour at 30 °C. It was then kept soaked in the solution for 24 h. Then the Al_{30}/B filtered from the mixture, washed with distilled water and, air dried for 24 h, then calcined at 300 °C for three hours.

2.3. Surface characterizations

Ferron assay has been performed as an important method for aluminum speciation analysis (Jardine & Zelazny, 1986). Absorbance of Al-Ferron complexes were monitored by using advanced (HACH, DR3900 UV–visible spectrophotometer-USA). Scanning electron microscopy (SEM) images were examined with (QUANTA FEG250 instrument-Netherlands). The specific surface area and pore size of the adsorbents were carried out by nitrogen-adsorption/desorption method (Gregg et al., 1967) at 77 K (boiling point of nitrogen) with the aid of gas sorption analyzer (Nova touch LX^2, surface area and pore size analyzer–Quanta Chrome instruments). X-ray diffraction technique was conducted to Al_{30}/B sample using Cu Kα beam of wavelength λ = 1.54 Å emitted from D8 Discover, Bruker diffractometer–Germany, working at potential 40 kV and current 40 mA and a scanning rate of 1 scan/0.01° and 2θ° range between 3° and 80°.

2.4. Pesticides adsorption, separation and quantification

Batch adsorption experiments were performed by adding known amounts of Al_{30}/B to 25 mL solutions of 0.2 mg/L heptachlor epoxide, dieldrin and endrin each. The pH of the tested solutions were adjusted using 0.1 M NaOH and 0.1 M HCl
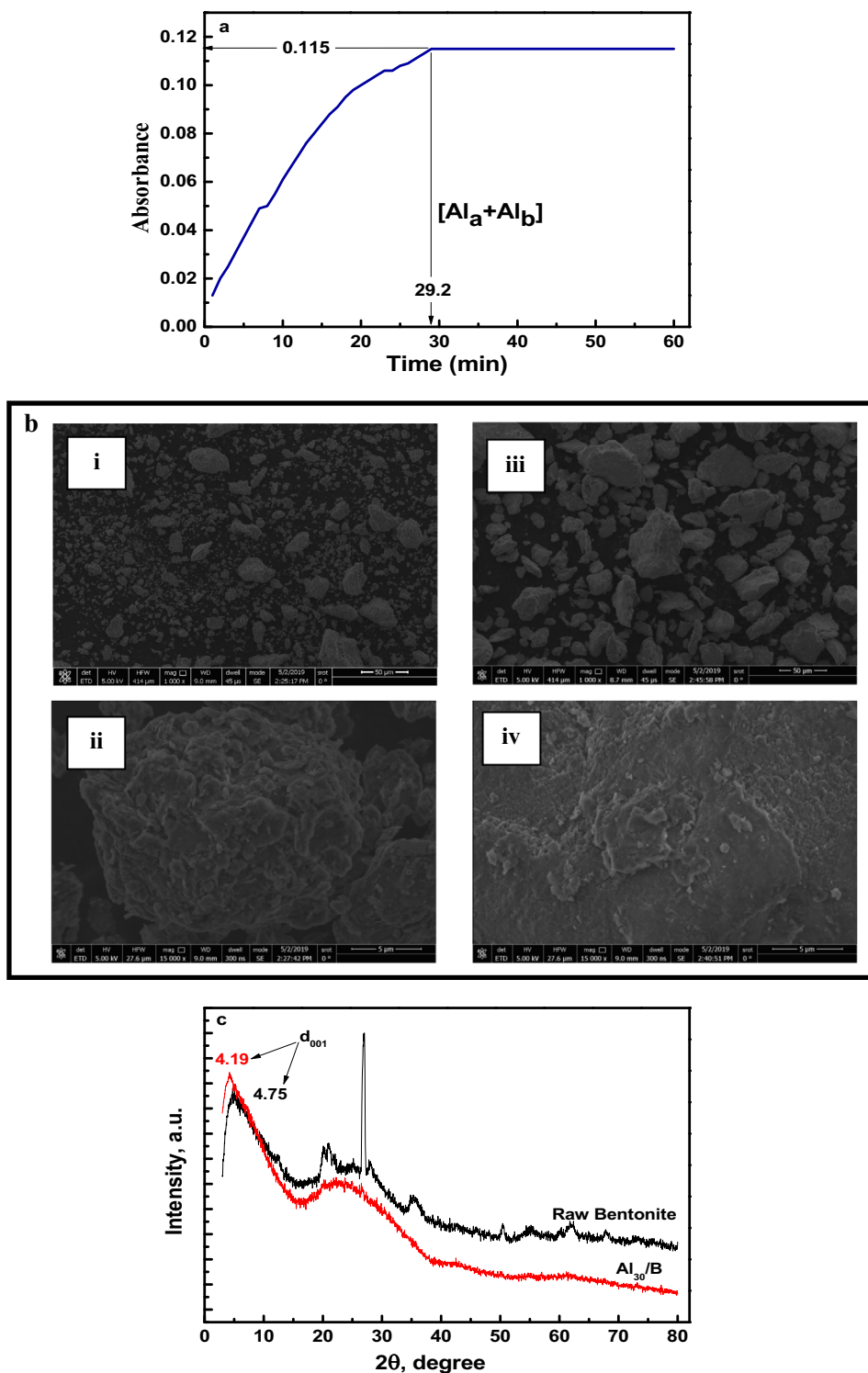
Fig. 1 Structure and characterization of modified Al_{30}/bentonite: (a) Timed Ferron colorimetric analysis of HPA solution ($[Al]_T = 2.4 \times 10^{-5}$ M) showing the increment in absorbance with progress of time. (b) SEM images for natural bentonite (i and iii) and Al_{30}/B (ii and iv) with different magnifications. (c) XRD pattern of raw bentonite and Al_{30}/B composite.

solutions to study the effect pH in the range from (3–10). The mixture was placed in a water bath shaker (120 rpm) for various temperature values ranging from 25 to 55 °C and duration time ranging from (0.5–20 h). After adsorption and filtration the residual heptachlor epoxide, dieldrin and endrin in filtrate was extracted according to EPA 508 (Graves et al., 1988). The concentration of each pesticide was measured using gas chromatography device (Agilent Technologies, 7890A GC System) coupled with mass spectrometer (Agilent Technologies, 5975C inert MSD with triple-axis Detector). The amount of pesticide
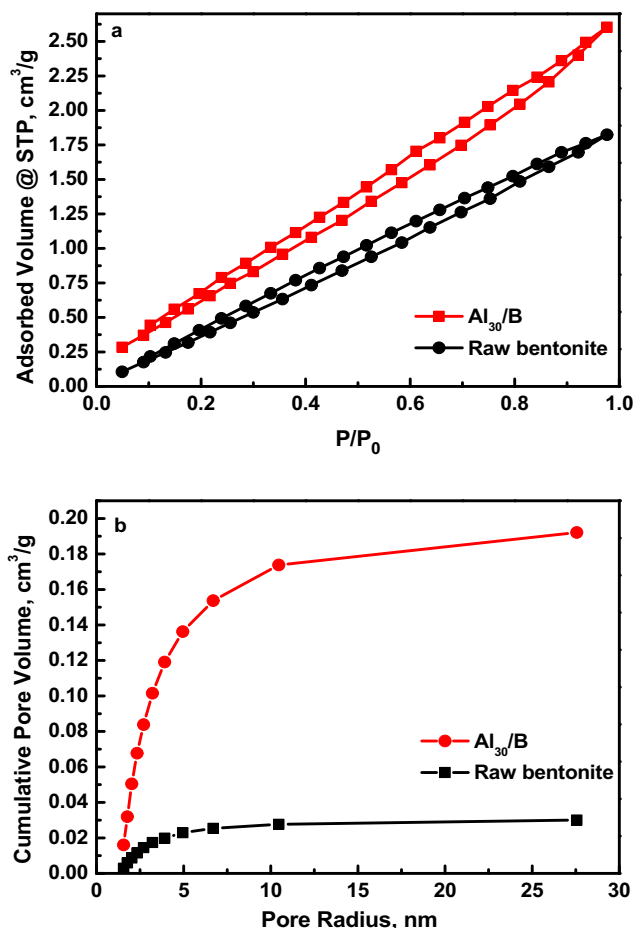
Fig. 2 (a) N$_2$ adsorption/desorption isotherms of raw bentonite and modified Al$_{30}$/B composite and (b) their corresponding pore size distribution curves.

Fig. 3 (a) Effect of contact time on the adsorption capacity of 0.2 mg/L organochlorine pesticides at pH 7.5 in presence of 25 mg of Al$_{30}$/B dosage at 25 °C. (b) The removal percent of organochlorine pesticides (0.2 mg/L) as a function of Al$_{30}$/B dose at natural pH 7.5 and ambient temperature 25 °C and with contacting time of 5 h.

adsorbed on the material surface at time of contact (t) can be calculated from the following equation:

$$q_t = (C_0 - C_t)V/W \qquad (1)$$

where q_t is the amount of pesticide adsorbed in mg/g, C_0 is the average initial concentration in mg/L (control sample concentration), C_t is the average concentration in mg/L of remaining pesticides (unadsorbed) after adsorption process at time (t), W is the adsorbent weight (g), and V is the volume of solution (L). At equilibrium conditions, C_t denoted C_e and q_t denoted q_e and called the equilibrium concentration and adsorption capacity, respectively. The removal efficiency can be calculated as follows:

$$\% \ \text{Removal} = ((C_0 - C_t)/C_0) \times 100 \qquad (2)$$

2.5. Adsorption, kinetics and thermodynamic studies

The pseudo-first order module describes the quantity of adsorbate on the heterogeneous adsorbent surface over time (t) (Lagergren, 1898), according to Eq. (3):
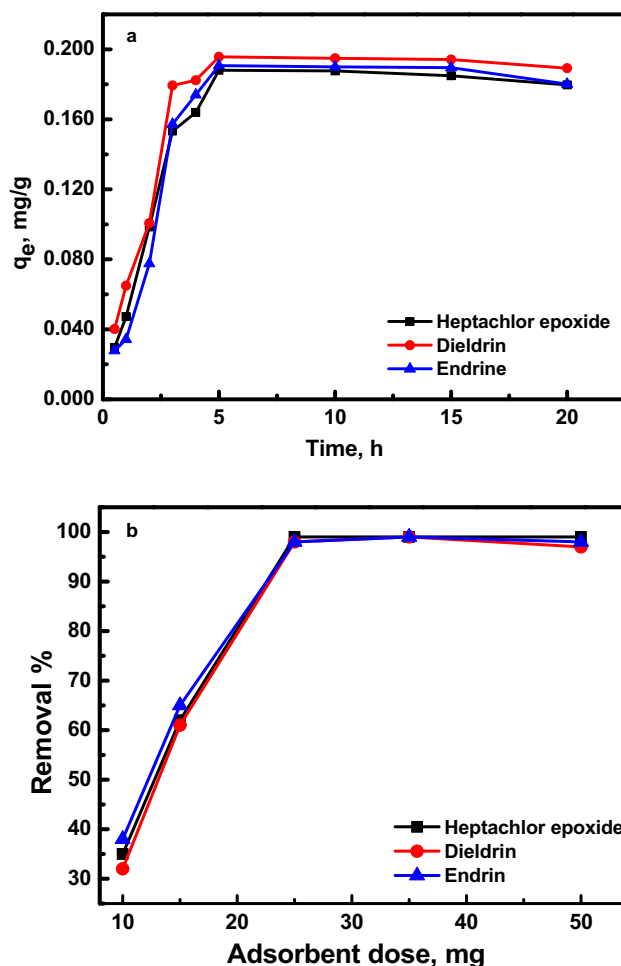
$$\log (q_e - q_t) = \log q_e - (k_1/2.303)t \qquad (3)$$

The pseudo-second order was established to simulate the real reaction as possible and considers a chemisorption reaction as the rate determining step (Ho, 2006). It is expressed by Eq. (4):

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \qquad (4)$$

where q_e and q_t are the amount of pesticides adsorbed on material surface at equilibrium and at time t, respectively, in mg/g, and k_1 and k_2 are the first order and second order rate constants, respectively.

Many isotherms are established to prove the adsorption processes such as Langmuir and Freundlich isotherms which are valid for most of the adsorption reactions. Langmuir isotherm suggests that maximum adsorption capacity is a monolayer of adsorbate covers the adsorbent surface where the homogeneous surface possess equal chances for adsorbate molecules adsorption, and no interaction between adsorbate molecules themselves (Langmuir, 1918). The Langmuir equation is represented by:
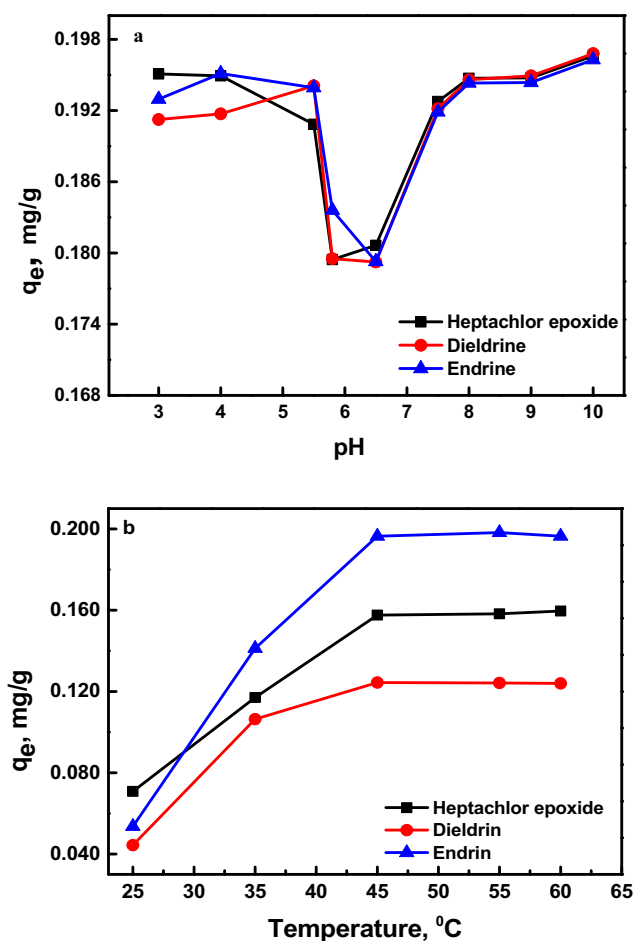
$$C_e/q_e = C_e/q_m + 1/K_L q_m \qquad (5)$$

Fig. 4 (a) Effect of solution pH on the adsorption capacity of 2.00 mg/L pesticides on 25 mg Al$_{30}$/B dosage after 5 h at 25 °C. (b) Effect of solution temperature on the amount of pesticides (initially 2.00 mg/L) adsorbed on 25 mg Al$_{30}$/B dosage at pH 7.5 after 5 h.

where q$_m$ is the maximum adsorption capacity (the amount of pesticides needed to form monolayer in mg/g and K$_L$ is the Langmuir constant in L/mg. A dimensionless factor called separation factor R$_L$ obtained from Langmuir isotherm module and defined as:

$$R_L = 1/(1 + K_L C_0) \qquad (6)$$

where C$_0$ is the maximum pesticides concentration. The value of R$_L$ indicates the type of the isotherm to be either unfavorable (R$_L$ > 1), linear (R$_L$ = 1), favorable (0 < R$_L$ < 1) or irreversible (R$_L$ = 0) (Langmuir, 1918)

On the other side, Freundlich isotherm module suggests an interaction between adsorbate molecules which represent surface heterogeneity (Freundlich, 1907), according to Freundlich equation:

$$\log q_e = \log K_F + (1/n)\log C_e \qquad (7)$$

where K$_F$ is the Freundlich constant and n value indicates the reaction favorability.

The thermodynamic parameters, enthalpy (ΔH°, J/mole), Gibbs free energy (ΔG°, J/mole) and entropy (ΔS°, J/mole/K) were determined to define the adsorption reaction (Yang & Al-Duri, 2005).

3. Results and discussion

3.1. Structure and characterization of modified Al$_{30}$/bentonite

3.1.1. Studies of time-developed Al-Ferron complex colorimetry

Ferron kinetic method was used to evaluate Al$_{30}$ content in Al$_{30}$/B. The absorbance/time curve of hydrolytic polymeric aluminum (HPA) solutions measured by Al-Ferron method is shown in Fig. 1a. The change in absorbance was monitored for 60 min and the Al reacted at 30 min was assumed to represent [Al$_a$ + Al$_b$] (Parker & Bertsch, 1992). The quantity [Al$_c$] was computed as the difference between [Al]$_T$ and [Al$_a$ + Al$_b$]. The quantitative calculation results of three species, Al monomer (Al$_a$), oligomer (Al$_b$), and polymer (Al$_c$), as well as rate constant (k) concluded that the real content of [Al$_{30}$] is 78.2% which means success formation of keggin Al$_{30}$ (Chen et al., 2007). With increasing total Al concentration, Al$_a$ and Al$_b$ contents decrease, while Al$_c$ content increases indicating Al$_{30}$ polymeric formation. This could be explained based on the fact that during aluminum hydrolysis both Al$_{13}$ and Al$_{30}$ species are kinetically intermediate products and the highly charged Al$_{30}$ is more stable than Al$_{13}$ as it is consists of two δ-Al$_{13}$ Keggin units connected by a crown made of four hexa-coordinated aluminum (AlO$_6$) (L. Allouche et al., 2000; L. Allouche & Taulelle, 2003).

3.1.2. Morphological studies

SEM analyses have been used to compare the surface morphologies and micro-structures changes before and after modification of bentonite. Fig. 1b(i, iii) shows that raw bentonite displays rock-like macro particles with rough and heterogeneous surfaces. After Al$_{30}$ modification, meso particles were noticed giving compact, large surface area and lamellae like structure were also observed on the surface of the Al$_{30}$/B (Fig. 1b(ii, iv)), indicating the partial exfoliation of the bentonite layer during Al$_{30}$ modification process.

The XRD patterns of the bentonite was studied to confirm the intercalation of the Al$_{30}$ into the bentonite layers and presented in Fig. 1c. Sharp peak of quartz was observed in raw bentonite, 2θ, 27.0°, and attributed to impurity of the sample. During modification processes, the basal spacing reflection of bentonite shifts gradually from 2θ, 4.75° to 4.19°, implying the formation of micro and meso porous structure resulting from the Al polycation addition. Also, a broad peak was noticed at 22° after modification confirming that the Al$_{30}$/B was successfully synthesized.

The raw and modified-bentonite samples showed a similar N$_2$-adsorption/desorption isotherm behavior of H$_2$-type hysteresis loop for aggregates of plate-like particles according to IUPAC classification giving rise to meso and micro pores (Fig. 2a) with higher performance for Al$_{30}$/B if compared with raw bentonite. The microporosity of the Al$_{30}$/B allows their use in the adsorption and separation of small ions, while the mesoporosity favors the adsorption of bigger molecules, such as aromatic compounds even biomolecules.
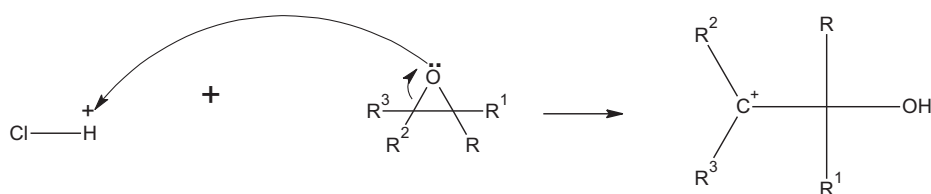
The specific surface areas were estimated to be 164.2 and 29.6 m^2/g for modified and raw bentonite, respectively. The higher surface area of modified bentonite is attributed to generation of micro and meso pores after success pillaring

of bentonite surface under the hydrothermal conditions. The raw and modified bentonite exhibited uniform pore size distribution of 5 and 10 nm, respectively (Fig. 2b). It was concluded that, Al$_{30}$/B has more attractive receptor sites compared to raw-bentonite confirming the effect exerted by inserting Al$_{30}$ onto bentonite layers, as proved by XRD characterization. Therefore, the higher pore size distribution for modified bentonite could play a significant role in pesticides adsorption.

3.2. Adsorption study of chlorinated pesticides

3.2.1. Effect of contact time and adsorbent dosage

The effect of contact time on adsorption of pesticides was explored in presence of 0.2 mg/L pesticides onto 25 mg of Al$_{30}$/B in a solution of pH 7.5 at 25 °C (Fig. 3a). The results revealed that ~95% of the three pesticides were adsorbed onto Al$_{30}$/B surface in the first 5 h followed by equilibrium for the three chosen pesticides. The rapid increase in the adsorbed amount of pesticides was attributed to the available pores and vacant adsorption sites in Al$_{30}$/B, which fill up gradually

effect was noticed. Consequently, the subsequent experiments were conducted during a contact time of 5 h and Al$_{30}$/B dose of 25 mg as optimum conditions.

3.2.2. Effect of solution pH

It is well known that, the adsorption is affected greatly by the pH of solution. All the tested pesticides have epoxide group, i.e. oxacyclopropane or oxirane which is the main active site in their structures. This group is strained and easily affected by adjacent substituents acids and bases (Grabowsky et al., 2011). In aqueous solution, oxacyclopropane group maintains a positive charge ion, while the bentonite surface is negatively charged. Thus, the solution pH affected both the surface charge of the modified bentonite and the degree of polarization of pesticides molecules. Thus, as the solution pH increases the adsorption of pesticides on modified bentonite increases (Fig. 4a). The adsorption is an electrophilic attack of pesticide carbon [C$^+$] on bentonite surface. In presence of acid, there are two contrary actions; the first is the catalyzed ring breakage and a true positive charge on carbon atom according to the following mechanism.


and the adsorption becomes slower with time till achieving complete saturation. It was observed that the adsorption capacities, q$_e$, were 0.188, 0.196 and 0.191 mg/g after 5 h for heptachlor epoxide, dieldrin and endrin, respectively. The adsorbent dosage effect was also studied by varying the mass of Al$_{30}$/B from 10 to 50 mg in a solution of pH 7.5 containing pesticides of 0.2 mg/L at 25 °C and for contacting time of 5 h (Fig. 3b). The removal efficiency of modified bentonite for pesticides was increased from 40% to 95%, which might be attributed to increase in the total surface area of modified bentonite sample (Alzahrani & Ahmed, 2016; Alzahrani et al., 2020;

The true cationic pesticide moiety is enforced to adsorb on Al$_{30}$/B and the amount of pesticides adsorbed increased as shown in Fig. 4a. The second is a competition between the H$^+$ proton in the acid and the slightly positive carbon in pesticide molecule to adsorb on the Al$_{30}$/B surface (Hameed et al., 2008). So the amount of pesticide adsorbed was decreased and this can be noticed at pH values 5.5 and 6.5 (i.e. in slightly acidic solutions). In case of basic solution, the OH group of the base attacks the slightly positive carbon and ring opening takes place to give a negatively charged ionized oxygen R-O$^-$ Na$^+$ as shown in the mechanism.
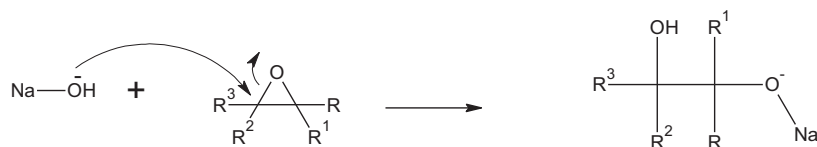
Mudzielwana et al., 2019; Nameni et al., 2008). It was observed that, as the adsorbent dosage increases, the removal efficiency increases till 25 mg adsorbent and then no significant

In addition, the Lewis acidity of bentonite was enhanced by pillaring with Al$_{30}$ (TOMUL & Balci, 2008), and therefore the pillars of Al$_2$O$_3$ attract pesticides molecules of negatively

Table 1 Comparison of adsorption capacities and other parameters for the removal of pesticides in different adsorbent materials and modifications of bentonite in other studies.

Adsorbents	Adsorbate	Surface Area/ Particle Size of Adsorbent (m^2/g)	Adsorption Capacity (mg/g)	Concentration Range (mg/L)	Contact Time (h)	Temp. (°C)	pH	Percent Adsorption	Reference
Triolein embedded activated carbon composite	dieldrin	721	0.002	0.001–0.05	48	25	4–8	—	Ru et al. (2007)
Pine bark sawdust	Heptachlor	—	—	2–1000	24	—	—	93.6	Ratola et al. (2003)
Organo-bentonite complexes	bromoxynil residues	—	—	1.2–31	48	5	3–7	88	El-Nahhal and Safi (2008)
Montmorillonite Kaolinite clays	endrin	14.1 17.7		500–5000	—		5.4–7.2		Peng et al. (2009)
Fe_3O_4 magnetic nanospheres coated with polystyrene	heptachlor epoxide dieldrin endrin	129	—	0.01	1	25		93.3	Lan et al. (2014)
Al_{30}/bentonite	heptachlor epoxide dieldrin endrin	164.2	0.188 0.196 0.191	0.2	5	45	7.5	95	Our work

oxygen at high pH so the amount of pesticides adsorbed increases with rise of pH as illustrated in Fig. 4a.

3.2.3. Effect of temperature

The effect of temperature on the adsorption of pesticides was also investigated in presence of 25 mg of modified bentonite sample and 0.2 mg/L initial pesticides concentration at pH 7.5 for 5 h contact time. The results showed that as the temperature increases the amount of pesticides adsorbed increases from 25 to 45 °C then no noticeable increase was observed up to about 60 °C (Fig. 4b). Hence, increasing temperature can affect solubility of pesticides and their orientation on bentonite surfaces (El-Sayed, 2011). Moreover, high temperature activates Al_{30}/B active sites which enhance adsorption of sparingly soluble pesticides, so the optimum temperature was chosen to be 45 °C. In Table 1, the Adsorption capacities and other parameters for the removal of pesticides in different adsorbent materials and modifications of bentonite of the proposed method are compared with those obtained by some reported methods. In comparison with some other adsorbent materials, Al_{30}/B showed advantages in several aspects. The modified bentonite is prepared in simple way. This gives the Al_{30}/B more advantages over other adsorbent used in the literature. Al_{30}/B bentonite showed relatively higher percent adsorption in neutral medium.

3.3. Adsorption kinetics and isotherms

3.3.1. Adsorption kinetics

The kinetic of organochlorine pesticides removal by Al_{30}/B have been evaluated in this study using the pseudo-first order and pseudo-second order kinetics. The various model parameters are illustrated in Table 2 and the fitting plots are illustrated in Fig. 5(a–b). A good fit for either kinetic model would require correlation coefficient (R^2) values close to unity as well as calculated adsorption capacity (q_e) values that come in a good agreement with the experimental values (Toor & Jin, 2012). In both regards, it was observed that the pseudo-first order kinetics gave the best fits and was more appropriate in describing the adsorption of pesticides on Al_{30}/B than the second order kinetics. Although the correlation coefficient values for the latter are around 0.98, the experimental q_e values do not agree with the calculated ones, obtained from the second order linear plots (Table 2).

3.3.2. Adsorption isotherms

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between solute and adsorbent, and is important for the design of adsorption system Fig. 6a. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the

Table 2 Kinetic parameters for adsorption of organochlorine pesticides on Al_{30}/B.

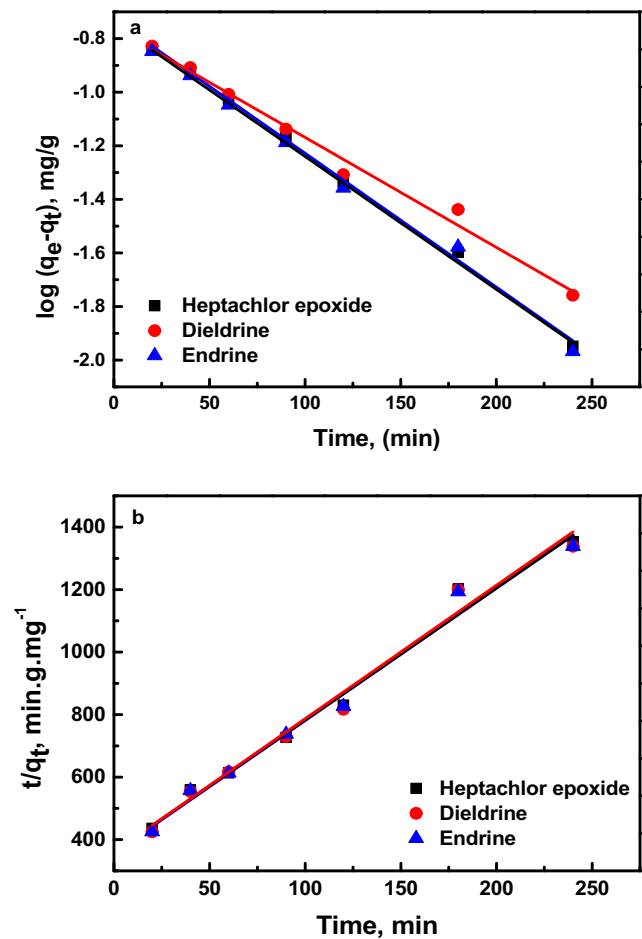| Organochlorine pesticides	Pseudo-first order			Pseudo-second order		
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg/g)	R^2
Heptachlor epoxide	0.0114	0.190	0.995	0.041	0.234	0.987
Dieldrin	0.0115	0.185	0.997	0.050	0.236	0.983
Endrin	0.0115	0.192	0.998	0.049	0.237	0.986

Fig. 5 (a) Pseudo-first order and (b) Pseudo-second order kinetics for adsorption of organochlorine pesticides on Al$_{30}$/B at 45 °C.

suitable model that can be used for design purpose. Adsorption isotherm study is carried out on two well-known isotherms, Langmuir and Freundlich. Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. While, Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage. The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2. Table 3 shows the values of the parameters of the two isotherms and the related correlation coefficients. A comparison is also made between two isotherms plotted in Fig. 6(b-c), which shows the experimental data points and the fitted lines for the three organochlorine pesticides examined for different initial concentrations at pH 7.5 and 45 °C. As seen from Table 3, the Freundlich model yields better fit ($R^2 \sim 0.99$) than the Freundlich model ($R^2 \sim 0.97$). In addition, the maximum monolayer adsorption capacity, q$_m$, calculated using Langmuir isotherm, as predicted by Eq. (5), do not agree with the experimental values (derived from the effect of contact time study at 5 h which are 0.188, 0.196 and 0.191 mg/g for heptachlor epoxide, dieldrin and endrin, respectively). As also illustrated in Table 3, the values of 1/
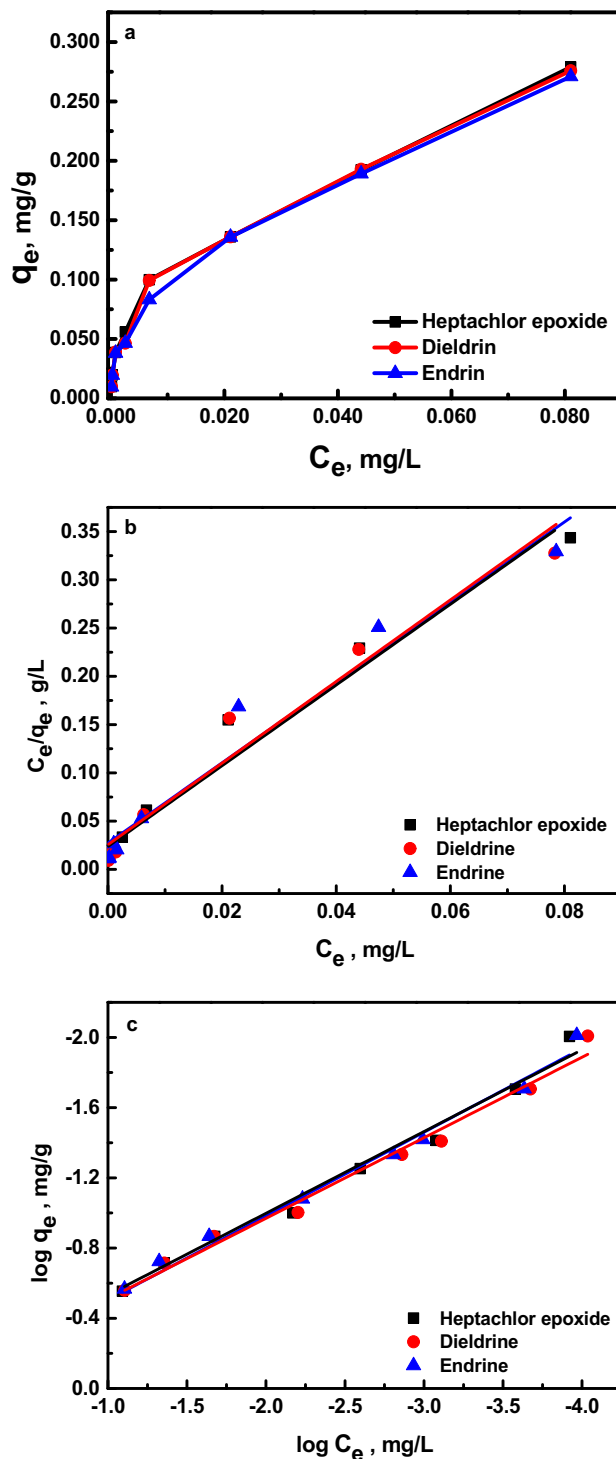

Fig. 6 (a) The equilibrium adsorption (b) Langmuir adsorption and (c) Freundlich adsorption isotherms of organochlorine pesticides on Al$_{30}$/B at 45 °C.

n (the slope of Freundlich linear Eq. (7)) are 2.09, 2.18 and 2.15 for heptachlor epoxide, dieldrin and endrin, respectively. The three 1/n values are greater than one which indicate favorable and cooperative adsorption.

Langmuir isotherm assumes monolayer coverage on a homogeneous surface with identical adsorption sites. But

Table 3 The model parameters of Langmuir and Freundlich isotherms for adsorption of organochlorine pesticides on Al_{30}/B at 45 °C.

Organochlorine pesticides	Langmuir isotherm				Freundlich isotherm		
	q_m (mg/g)	k_L (L/mg)	R^2	R_L	K_F	$1/n$	R^2
Heptachlor epoxide	0.241	152.3	0.972	0.032	0.940	2.09	0.989
Dieldrin	0.239	175.7	0.966	0.028	0.889	2.18	0.986
Endrin	0.237	164.4	0.962	0.030	0.858	2.15	0.989
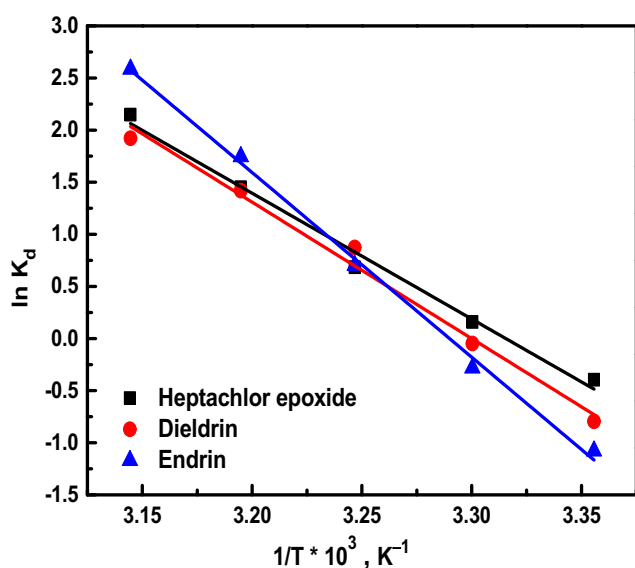
Fig. 7 Plot of ln K_d against $1/T$ for adsorption organochlorine pesticides on Al_{30}/B.

Table 4 Thermodynamic parameters of adsorption of organochlorine pesticides onto Al_{30}/B.

Organochlorine pesticides	$\Delta H°$ kJ. Mol^{-1}	$\Delta S°$ kJ. Mol^{-1}. K^{-1}	$\Delta G°$ at 45 °C kJ. Mol^{-1}
Heptachlor epoxide	100	0.33	−4.57
Dieldrin	109	0.36	−5.38
Endrin	149	0.48	−6.81

has more pores and sites to catch pesticides molecules after the monolayer accomplished by a different way. In conclusion, Freundlich isotherm model shows the best fit compared to Langmuir isotherm for adsorption of organochlorine pesticides on Al_{30}/B at the experimental conditions applied in this study.

3.3.3. Thermodynamic study

Fig. 7 shows a relation between ln K_L versus $1/T$ represented as a straight line with the gradient $(-\Delta H°/R)$ from which $\Delta H°$ may be calculated using the least-squares method (Table 4) which confirms the endothermic nature of the process. This conclusion coincides with the results obtained from the effect of temperature experiment. In addition, the higher magnitude of $\Delta H°$ (>20 kJ. mol^{-1}) suggests that the organochlorine pesticides are chemisorbed on Al_{30}/B.

The positive values of $\Delta S°$ (Table 4) suggest the increased randomness at the solid-solution interface with the increasing of temperature (Lian, Guo, & Guo, 2009). Taken into consideration the values of both $\Delta H°$ and $\Delta S°$, the Gibbs free energy, $\Delta G°$, at 45 °C was calculated as depicted in Table 4. The negative values of $\Delta G°$ for the three investigated pesticides indicates that the adsorption of these pesticides on Al_{30}/B are spontaneous and feasible (Dawood & Sen, 2012).

4. Conclusion

A Successful Al_{30}/B was prepared from raw bentonite and Al_{30} and was used in adsorption of three important pesticides from aqueous solutions. The Al_{30}/B has more porosity and larger surface area compared to raw-bentonite confirming the effect exerted by Al_{30} cations on the surface of bentonite, as proved by SEM and XRD characterization. The results of N_2 adsorption-desorption isotherms indicated that the new mesoporous and microporous structure was significantly increased after the insertion of Al_{30} allowing adsorption of large organic molecules. The parameters affecting the adsorption of pesticides were studied. The results obtained showed that the optimal adsorbent dose and the contact time to reach equilibrium were 25 mg and 5 h, respectively. Also, the adsorption was strongly influenced by temperature which had a positive effect on pesticides adsorption by Al_{30}/B. In addition, the adsorption of pesticides was better at neutral pH. The overall kinetic study showed pseudo first-order kinetic model with correlation coefficient close to unity. Adsorption behavior was best described by a Freundlich type isotherm. The thermodynamic study indicated that the adsorption was chemisorption, spontaneous and endothermic in nature. Al_{30}/B has a promising potential in environment

these assumptions are valid for gas adsorption on solid surface. In solution-solid systems, with the hydration forces, mass transport effects etc. the system is much more dynamic and complicated, and Langmuir isotherm does not necessarily reflect the validity of the aforementioned assumptions. In such systems, the isotherm adequacy can be seriously affected by the experimental conditions, in particular, the range of concentration of the solute/adsorbate (Jeppu & Clement, 2012; Potgieter, 1991). In the current system, the adsorbate pesticide concentration range is significantly small and the Al_{30}/B adsorbent possesses more available sites for extra adsorbates. Furthermore, the Al-pillared adsorbent

fields as an effective, economical, and ecological adsorbent for the removal of pesticides from aqueous medium.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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