



Influence of salts and humic acid on 2,4-dichlorophenoxyacetic acid removing from aqueous solution by peanut shell activated carbon

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ABSTRACT

The activated carbon (AC) was prepared from peanut shell and then used as adsorbent for 2,4-dichlorophenoxyacetic acid (2,4-D) removal from aqueous solution. The prepared AC was characterized by Fourier transform infrared spectroscopy and scanning electron microscopy. The effects of sodium chloride, calcium chloride, and humic acid (HA) were investigated on adsorption process. The kinetics results yield well the pseudo-second-order model than pseudo-first-order kinetic. The L-shape type isotherm obtained with influence of salts were became S-shape type with simultaneous influence of salts and HA. The experimental data were best fitted with the Langmuir model with influence of salts, and best suitable with the competitive Langmuir with combined influence of HA and salts. The adsorption capacities were 281.22, 86.12, 160.32, and 154.96 mg g⁻¹ with adsorption of 2,4-D only, and with influence of 0.01 M NaCl, 0.01 M CaCl₂ and HA solutions respectively. The reusability property of AC slightly decreased during the first three cycles performed while the regeneration efficiency was remained higher after the five cycles attempted.

Keywords: Peanut shell; Pesticides; Adsorption; Salts; Humic acid

1. Introduction

In recent decades, the high consumption of herbicides in agriculture leads to the contamination of surface water and groundwater by leaching, percolate and infiltration of treated soils, which means important environmental pollution and also causes human disease [1,2]. In Benin, to increase the production of cotton, maize, soybeans, and other cereals, large quantities of organochlorine and organophosphorus

pesticides were spreading on crops, generating water and sediment pollution as a disadvantage. So, the high concentrations exceeding environmental quality standards of some pesticides such as atrazine, metazachlor, chlorpyrifos and 2,4-dichlorophenoxyacetic acid (2,4-D) were found in Oueme River water and sediments [3–5]. The 2,4-D is an active compound in over of thousand herbicides mostly used in agriculture because of its efficiency and selectivity [6]. 2,4-D was also highly soluble in water and has often been detected in the aquatic environment. Also, 2,4-D is dangerous for human health and the environment even at low concentration [7].

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Thereby, numerous methods have been applied for 2,4-D removal from aqueous medium. Most of them have related to advanced oxidation [8], ozonation [9], photodegradation [10], electrochemical process [11] and adsorption [12,13]. However, activated carbon (AC) is widely used as an adsorbent for pollutants removal from wastewater because of its efficiency, selectivity, and ecological advantages. But, the high cost of commercial AC has motivated the production of AC from non-conventional compounds from agricultural wastes such as coconut shell [14], corncob [15], orange peel [16], grape seeds [17], rice husk [18] and groundnut shell [19].

Furthermore, when herbicides are sprayed over crops, some of the products are spread on the treated soils. Given the soil's composition in humic substances (HS) and mineral salts, the mobility of herbicide molecules from soil to water and sediment may be influenced by salts and HS concentrations. HS is the major component playing important roles in the distribution, mobilization and degradation of soil pollutants like pesticides [20]. So, the study of the influence of salts and HS on pesticide removal has been investigated by several searchers. Thus, Kurtoglu and Atun [21] reported that the removal efficiency of 2,4-D in the presence of Na^+ ion slightly increased, while Gonzalez-Marquez et al. [22] observed the decrease in the atrazine removal at high concentration of salts. Tian et al. [20] and El-Nahhal et al. [23] also found that the removal efficiency of linuron and atrazine decreased in the presence of NaCl and dissolved organic matter respectively.

Arachis hypogaea commonly called the peanut is a leguminous produced in Benin for its oilseeds. After oil extraction, the shells are abandoned in garbage which leads to environmental pollution. Therefore, peanut shells are widely available, cheapest biomaterial and highly biodegradable. Thus, the use of peanut shells as an adsorbent for pollutant removal may contribute to environmental protection. The aim of the study was the preparation of AC from the peanut shell by chemical activation with H_3PO_4 . The prepared AC was characterized by Fourier transform infrared spectroscopy (FTIR), zero-point charge, Boehm titration, specific surface area Brunauer–Emmett–Teller (BET) and scanning electron microscopy (SEM), and then used as an adsorbent for removal of 2,4-D through the batch mode. The outcome of this work would improve the influence of the simultaneous presence of salts and humic acid (HA) on the 2,4-D adsorption process. The effects of pH, contact time, temperature, adsorbent dosage and concentration of 2,4-D, salts and HA were investigated. The adsorption kinetics, isotherms, and thermodynamic behavior were also performed to explain the adsorption mechanism.

2. Materials and methods

2.1. Reagents

H_3PO_4 (85%, $d = 1.71$), HCl (36%, $d = 1.18$), NaOH, 2,4-D ($\text{C}_8\text{H}_6\text{O}_3\text{Cl}_2$) (2,4-D), NaCl, CaCl_2 were supplied by Sigma Aldrich (England) and all the others chemical reagents are analytical grade. The peanut shells wastes were collected from women cooperative who sell the peanut seeds in Natitingou town, (Benin). The HA was extracted from peat Nokoue Lake using the International Humics Substances Society method previously reported by Fatombi et al. [24].

The stocks solutions of 2,4-D and HA were prepared by dissolving 1 g of 2,4-D in 100 mL of 96% ethanol, and 1 g of HA in 100 mL of 0.1 M NaOH solution, then, each the mixture was diluted to 1 L with distilled water.

2.2. Preparation of AC

AC was prepared as previously reported by Shahraki et al. [25]. The peanut shells were washed several times by tap water and dried under sunlight for several days. The dried peanut shells were crushed and sifted from 0.8 to 1 mm. The obtained powder was mixed with H_3PO_4 30% at 1:3 impregnation ratio (weight of peanut shell/weight of H_3PO_4). The mixture was heated with reflux during 2 h, then oven-dried at 60°C for 24 h. Then, the dried mixture was heated in a tubular furnace (Carbolite Scientific) at 170°C at a rate of 10°C/min during 1 h, and then at 450°C for 3 h. The obtained coal was washed several times by distilled water until neutral pH, then, dried in a tubular furnace at 110°C for 12 h and labeled as AC.

2.3. Characterization of AC

The prepared AC was characterized by several analytical technics. The point of zero-charge $\text{pH}_{(\text{ZPC})}$ was carried out using the previously reported by Mathias et al. [26]. 0.15 g of AC was put in conical glass flasks containing 50 mL of 0.1 M NaCl solution at initial pH ($\text{pH}_{(\text{initial})}$) adjusted between 2 and 10 with 0.1 M HCl and 0.1 M NaOH solutions. The mixture was continuously stirred during 48 h at 300 rpm and room temperature, then, the final pH ($\text{pH}_{(\text{final})}$) was measured. The $\text{pH}_{(\text{ZPC})}$ was obtained by plotting the pH change ($\text{pH}_{(\text{final})} - \text{pH}_{(\text{initial})}$) against ($\text{pH}_{(\text{initial})}$), where the ($\text{pH}_{(\text{final})} - \text{pH}_{(\text{initial})} = 0$) was taken as $\text{pH}_{(\text{ZPC})}$ value. The active functional groups from the AC surface were studied by Boehm titration [27]. Boehm titration was performed with 1.5 g of AC mixed at room temperature with 50 mL of 0.05 M Na_2CO_3 , 0.05 M NaHCO_3 and 0.05 M NaOH solutions. The mixture was continuously stirred for 24 h and then filtered. A volume of 10 mL of filtrate of the reaction with Na_2CO_3 , NaHCO_3 or NaOH was titrated by 0.05 M HCl solution. The amounts of carboxylic, lactonic and phenolic functional groups were quantified from the amounts of HCl used. The specific surface area BET and the pore size were determined from N_2 adsorption/desorption isotherm at 77 K on Micromeritics 2010 (USA). The FTIR analysis was performed on Perkin Elmer 100 Series spectrometer FTIR (United Kingdom). The samples were mixing with potassium bromide (1/100 by weight) in 13 mm diameter pellets. Spectra were recorded under 4 cm^{-1} resolution within the range of a 400–4,000 cm^{-1} wavenumber. The morphology of AC was carried out with a SEM-FE-1540XB.

2.4. Adsorption experiments

The batch experiments were carried out by putting 50 mg of AC in a conical glass flask containing 50 mL of 50 mg L^{-1} 2,4-D solution. The initial pH of the 2,4-D solution was adjusted to the needed value with 0.10 M HNO_3 solution or 0.10 M NaOH solution. The mixture was stirred at 100 rpm over the desired contact time, then, the mixture was withdrawn from the stirrer and filtered through Whatman filter

paper N°1. The residual concentration of 2,4-D in solution was quantified by the calibration curve method after spectrophotometric absorbance measurement on UV/Vis 1600 PC spectrophotometer at 283 nm. The effects of concentration of 2,4-D solution (10–100 mg L⁻¹), pH (2–10), AC dosage (0.01–0.1 g), contact time (0–120 min) and temperature (30°C–75°C) were also investigated.

The influence of concentrations of NaCl and CaCl₂ and HA was performed on adsorption process by adding to an appropriate aliquot of the 2,4-D solution, the amounts of NaCl, CaCl₂ or HA solution until final concentration range 0.01–0.1 M for NaCl or CaCl₂, and 10–100 mg L⁻¹ for HA are reached in the mixture. The concentration of HA in solution was also quantified after measurement of absorbance at 272 nm. The concentration of 2,4-D in (2,4-D + HA) mixture was calculated using the subtraction absorbance method. The representative UV spectra recorded in the 250–350 nm range were shown in Fig. 1.

The removal efficiency RE(%) and the amount of 2,4-D adsorbed on the unit weight of AC (q) were calculated as follows:

$$RE(\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$q = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

where C_0 (mg L⁻¹) is the initial 2,4-D concentration, C_t (mg L⁻¹) is the 2,4-D concentration at any contact time t , m (g) is AC weight and V (L) is the solution volume.

2.5. Desorption and recovery study

Desorption experiments were also carried out in batch mode with 0.1 M NaOH solution used as eluant. The AC-loaded 2,4-D collected from the adsorption experiment was washed with distilled water, and oven-dried at 60°C for 12 h, then mixed with 100 mL of 0.1 M NaOH solution. After stirring at 100 rpm at room temperature during 6 h, the mixture was filtered and the final concentration of 2,4-D in the filtrate was quantified. The desorbed AC was washed with distilled water until neutral pH, oven-dried, and then reused to perform the next adsorption/desorption cycle repeated for five times. The effects of concentration of salts were also performed on desorption study. The regeneration efficiency D (%) was calculated as follows:

$$D(\%) = \frac{m_{\text{des}}}{m_{\text{ads}}} \times 100 \quad (3)$$

where m_{ads} (mg) is the weight of adsorbed 2,4-D and m_{des} (mg) is the weight of desorbed 2,4-D.

3. Results and discussion

3.1. Characteristics of AC

The textural parameters of AC were 458.23 m² g⁻¹, 0.23 cm³ g⁻¹ and 2.00 nm for surface area, total pore volume and mean pore diameter respectively. The results suggested

that the prepared AC has the mesoporous structure according to the International Union of Pure and Applied Chemistry classification and also indicated that AC has a high specific area surface than other carbonaceous materials [21,28].

The FTIR study of AC was performed before and after the adsorption process. From the AC spectrum shown in Fig. 2a, the broadband at 3436 cm⁻¹ may be assigned to the O–H stretching vibration in alcohols and phenols. The peak at 2928 cm⁻¹ was ascribed to C–H aliphatic stretching while the peaks at 1689 and 1610 cm⁻¹ were attributed to the vibrations of C=O in carbonyl, lactonic and carboxyl groups and stretching vibration of O–H in carboxylic acid, respectively [16]. The band at 1609 cm⁻¹ and the peak at 718 cm⁻¹ were assigned to C=C and C–H stretching vibrations in the aromatic rings [29]. The spectra of AC-loaded 2,4-D, AC-loaded HA and AC-loaded (2,4-D + HA) (Fig. 2b–d) showed the same trend

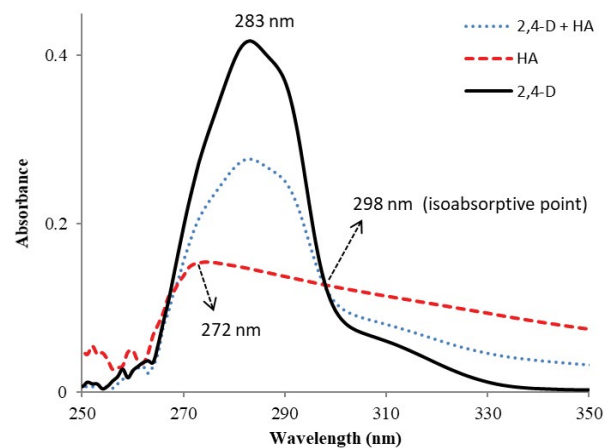


Fig. 1. UV spectra of 2,4-D, HA and (2,4-D + HA) mixture. (Concentration of: 2,4-D in single solution 50 mg L⁻¹, in mixture 25 mg L⁻¹, HA concentration in single solution 20 mg L⁻¹, in mixture 10 mg L⁻¹).

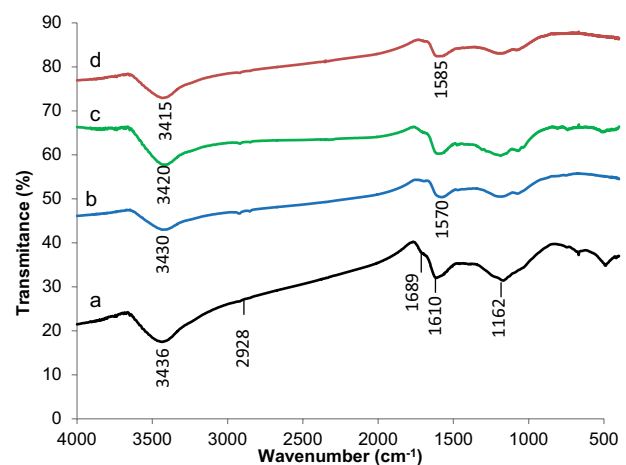


Fig. 2. FTIR spectra: (a) AC, (b) AC-loaded (2,4-D + HA), (c) AC-loaded 2,4-D, and (d) AC-loaded HA.

as the spectrum of AC (Fig. 2(a)). FTIR spectra analysis after adsorption revealed that the peak at $3,436\text{ cm}^{-1}$ corresponding to $-\text{OH}$ groups in the AC spectrum has been shifted to $3,420$, $3,415$ and $3,430\text{ cm}^{-1}$ in AC-loaded 2,4-D, AC-loaded HA and AC-loaded (2,4-D + HA) spectra respectively. These shifts may be attributed to weak interactions such as van der Waals forces and H-bondings between AC surface and 2,4-D and HA molecules, and also suggested that the adsorption process of 2,4-D was controlled by physisorption.

The scanning electron micrographs of AC before and after simultaneous adsorption of 2,4-D and HA at 2000x magnification are shown in Fig. 3. It is seen from Fig. 3a that the AC surface was rough with numerous pores which 2,4-D and HA molecules could be trapped and adsorbed. The surface of AC-loaded (2,4-D + HA) (Fig. 3b) showed a compact and smooth block without pores. These observations suggested that 2,4-D and HA molecules have been successfully adsorbed on the AC surface.

3.2. Effect of pH of solution

The pH of the solution plays an important role in the adsorption process. In this study, the effect of pH of the solution was performed in the pH range 2–10. The results (Fig. 4) indicated that the uptake of 2,4-D slightly decreased from 90% to 75% with an increase in the pH from 2 to 8, and then, the decrease was sharply until the removal efficiency of 12% was reached at pH = 10. The pKa of 2,4-D was found to be 2.80 [13], so, at pH > 2.80, the carboxylic group from 2,4-D molecules get partially dissociated and 2,4-D molecules became in the anionic ($2,4\text{-D}^-$) ions. Moreover, Boehm titration results indicated the presence of acidic functional groups on the AC

surface. The amounts of carboxylic, phenolic and lactonic groups were 2.75, 0.017 and 0.083 mmol g^{-1} respectively. Also, the pH_{PZC} of AC was 3.2 (Fig. 4). Therefore, at pH < 3.2, the carboxylic and phenolic functional groups from AC were protonated and the AC surface gets positively loaded, thus, the adsorption of 2,4-D occurred by electrostatic attractions between the positive load of AC surface and the anionic $2,4\text{-D}^-$ ions. At pH > 3.2, the carboxylic groups from AC were dissociated and the AC surface became negatively loaded which resulted in electrostatic repulsion between the both negatively charged species, so, the adsorption decreased [30].

Besides electrostatic interactions and H-bondings, some other forces are responsible for adsorption of 2,4-D by AC. AC and 2,4-D have hydrophobic properties due to the π bonds in aromatic rings from 2,4-D and AC structures. Thus,

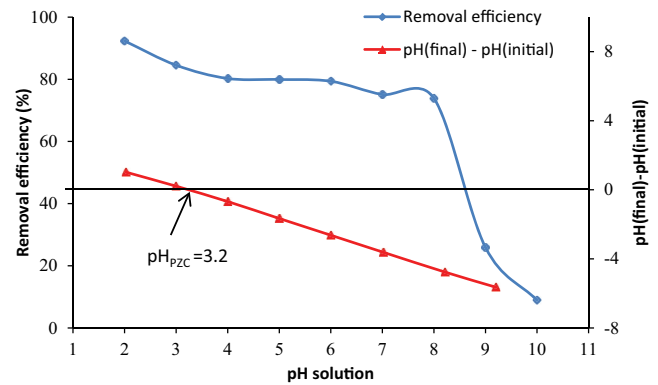


Fig. 4. Effect of pH of the solution and pH_{PZC} determination.

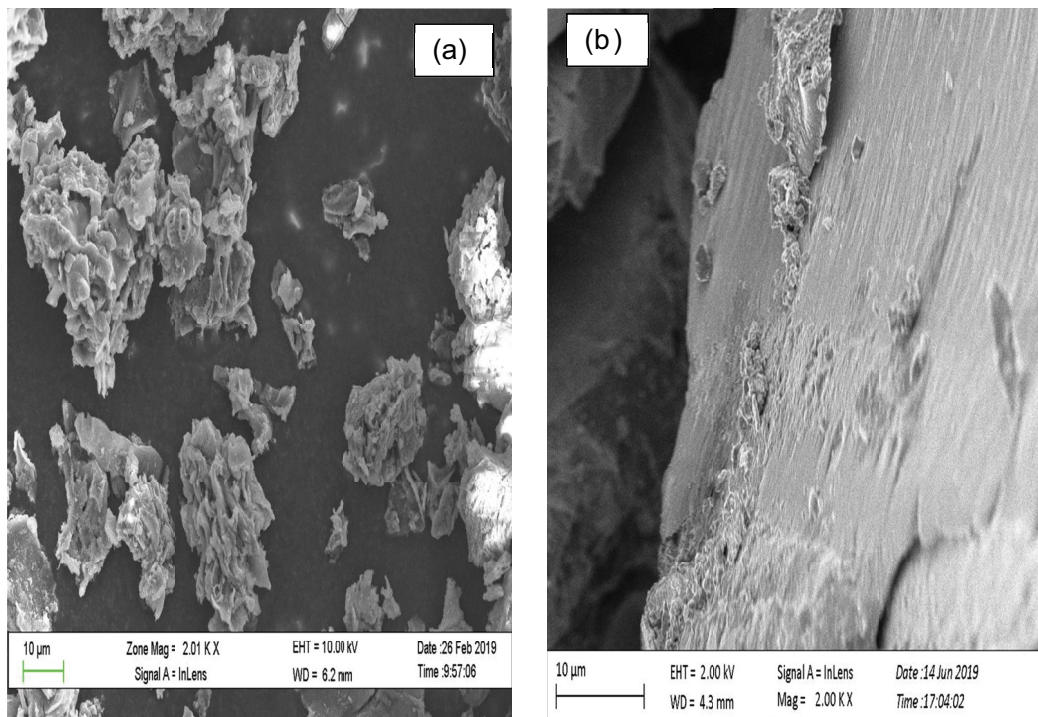


Fig. 3. SEM images: (a) AC before adsorption and (b) AC after adsorption of (2,4-D + HA).

there are hydrophobic-hydrophobic interactions between a part of the hydrophobic property of AC and the one of 2,4-D, hence, adsorption of 2,4-D occurred. From Fig. 4, the maximum adsorption of 2,4-D was reached at pH = 2, but, considering the effect of HA that will be performed on the 2,4-D adsorption, pH 3 was selected as the optimum pH. Indeed, it has been reported in the literature that the HA could be precipitated at a pH value lower than 2 [31].

3.3. Effect of adsorbent dosage

The effect of AC dosage on the adsorption process was studied with an initial concentration of 2,4-D of 50 mg L⁻¹ and using AC dosage range 0.01–0.1 g at pH = 3 and at room temperature. Fig. 5 showed the plot of the adsorbed amount of 2,4-D at different AC doses. It was observed that the adsorption capacity decreased from 176.33 to 44.69 mg g⁻¹ with increasing in AC dosage from 0.01 to 0.1 g due to the decrease in the number of the active sites on the AC surface. With AC dosage increased, more active sites are provided for adsorption, so some active adsorption sites remained unsaturated during the adsorption process and the 2,4-D molecules had not fully covered the active sites of AC surface. Therefore, increasing the AC dosage causing a decrease in adsorption capacity [32].

3.4. Effect of contact time and adsorption kinetic

The effect of contact time on the adsorption process was studied with 50 mg L⁻¹ of 2,4-D solution, at pH = 3 and at room temperature. Other conditions used were 0.01 M and 0.1 M NaCl and CaCl₂ solutions and 50 mg L⁻¹ HA solution. The experiments were performed during a contact time range 0–120 min, and the obtained results were displayed in Fig. 6a. The results showed that the plots of the amount of adsorbed 2,4-D against contact time increased with an increase in the contact time until the equilibrium state was reached. The results also revealed that the adsorption is fast at the initial stage and became slower as it approaches an

equilibrium state. This could be attributed to a larger number of vacant available sites on the AC surface at the initial stage than the later stage. With increasing contact time, most of the active sites of the AC surface became occupied and leading to the repulsive interaction between adsorbed 2,4-D and unadsorbed 2,4-D at the later stage [33]. From Fig. 6b, it is seen that the equilibrium state was achieved at about 60 min, but a contact time of 120 min was taken as contact time to perform all experiments in this study. This contact time is in good agreement with that reported by Tian and Zhou et al. [20,33].

To describe the adsorption mechanism, the pseudo-first-order [34], pseudo-second-order [35] and intraparticle diffusion [36] kinetic models were applied. The linear form of pseudo-first-order and pseudo-second-order models was expressed as Eqs. (4) and (5), respectively.

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

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

The intraparticle diffusion model Eq. (6) is expressed as follows:

$$q_t = k_{id} \cdot t^{1/2} + C \quad (6)$$

where q_e (mg g⁻¹) is the amount adsorbed at equilibrium, q_t (mg g⁻¹) is the amount adsorbed at any time t , k_1 (min⁻¹) is the pseudo-first-order rate constant, k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant, k_{id} (mg g⁻¹ min^{-1/2}) is the intraparticle diffusion rate constant, C (mg g⁻¹) is the intercept related to the boundary layer effect and t (min) is the contact time.

The influence of concentration of salts and HA solutions was also investigated on adsorption kinetic study. The obtained results at room temperature (30°C) were shown in Fig. 6b–d and the kinetic parameters were calculated and summarized in Table 1. From data showed in Table 1, it appeared that the pseudo-second-order kinetic model had a highly reliable correlation coefficient R^2 close to the unit for all assays performed. The experimental data showed good agreement with the calculated adsorption capacities according to the pseudo-second-order kinetic model (Table 1). Moreover, it was also seen from Table 1, a clear difference between the calculated values according to the pseudo-first-order kinetic model and the experimental results. Hence, the adsorption of 2,4-D with the influence of salts and HA is described well by the pseudo-second-order kinetic model.

The diffusion of adsorbate molecules in adsorbent pores could not be described well only by pseudo-first-order and pseudo-second-order kinetic models. So, the intraparticle diffusion model was also used in this work to describe the adsorption mechanism. From intraparticle diffusion results shown in Fig. 6d, it is seen that the plots q_t against $t^{1/2}$ has two linear portions with R^2 values greater than 0.859 indicating two stages during the adsorption process. The first linear portion, from 1 to 20 min described the adsorption on an external surface of pores while the second portion, from 20 to 120 min was assigned to the gradual and final adsorption,

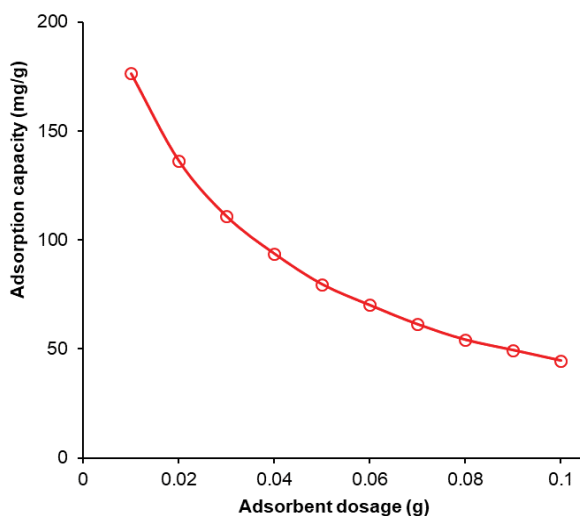


Fig. 5. Effect of adsorbent dosage.

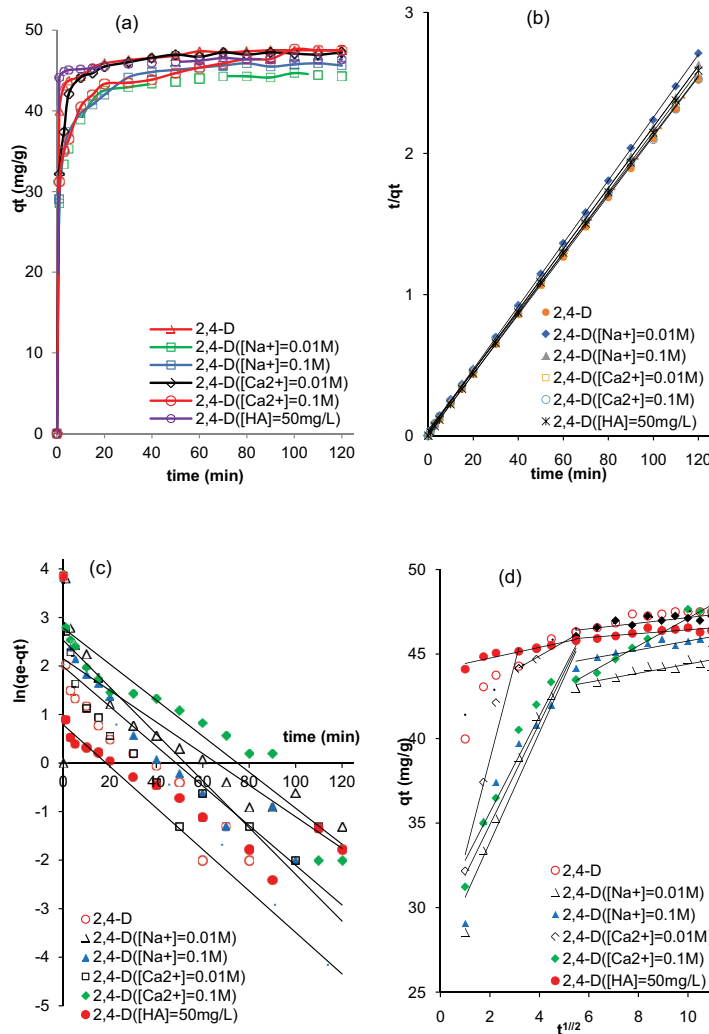


Fig. 6. (a) Effect of contact time, (b) pseudo-first-order kinetic, (c) pseudo-second-order kinetic, and (d) intraparticle diffusion model.

Table 1
Kinetic parameters of adsorption of 2,4-D with the influence of salts and HA

	$q_{e(\text{exp})}$ (mg g^{-1})	Pseudo-first-order model			Pseudo-second-order model			Intraparticle diffusion model		
		k_1 (min^{-1})	$q_{e(\text{cal})}$ (mg g^{-1})	R^2	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	$q_{e(\text{cal})}$ (mg g^{-1})	R^2	k ($\text{mg g}^{-1} \text{min}^{-1/2}$)	C (mg g^{-1})	R^2
[2,4-D] = 50 mg L^{-1}	47.52	0.054	7.62	0.840	0.040	47.62	0.999	1.258	40.14	0.859
2,4-D + [Na ⁺] = 0.01 M	44.29	0.032	8.56	0.720	0.019	45.45	0.999	3.250	27.36	0.921
2,4-D + [Na ⁺] = 0.1 M	45.63	0.048	12.49	0.901	0.018	47.62	0.999	2.999	28.91	0.897
2,4-D + [Ca ²⁺] = 0.01 M	47.24	0.042	7.26	0.772	0.034	47.62	0.999	5.651	27.48	0.924
2,4-D + [Ca ²⁺] = 0.1 M	47.51	0.037	16.12	0.902	0.010	50.00	0.999	2.839	29.95	0.919
2,4-D + [HA] = 50 mg L^{-1}	46.55	0.042	16.20	0.716	0.088	47.62	0.999	0.317	44.12	0.883

which was controlled by the intraparticle diffusion. The values of the C parameter were 40.14, 27.36, and 27.48 mg g^{-1} for 2,4-D and with the influence of 0.01 M NaCl and 0.01 M CaCl_2 solutions respectively (Table 1) indicating a decrease in the thickness and the effect of the boundary layer. It was also

observed that the plots did not pass through the origin, suggesting that the intraparticle diffusion was involved in the adsorption process, but was not the only rate-limiting step. Similar observations were reported by Lelifajri et al. [30] and Hue et al. [37].

3.5. Effect of concentration and adsorption isotherm study

The effect of the initial concentration of 2,4-D on the adsorption process was carried out in the concentration range 10 to 100 mg L⁻¹, at pH 3 and at room temperature. The results showed in Fig. 7a indicated that the adsorption efficiency of 2,4-D decreased from 65.15% to 36.17% with an increase in the initial concentration of 2,4-D from 10 to 100 mg L⁻¹. This may be attributed to the fact that, at a lower concentration of adsorbate, there were many unoccupied adsorption active sites available on the adsorbent surface. However, at a higher concentration of 2,4-D, the competition occurred between 2,4-D molecules to interact with the binding sites, hence, all binding sites get saturated and leading to a decrease in adsorption efficiency [38,39].

The study of the adsorption process requires the adsorption isotherm ascertainment to better understand the adsorption mechanism. To perform the best adjustment of the experimental equilibrium data with the isotherm models, the Langmuir isotherm [40], Freundlich isotherm [41] and Temkin isotherm [42] models were studied.

The Langmuir model assumes the monolayer adsorption on a homogeneous surface, and all active sites are energetically equivalent. A non-linear form of Langmuir Eq. (7) is written as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

where q_e (mg g⁻¹) is the adsorption capacity at the equilibrium, q_m (mg g⁻¹) is the maximum adsorption capacity, C_e (mg L⁻¹) is the equilibrium concentration of 2,4-D and K_L (L mg⁻¹) is the Langmuir isotherm constant.

The dimensionless constant (separator factor) R_L , was utilized to evaluate when the adsorption is favorable ($0 < R_L < 1$) or, unfavorable ($R_L > 1$), linear ($R_L = 1$) and irreversible ($R_L = 0$). R_L expression was defined by Weber and Chakravorti [43] as follows:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (8)$$

where C_0 (mg L⁻¹) is the initial concentration of 2,4-D solution.

The Freundlich isotherm is an empirical model used to describe the non-ideal multilayer adsorption on heterogeneous surfaces. A non-linear form of Freundlich isotherm model is expressed as follows:

$$q_e = K_f C_e^{1/n} \quad (9)$$

where K_f (mg g⁻¹ (L mg⁻¹)^{1/n}) is Freundlich capacity constant and $1/n$ is related to adsorption intensity and heterogeneity factor.

The Temkin isotherm assumes that the heat of the adsorption of adsorbate molecules in the adsorbent layer would decrease linearly with the adsorbent-adsorbate interactions are moderate [44]. The non-linear form of the Temkin model is written as follows:

$$q_e = B \ln(A_T C_e) \quad (10)$$

where $B=RT/b_T$, A_T (L g⁻¹) and b_T (J mol⁻¹) are the Temkin isotherm constants, R (8.314 J mol⁻¹ K⁻¹) is the gas constant and T (K) is the absolute temperature.

The influence of HA concentration was studied in a binary system. The competitive Langmuir isotherm [45] was used as the isotherm model to describe the adsorption mechanism of 2,4-D towards AC in the presence of HA. The competitive Langmuir isotherm model expression is written as follows:

$$q_{ei} = \frac{q_{mi} K_{Li} C_{ei}}{1 + \sum_{j=1}^2 K_{Lj} C_{ej}} \quad \text{for } i = 1, 2 \quad (11)$$

where q_{mi} (mg g⁻¹) is the maximum adsorption capacity, K_{Li} and K_{Lj} (L mg⁻¹) are the competitive Langmuir isotherm

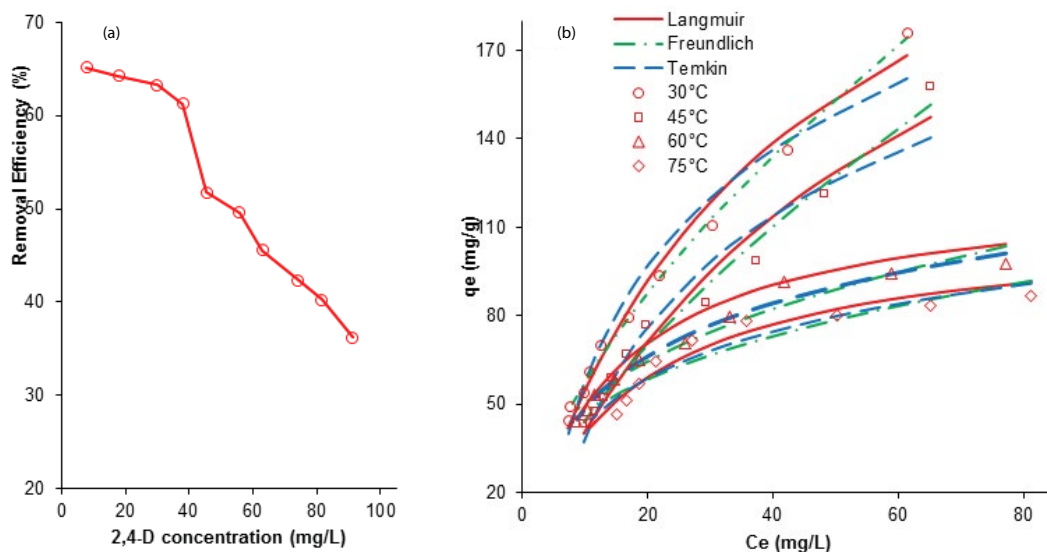


Fig. 7. (a) Effect of 2,4-D concentration and (b) adsorption isotherm of 2,4-D.

constants. The values of $q_{\text{m}}, K_{\text{Li}}$ and K_{Lj} parameters are obtained from binary adsorption data.

To identify if the isotherm model was suitable or not with experimental data, the non-linear Chi-square (χ^2) values were determined. The corresponding statistical expression is written as follows [44]:

$$\chi^2 = \frac{\sum (q_{\text{e,exp}} - q_{\text{e,cal}})^2}{q_{\text{e,cal}}} \quad (12)$$

where $q_{\text{e,exp}}$ (mg g^{-1}) is the experimental adsorption capacity and $q_{\text{e,cal}}$ (mg g^{-1}) is the calculated adsorption capacity according to the model.

3.6. Adsorption isotherm without influence of concentration of salts and HA

Adsorption isotherms obtained at different temperatures ranged between 30°C and 75°C were shown in Fig. 7b and the isotherm parameter values were calculated and summarized in Table 2. It is seen from results a decrease in adsorption capacity with an increase in the temperature which suggested an exothermic behavior of 2,4-D adsorption. The final experimental values of q_e were 174.54, 157.49, 97.59, and 86.82 mg g^{-1} at 30°C, 45°C, 60°C, and 75°C respectively. The results also indicated that the shape of all isotherms plots is of L type according to Giles et al. [46] indicating favorable adsorption at all temperatures studied. The L type isotherm

is typical of systems in which more sites of adsorbent surface are filled and became increasingly difficult for adsorbate molecules to find a vacant available site. It is also seen that the Freundlich isotherm yield the best fit with the experimental data at 30°C and 45°C than either Langmuir and Temkin isotherms, whereas, the Temkin isotherm has a better suitable with experimental data at 60°C and 75°C as confirmed by a high value of R^2 and small value of non-linear chi-square (Table 2). The values of the Temkin isotherm constant b_T were positive and increased from 44.47 to 125.93 J mol^{-1} with increasing in the temperature from 30°C to 75°C suggesting that the adsorption process was exothermic and occurred by physisorption [38]. The better fit of experimental data with the Freundlich model suggested that the removal of 2,4-D may take place by multilayer adsorption with interactions between the 2,4-D and the heterogeneous surface of AC. Also, the values of Freundlich isotherm constant n were >1 and included between 1 and 10 (Table 2), this implied a normal and favorable adsorption process [47]. The values of separator factor R_L from the Langmuir model are ranged between 0 and 1, therefore, the adsorption process was favorable.

Moreover, adsorption capacities obtained according to the Langmuir isotherm model were 281.22, 278.95, 125.00, and 111.11 mg g^{-1} at 30°C, 45°C, 60°C, and 75°C, respectively. The values were compared with monolayer adsorption capacities obtained with other AC reported in the literature. The results from Table 3 highlighted that the prepared AC has a relatively higher monolayer adsorption capacity than

Table 2 Isotherm parameters of 2,4-D adsorption

T (°C)	Langmuir				Freundlich				Temkin				
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	χ^2	K_f ($\text{mg g}^{-1} (\text{L mg}^{-1})^{1/n}$)	n	R^2	χ^2	B	A_T (L g^{-1})	b_T (J mol^{-1})	R^2	χ^2
30	281.22	0.024	0.993	3.005	14.16	1.64	0.998	0.690	56.65	0.277	44.47	0.982	6.218
45	278.95	0.017	0.983	4.374	9.97	1.53	0.991	2.43	54.39	0.203	48.60	0.972	6.196
60	125.00	0.0656	0.992	4.857	22.67	2.86	0.980	1.842	25.79	0.656	107.35	0.991	0.735
75	111.11	0.057	0.977	4.623	22.26	3.10	0.9457	3.88	22.97	0.647	125.93	0.965	2.427

Table 3 Monolayer adsorption capacities of 2,4-D by various activated carbons

Adsorbents	q_m (mg g^{-1})	pH	Contact time	Temperature (°C)	References
AC fiber modified by nitric acid	555.6	6	90 min	30	[39]
Powdered activated carbon	60.1	2.91	4 h	25	[21]
Date stone activated carbon	238.1	3.6	9 h 30 min	30	[48]
Pumpkin seed hull activated carbon	260.79	na	na	30	[49]
Corn cob activated carbon	300.17	3.5	12 h	30	[15]
Langsat empty fruit bunch activated carbon	261.2	na	na	30	[50]
Commercial powdered activated carbon	178.57	na	na	10	[37]
Red-mud carbon composite	111.11	3	60 min	25	[38]
Carbonaceous material C-C ₆ Cl ₆	89.5	3	30 min	na	[28]
Peanut shell activated carbon	281.22	3	120 min	30	This study

na: not available

other carbonaceous materials and may be used as potential adsorbent for removing the pesticides from contaminated water.

3.7. Influence of coexisting of ions

2,4-D cannot exist alone in water but with coexisting of ions such as Na^+ and Ca^{2+} , so, the influence of NaCl and CaCl_2 at different concentrations was investigated at pH 3 and at room temperature on the adsorption process. The results shown in Fig. 8 indicated that the experimental data were in good agreement with the Langmuir isotherm model. The adsorption capacity increased from 86.12 to 89.49 mg g^{-1} , then from 160.32 to 300.27 mg g^{-1} (Table 4) with a decrease in the concentrations of Na^+ and Ca^{2+} from 0.1 M to 0.01 M respectively. It was also seen that the adsorption capacity was lower with the influence of Na^+ ion than with the influence of Ca^{2+} ion. It appeared that, the divalent cation (Ca^{2+}) was a positive effect on 2,4-D adsorption than monovalent cation (Na^+). This was due to the higher polarizability effect

of Ca^{2+} ion than Na^+ ion which has a great effect on the thickness of the double layer and leads to higher adsorption efficiency than with of monovalent cation [28]. Also, for the same cation, the adsorbed amount of 2,4-D increased with a decrease in the ionic strength. This may be explained by increasing ionic strength which increased with the salts concentration and resulting in increasing in dissociation degree of 2,4-D molecules. Thus, the attractive interactions between the positive load of cations and the anionic 2,4- D^- occurred and induced the competition with electrostatic interactions between 2,4- D^- and AC surface, so the adsorbed amount of 2,4-D decreased [51]. Besides, the Ca^{2+} ions could screen the negative charge of 2,4- D^- better than Na^+ ions because Ca^{2+} ions have the possibility of forming intermolecular bridges between the carboxylic group of 2,4- D^- and Ca^{2+} . The formed complexes ($\text{R}-\text{COO}-\text{Ca}^{2+}-\text{OOC}-\text{R}$) better screen the negative load of 2,4- D^- and justified the increase in the adsorbed amount of 2,4-D [52].

3.8. Effects of simultaneous influence of HA and salts

The effect of HA was studied on adsorption of 2,4-D with a concentration of HA solution range 10–50 mg L^{-1} and with 0.01 M and 0.1 M NaCl and CaCl_2 solutions. The results obtained are presented in Fig. 9 and the isotherm parameters calculated according to the competitive Langmuir model are summarized in Table 5. From results showed in Fig. 9, the shape of adsorption isotherm with the influence of HA was H-type isotherm, indicating a high affinity of 2,4-D with AC. In the absence of ionic strength, the 2,4-D molecules are weakly dissociated, so, the intermolecular interactions such as van der Waals forces and H-bondings occurred between 2,4-D molecules and active functional groups from the AC surface. Also, the low adsorbed amount 154.96 mg g^{-1} of 2,4-D observed in the presence of HA compared to 281.22 mg g^{-1} obtained in its absence may be due to competitive adsorption between 2,4-D and HA molecules [21]. Furthermore, with an increase in the ionic strength due to Na^+ and Ca^{2+} ions in the presence of HA, the electrostatic attractions between the cations and 2,4- D^- or HA^- occurred and leading to the decrease in 2,4-D adsorption. The S-type isotherm obtained with the simultaneous influence of HA and salts suggested that 2,4-D have a moderate intermolecular attraction with AC surface and also met strong competition for access to AC active sites from HA [46]. The data from Table 5 showed that the adsorption capacity

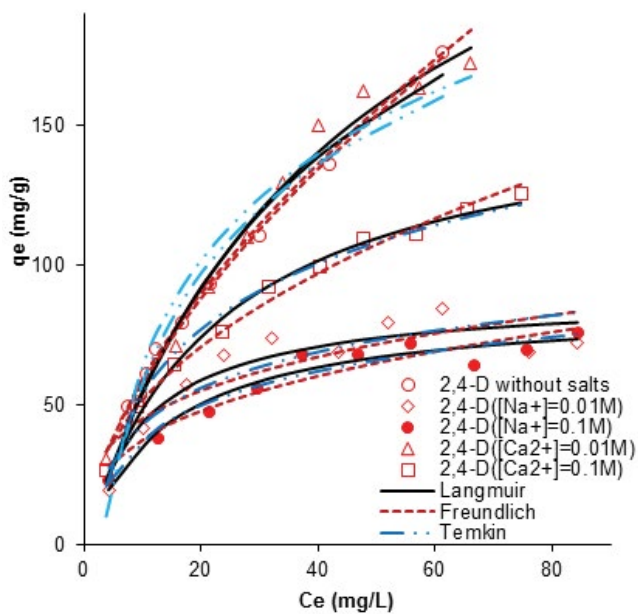


Fig. 8. Adsorption isotherm of 2,4-D with the influence of salts.

Table 4
Isotherm parameters of 2,4-D adsorption with the influence of concentration of salts

	Langmuir				K_f (mg g^{-1} (L mg^{-1}) ^{1/n})	Freundlich			Temkin				
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	χ^2		n	R^2	χ^2	B	A_T (L g^{-1})	b_T (J mol^{-1})	R^2	χ^2
2,4-D	281.22	0.024	0.993	3.00	14.16	1.64	0.998	0.690	56.65	0.277	44.47	0.982	6.22
2,4-D([Na^+] = 0.01 M)	89.49	0.096	0.948	6.13	23.32	3.47	0.865	16.05	18.78	0.995	122.43	0.913	9.27
2,4-D([Na^+] = 0.1 M)	86.12	0.071	0.971	2.92	17.67	2.99	0.950	4.59	17.71	0.841	129.83	0.966	2.88
2,4-D([Ca^{2+}] = 0.01 M)	300.27	0.022	0.993	4.65	14.97	1.67	0.987	4.82	55.12	0.317	41.73	0.969	49.88
2,4-D([Ca^{2+}] = 0.1 M)	160.32	0.035	0.996	1.71	18.24	2.20	0.994	1.98	33.83	0.491	67.97	0.993	2.71

154.96 mg g⁻¹ obtained with the presence of HA decreased to 37.76 and 30.75 mg g⁻¹ with increasing in the ionic strength due to Na⁺ ions. Therefore, when the ionic strength was induced by Ca²⁺ ions, the amount of adsorbed 2,4-D decreased from 292.80 to 117.76 mg g⁻¹ with the concentration of Ca²⁺ ions increased from 0.01 to 0.1 M. The results highlighted that Na⁺ ions increased the competition between 2,4-D⁻ and HA⁻. But, Ca²⁺ ions would form complexes with 2,4-D⁻ or HA⁻ which leads to an increase in the adsorption of 2,4-D [52].

The suggested schematic mechanism of the adsorption process was shown in Fig. 9b and c. It is seen that at pH < p*H*_{pzc} the electrostatic attractions between Na⁺ or Ca²⁺ and 2,4-D⁻ occurred and leading to competition with electrostatic interactions between 2,4-D⁻ and AC surface. Moreover, with pH > p*H*_{pzc} in addition to attractive interactions between Na⁺ or Ca²⁺ and 2,4-D⁻, there is also a repulsion interaction between 2,4-D⁻ and negative load from the AC surface.

3.9. Effect of temperature and thermodynamic study

The effect of temperature on the adsorption process was investigated with a temperature range of 30°C–75°C. It is seen from Fig. 10a and b that, with an increase in temperature from 30°C to 75°C, the uptake of 2,4-D slightly decreased regardless of the influence of salts and HA. The results suggested that the adsorption process occurred through an exothermic process. To confirm the exothermic behavior and identify if the adsorption process was spontaneous, the thermodynamic parameters such as standard free enthalpy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated. According to thermodynamic law, ΔG° is expressed as follows:

$$\Delta G^\circ = -RT \ln K \quad (13)$$

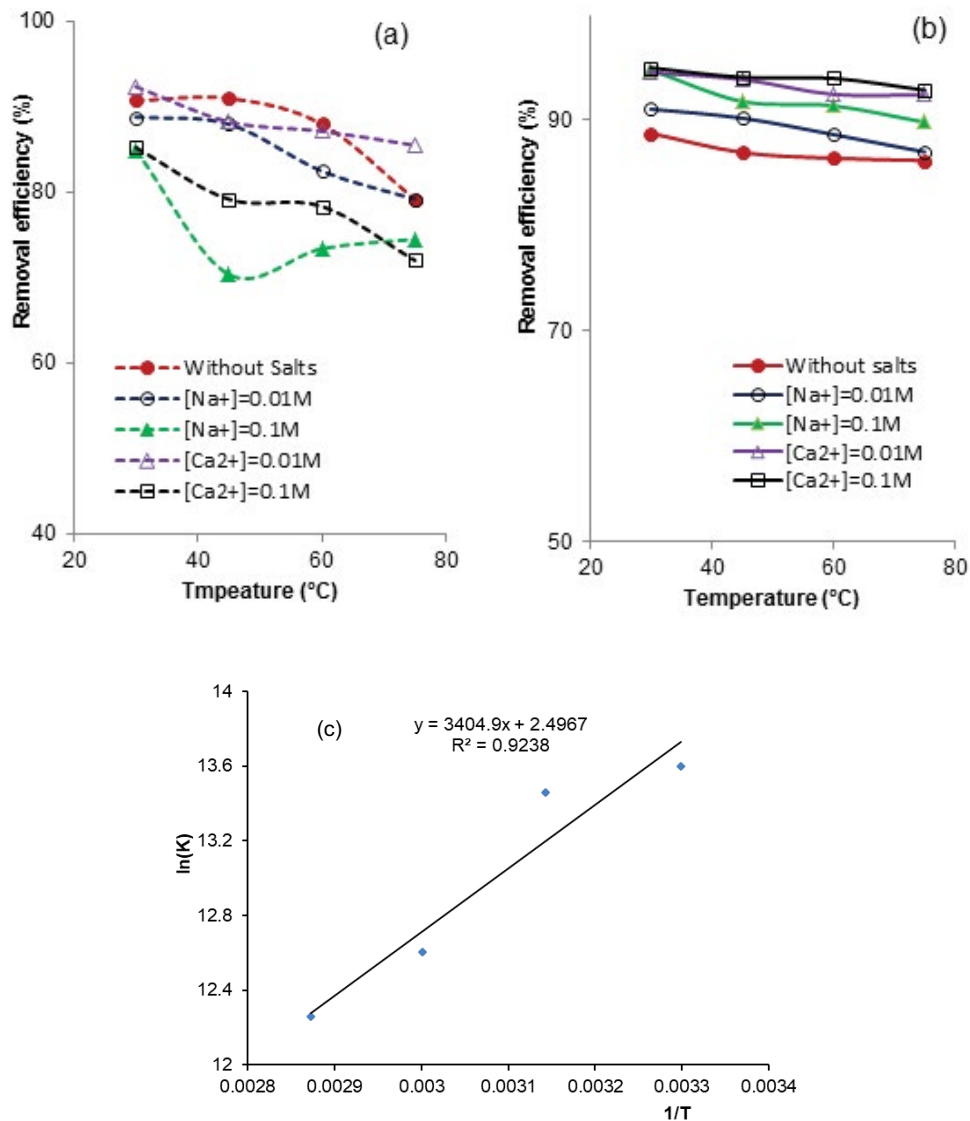


Fig. 10. (a) Effect of temperature with the influence of salts, (b) HA and salts, and (c) thermodynamic study.

where K is the thermodynamic equilibrium constant without unit, R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the gas constant and T (K) is the absolute temperature.

The relationship between ΔG° , ΔH° , and ΔS° is expressed as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (14)$$

The values of ΔH° and ΔS° were calculated from the plot of $\ln K$ against $1/T$.

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

According to Liu [53], Zhou et al. [54] and Anastopoulos et al. [55], the thermodynamic equilibrium constant can be calculated from Langmuir isotherm constant as follows:

$$K = K_L \times M \times 1,000 \times 55.55 \quad (16)$$

where K_L (L mg^{-1}) is the Langmuir isotherm constant, M (g mol^{-1}) is the 2,4-D molecular weight and 55.55 is the concentration (mol L^{-1}) of water.

The thermodynamic parameters were obtained from the adjustment of the van't Hoff equation at temperatures 303, 318, 333 and 348 K and the results were summarized in Fig. 10c and Table 6. The negative value of

ΔH° ($-28.287 \text{ kJ mol}^{-1}$) and the positive value of ΔS° ($20.741 \text{ J K}^{-1} \text{ mol}^{-1}$) highlighted that the adsorption process was exothermic and the solid–liquid interface was more increased in the randomness [56]. Also, the magnitude of ΔH° was lower than 40 kJ mol^{-1} , hence, the adsorption process was physisorption [37]. The negative values of ΔG° at different temperatures indicated that the adsorption process was feasible and spontaneous [57].

4. Desorption and regeneration study

The regeneration process of AC was investigated through five consecutive adsorption/desorption cycles. The adsorption experiments were performed at pH 3 while the desorption assays with AC-loaded 2,4-D were conducted using 0.1 M NaOH solution as eluant. The influence of salts concentration was also performed on adsorption/desorption cycles. It is showed in Fig. 11a and b, that the adsorption efficiency slightly decreased from 99% to 81% regardless of the influence of concentration of salts with increasing in the cycling time from 1 to 3, and then, the decrease was fast and achieved to 11% at the last cycle time. The results suggested an erosion of the AC particles [58]. Moreover, the regeneration efficiency was still higher after the five cycles attempted which confirmed the physisorption mechanism of the 2,4-D adsorption process. The results implied that AC presented a good potential adsorbent for 2,4-D removal from wastewater.

Table 6
Thermodynamic parameters

T ($^\circ\text{C}$)	K_L (L mg^{-1})	K	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° ($\text{J K}^{-1} \text{ mol}^{-1}$)
30	0.0655	8.042×10^5	-34.575	-28.287	20,741
45	0.0570	6.99×10^5	-34.886		
60	0.0243	2.98×10^5	-35.197		
75	0.0172	2.11×10^5	-35.508		

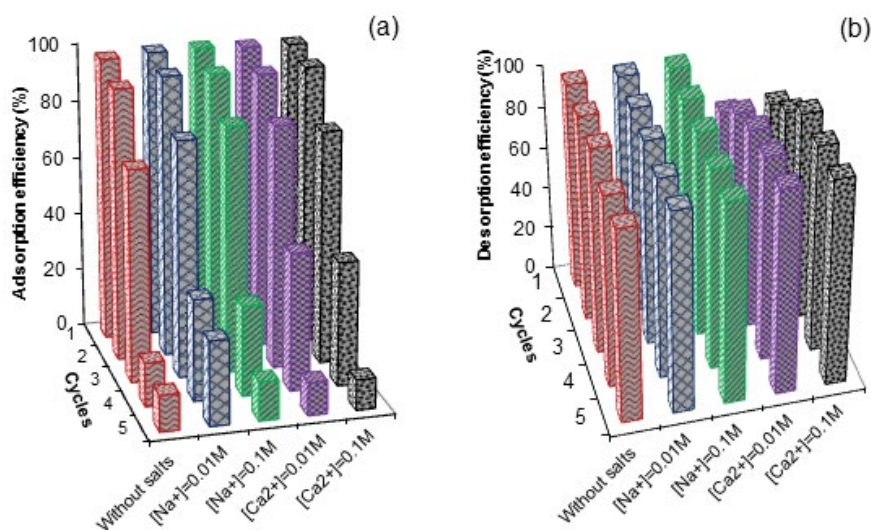


Fig. 11. (a) Adsorption and (b) desorption.

5. Conclusions

The results of this study revealed that AC prepared from peanut shell has suitable adsorption efficiency for the removal of 2,4-D from aqueous solution. The equilibrium isotherms at different temperatures were best fitted with Freundlich and Temkin isotherm models. The adsorption process was spontaneous and exothermic. The influence of NaCl, CaCl₂ and HA investigated, showed that NaCl has a negative effect on 2,4-D adsorption than CaCl₂. Influence of combined effects of HA and salts induced high competition between 2,4-D molecules and HA molecules. The reusability property study of AC highlighted a slight decrease in adsorption efficiency during the first three cycles performed while a negligible decrease in regeneration efficiency was acted during the five cycles tested. The prepared AC could be used as a good adsorbent for 2,4-D removal from contaminated water.

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