

Phenol Adsorption on Modified Adsorbents NH₃-Activated Carbon, NaOH-Activated Carbon: Characterization, Kinetic and Isotherm Modeling

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ABSTRACT: In the present study, an organic wastewater industrial pollutant such as a phenol was removed by the improved modified adsorbents: NH₃-activated carbon, and NaOH-activated. When the activated carbon ACDK was recovered from agricultural waste Date Kernel and prepared via pyrolysis and thermal activation at 850 ° C. The modification of the activated carbon surface ACDK was ready chemically with the impregnation in the 10wt % ammonia solution to obtain a modified adsorbent: NH₃-ACDK, the impregnation of ACDK in 10 wt% Sodium Hydroxide solution for the second modified adsorbent: NaOH-ACDK. The modified functional samples were characterized by SEM, FT-IR and DRX, TGA-DSC. The results established that phenol molecules were favorable for adsorption on the nitrogen group and hydroxide group of activated carbon at pH 4, solution temperature (28°C), and contact time (60-100 minutes). The adsorption kinetics of phenol on the modified adsorbents were better adapted to the pseudo-second-order adsorption model with ($R^2 = 0.985$) for NH₃-ACDK, ($R^2 = 0.980$) for NaOH-ACDK. The adsorption isotherm follows the Langmuir design and is fitted well compared to Freundlich models with ($R^2 = 0.999$) for NaOH-ACDK, Langmuir, and Freundlich isotherms models fit the experimental equilibrium data for NH₃-ACDK) with correlation coefficient ($R^2 \geq 0.989$). The removal percentage of phenol on NH₃-ACDK, and NaOH-ACDK was 97,6 % and 70,3%, respectively.

KEYWORDS: Modified adsorbents; Phenol adsorption; Characterization; Kinetic; Isotherm.

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INTRODUCTION

The phenolic components are among the persistent organic pollutants (POPs) in wastewater. Phenol is widely found in emissions from pharmaceutical, pesticide, polymer, coke processing, petrochemical industries, and consumer products [1-3]. The toxicity of phenol can result in many serious health conditions, including problems with breathing, coma and damage of human vital organs [4]. Phenol and its derivatives are classified as mutagenic, carcinogenic and teratogenic elements because of their negative effects, on ecosystems and their toxic impacts on the aquatic environment [5]. Due to the increasing environmental awareness, many countries have set strict discharge limits for these substances in water [6]. In fact, several treatment technologies, recent researchers including physical, chemical and biological methods or combinations thereof have been investigated for removal of phenols and their recovery [7]. Various studies on phenol adsorption were published in the literature [8-11] that the adsorption technology and various aspects of the adsorption mechanism have a great potential in the removal of phenolic compounds pollutants from aqueous solutions due to its moderate energy consumption, its low cost, high efficiency and simple operation [1,3,5,8]. Activated carbon adsorption is extensively used because the method to eliminate phenols from aqueous solutions and its efficiency are well-known [12,13]. However, commercial activated carbon is very expensive, numerous researchers are trying to discover substitute adsorbents from raw materials (biomass) and valorization to low-cost adsorbent that can be prepared by physical or chemical activation [14- 18]. Some parameters for choosing the new adsorbent are surface area, porosity, regeneration, and expenses because the adsorption performance of activated carbon is mainly determined by its rich porosity, high surface area, and functional groups [19-20]. So, in order to prepare high-quality activated carbon, the micro- and mesopore structure must be tailored with a high specific surface area, and active sites must be generated through substitutional doping of heteroatoms such as nitrogen, sulphur, boron, and phosphorus... generation of active sites by the substitutional doping of heteroatoms such as nitrogen, sulfur, boron and phosphorus ...etc [19,21,22]. Nitrogen-containing groups on the AC surface, generally enhance the basicity that improves the removal efficiency

of phenolic compounds [21-24]. The Preparation of a highly microporous activated carbon using biomass as the starting material by pyrolysis and chemical activation with mineral elements: Oxygen or Hydroxide and/or nitrogen functionalization, as well as the removal of phenol on modified and functional activated carbons have been intensively investigated; So this paper reports that date kernel activated carbon was treated with ammonia solution and with sodium Hydroxide solution to modify its surface functional groups to obtain two adsorbents: (NH₃-ACDK) and (NaOH-ACDK). The adsorption performance of the two prepared functional activated carbon adsorbents: (NH₃-ACDK) and (NaOH-ACDK) on phenol was then evaluated.

EXPERIMENTAL SECTION

Chemical & Apparatus

- *Chemical reagents* for functional surface modification of activated carbon: (NH₃ 10Wt% solution, NaOH 10Wt% solution) of analytical grade prepared from stock solutions provided by Sigma-Aldrich society- Merck KGaA, Ammonia aqueous/ Ammonium hydroxide solution: reagent purity of 28.0-30.0% NH₃ basis, Formula: H₅NO. Sodium hydroxide (reagent purity \geq 97.0% Formula :NaOH.

- *Model adsorbate (organic pollutant)* used in this study: Phenol crystallized PA-ACS, with high purity was provided by PANREAC QUIMICA SA- C₆H₆O, a storage solution of phenol was prepared by dissolving 0,6 g phenol crystallized in 1,000 mL of distilled water. The wanted solutions with different concentration of phenol were prepared by dilution of storage solution of phenol.

Characterizations apparatus

(*SEM*): Scanning Electron Microscope (Neoscope JCM-5000) for investigating the surface morphology.

(*FT-IR*): Fourier Transform-Infrared Spectroscopy (spectrometer JASCO FT/IR) for determining the functional groups, in the scanning range of 4,000-500 cm⁻¹ and using (Attenuated Total Reflectance) technique.

X-ray (XRD): diffraction measurements were performed with a PAN analytical X'Pert Pro type diffractometer from Mohamed Boudiaf M'sila University, Algeria, using the K α line of copper for a wave length λ

= 1.54060 Å. The diffractograms were acquired in θ - 2 θ geometry for an angular range of 20 to 80 °.

TGA: The used apparatus was a thermal balance SDT Q600 V20.9 / TGA V4.5A from TA Instruments. The average mass of the analyzed samples was about 4.7110 mg and 12.1450 mg for activated carbon, mineral functional adsorbents.

Modified Adsorbents Preparation

Precursor of AC: Date Kernel were obtained from the waste pastry dates factories of Algerian desert. A raw precursor was cleaned with distilled water and mixed with HCl solution prepared at 50%, then washed with distilled water pending the pH of the filtrating solution became neutral, it was dried at 100°C for 1 day to eliminate water.

Activated Carbon ACDK: Granular biochar date Kernel were prepared by pyrolysis and thermal activation under N₂ at 850 °C [16,17,25]. The particle size of granular date kernel activated carbon was 5-15 mesh.

NH₃-ACDK: A quantity of 8 g of ACDK was impregnated in 300 mL of 10wt% ammonia solution with stirring for 2 days, at 25°C. After the granular solid was filtered and was then dried in an oven at 110°C for about 12 h, it was kept in a desiccator to protect it from moisture.

NaOH-ACDK: An amount of 8 g of ACDK was immersed in 300 mL of 10wt% sodium Hydroxide solution with stirring for 2 days, at 25°C, then the solid was filtrated and dried in an oven at 110°C for about 12 h, it was kept in a desiccator to protect them from moisture.

Adsorption Experiments

Adsorption was performed by Batch adsorption studies: in a set of 250 mL-Erlenmeyer flasks where 100mL of phenol solutions at pH 4 (used the pH Meter Lutron PH-208) with various initial concentrations (5–50 mg/L) were placed at room temperature 28 °C. Equal mass of functional adsorbents of about 0,5g was added to each flask at 200 rpm during selected laps of time to reach equilibrium with each modified adsorbent: NH₃-ACDK, and NaOH-ACDK, these conditions were also used to determine the isotherm models as well as the orders of the adsorption kinetics. Before and after adsorption all concentrations of phenol solution were analyzed using UV-Vis spectrometry (1800-SHIMADZU) at $\lambda_{max} = 270$ nm.

The solution concentration allowed us to determine the following parameters: Q_t (mg/g), Q_e (mg/g), and R (%) [16,17];

$$Q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

$$R\% = 100 \frac{(C_0 - C_e)}{C_0} \quad (3)$$

Where Q_t and Q_e are the adsorption capacities of the adsorbent at the selected time t and at the equilibrium, respectively. R (%) is the removal percentage of phenol. C₀ and C_t (mg/L) are the initial concentration and the concentration at the selected time t, respectively, of the adsorbate in the solution. V (L) is the volume of the phenol solution and m (g) is the mass of each used adsorbent.

Effect of mass of modified adsorbents

The effect of the mass to remove the phenol from the aqueous solution by the modified adsorbents NH₃-ACDK, NaOH-ACDK was studied via various masses (0,1- 0,3- 0,5-1-1,5 g), at the pH of the solution without adjustment, at temperature solution 28°C, initial phenol concentration of 5 mg/L and stirring speed of 200 rpm.

Effect of pH phenol solution

Effect of pH on phenol removal at pH 2,4,8 and 10, mass of 0,5 g of modified adsorbents, pH was adjusted using 0.1M HCl or 0.1M NaOH, initial phenol concentration of 5mg/L, temperature solution 28 °C, stirring time 60min with NH₃-ACDK and stirring speed of 200 rpm were studied and stirring time 100 min with NaOH-ACDK.

RESULTS AND DISCUSSION

Surface characterizations

Fig. 1 shows the SEM images of ACDK and modified adsorbents: NH₃-ACDK, NaOH-ACDK; a regular porous structure is created because of the decomposition of major compounds of date kernel (cellulose- hemicelluloses and lignin) at high temperature [16,17]; after pyrolysis and thermal activation for the figure of ACDK. Except for small white particles, slight morphology changes could be observed in the pore, the development of porosity is attributed to the impregnation of activated carbon ACDK

with ammonia NH_3 -ACDK. The SEM image of NaOH-ACDK) shows that the microporous structure of the sample is in the form of irregular cavities and that the sample

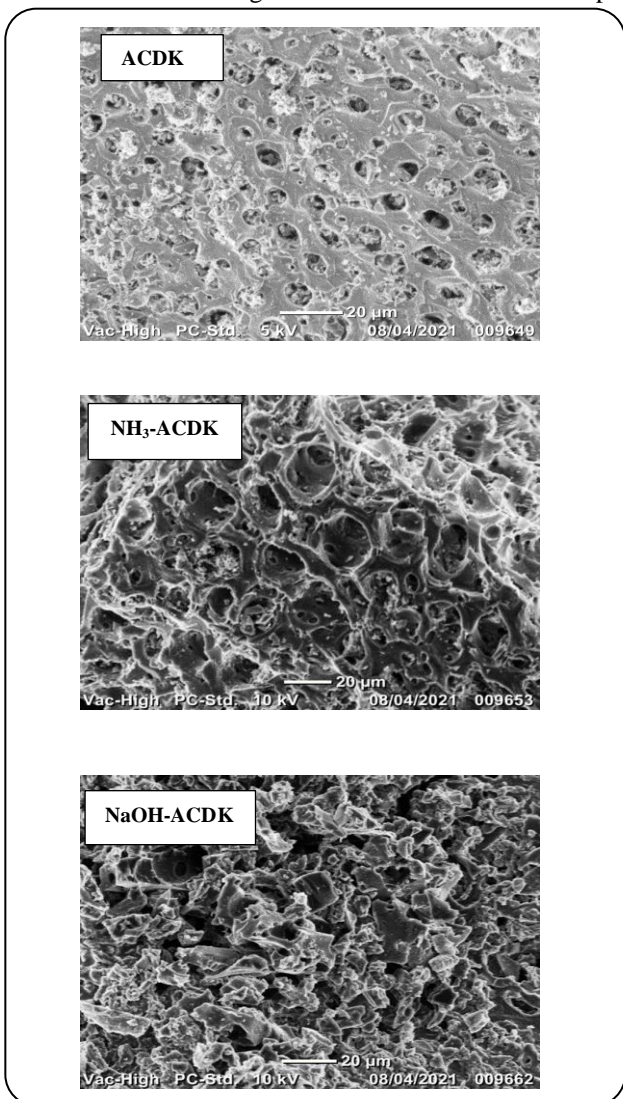


Fig 1: SEM images of ACDK and modified adsorbents: NH_3 -ACDK, NaOH-ACDK.

Fig. 2 shows FT-IR spectra of the ACDK and the NH_3 -ACDK; NaOH-ACDK. The bands located at 4000 and 3500 are corresponding to O-H stretching vibration in hydroxyl groups and C-O stretching molds in ethers [16,17,26,27]. The peaks at 2500 and 2340 cm^{-1} are assigned to C-H asymmetric stretching vibration in methyl and $\text{C} \equiv \text{C}$ group, respectively [24,28]. The appearance a bending vibration peak corresponding of C-N (at 1490 cm^{-1}) and vibration peak at 1570 cm^{-1} is associated with C=C [19] in spectra of NaOH-ACDK. The peak at 1543 cm^{-1} is

surfaces are not homogenous; expect deposition of sodium salt on the surface of ACDK due to impregnation by NaOH.

related to N-containing [29]: (the absorption intensities of the N-H and C-N peaks in NH_3 -ACDK are higher than that in ACDK and NaOH-ACDK, the bands at 1490 and 1050 cm^{-1} are for nitrogen groups and C-OH stretching molds in phenolic groups [26]. Peaks at 720 cm^{-1} is attributed to C-H deformation in cellulose [27,30].

The crystallinity of the samples for activated, modified activated carbons (NH_3 -ACDK) and (NaOH-ACDK) as characterized by XRD is fully reflected in Fig. 3, the range of $20^\circ \sim 25^\circ$, a typical (0 0 2) diffraction peak of carbon, the broad peak (C (002) and C(101) in the XRD spectrum for all materials indicates the presence of amorphous structure of carbon [31, 32, 33]. The activation process did not change the main characteristics of the X-ray spectra. The broad peak at 24° and 23.5° were attributed to the presence of the amorphous carbon structures, but the weak and the broad peak at 43° and 44.5° were attributed to the presence of the graphite structure [27,34, 35, 36]. A new peak shows that an anonymous (unidentified) line appears in XRD spectrums at $2\theta = 72^\circ$; for the samples of activated carbons with NaOH and NH_3 , which is sharp.

The thermograms of the thermal decomposition are shown in Fig. 4. So, the thermal curve corresponding to activated date Kernel ACDK is illustrated in (Fig. 4-A). From this TGA profile, we can observe two stages of the mass loss process. First, the mass loss (7,08 percent) resulting in moisture elimination comes to about 53° . The second one corresponds in the range of $500\text{-}600^\circ\text{C}$, an amount of mass loss (25,13 percent), (the second corresponds to a mass loss of 25.13 percent at temperatures ranging from 500 to 600°C).

The TGA thermal curve that corresponds to NH_3 -ACDK in (Fig 4-B) contains two stages of the mass loss process. The first stage extends from the start of the analysis to 51°C with a weight loss of about 5,65 (percent). The second stage corresponds to the NH_3 -ACDK decomposition, which is observed at 755.83°C with a mass loss of (15.96 percent). The TGA records of the NaOH-ACDK are shown in (Fig4-C), comprised of three stages of the mass loss process. The first weight loss is approximately (5.39%), caused by the release of adsorbed water at 94.5°C . The next two stages correspond to the mineral functional activated carbon NaOH-ACDK

decomposition, which is observed at 590 °C and 800 °C with respective mass losses of (11.05 per cent) and (8.64 per cent). All significant mass loss was observed which can be

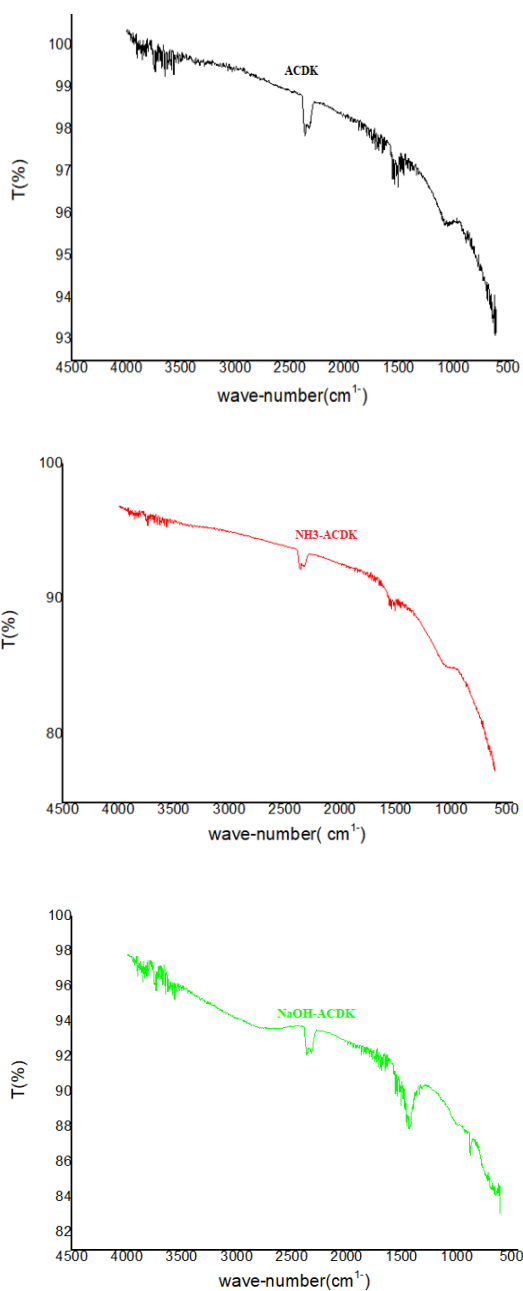


Fig. 2: FT-IR spectrum for ACDK, NH₃-ACDK, and NaOH-ACDK.

and lignin is more thermostable than both cellulose and hemicellulose, its range of decomposition is very wide [25].

Effect of the mass

attributed to the remaining lignin decomposition, however, cellulose destroys thermally among 300 and 400°C. Hemicellulose decomposition is in the range of 220-320°C,

The effect of the NH₃-ACDK and NaOH-ACDK modified adsorbents mass on the adsorption of phenol was examined by varying mass from 0.1 to 1,5 g for optimum contact time (60-100min). The results obtained from

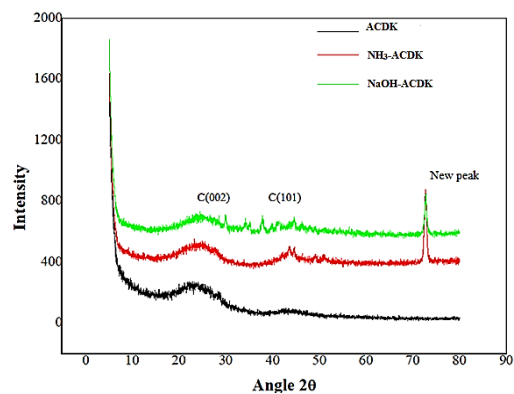


Fig. 3: XRD pattern of ACDK, NH₃-ACDK and NaOH-ACDK.

Fig. 5 show that the phenol adsorption capacity increased with an increase in adsorbent amount and reaches saturation at about 0.5 g, this is due to reduction of greater number of active adsorption sites, so 0.5g was chosen as the optimum modified adsorbents mass for advance experiments.

Impact of solution pH

The pH of the solution represents an important parameter in the adsorption process. Accordingly, different pH values (2,4,8,10) were evaluated and the graphs of phenol adsorption capacity (Q_e) by modified adsorbents were plotted versus the solution pH Fig. 6 it can be seen that the Q_e values were reduced at low and high pH values, since at low and high pHs, protons and phenol anions are the predominant species, respectively [48]. Therefore, the optimum pH value was determined as 4 at room temperature 28°C.

Adsorption kinetics and isotherms

In order to appreciate the dynamics of phenol adsorption on NH₃-ACDK, NaOH-ACDK. The experimental Q_t data at various contact times were fitted with some kinetic models, to better understand the dynamics of

phenol adsorption on NH₃-ACDK and NaOH-ACDK, the experimental Q_t data at different contact times were fitted with various kinetic models, including pseudo-first order, pseudo-second order, and kinetic models. Including

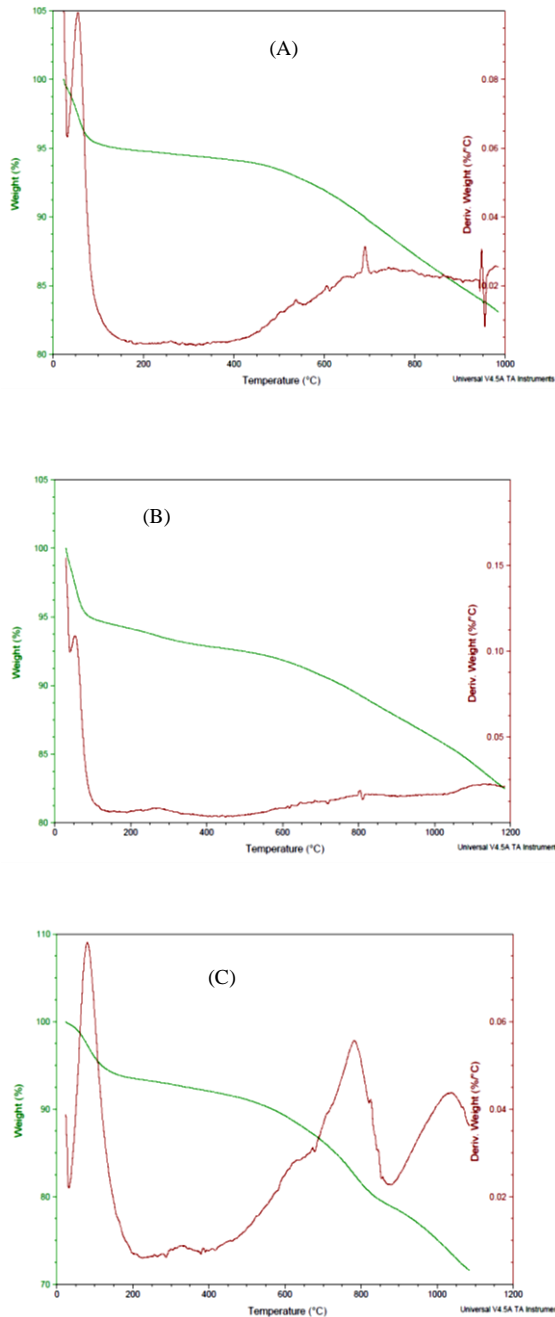


Fig. 4: TGA-DSC analysis of ACDK (A), NH₃-ACDK (B) and NaOH-ACDK (C).

- The PFO is expressed by the following Equation (4) [16, 37]

Pseudo-first order, Pseudo-second order, and kinetic models. Moreover, two common isotherm models, namely Freundlich and Langmuir were applied for the analysis of the equilibrium experimental data.

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (4)$$

Where K_1 is the first-order rate constant, whereas, Q_e and Q_t (mg/g) are the amount of phenol adsorbed at equilibria and at any time, respectively. According to the plot of $\ln(Q_e - Q_t)$ versus t , (Fig. 7(a), (b)). The K_1 and Q_e were calculated from the slope and intercept. The results of the pseudo-first-order kinetic model are listed in (Table 1). The R^2 values were 0.943, 0.974 from NaOH-ACDK and NH₃-ACDK respectively. Considering the values of R^2 , the pseudo-first-order kinetic model was therefore less likely to explain the adsorption behavior of modified adsorbents.

- The PSO model is described as [38]:

$$\frac{t}{Q_t} = \frac{1}{K_2 \times Q_e^2} + \frac{t}{Q_e} \quad (5)$$

Where K_2 is the second-order rate constant, and Q_e and Q_t (mg/g) are the amounts of phenol adsorbed at equilibria and at any time, respectively. The values of K_2 and Q_e were calculated from the slope and intercept of the linear plot of t/Q_t versus t , (Fig. 8(a), (b)). The parameters of the pseudo-second-order kinetic model for the modified adsorbents are listed in (Table 1). The R^2 values derived from the second-order kinetic model were greater than 0.99 for NaOH-ACDK and NH₃-ACDK. Consequently, the pseudo-second-order model was the suitable equation to designate the adsorption kinetics of phenol on the NaOH-ACDK and NH₃-ACDK. The kinetics of phenol adsorption on the NH₃-ACDK and NaOH-ACDK are well followed by the pseudo-second-order kinetic models proposed for phenol adsorption probably occurred through the distribution of electrons amid, the phenolic ring and basal plane of the activated carbon surface [22]. When nitrogen atoms were inserted into the surface of NH₃-ACDK; Oxygen or Hydroxide atoms were implanted into the surface of NaOH-ACDK [39].

The Langmuir and Freundlich isotherm models were used to the equilibrium data and to describe the relationship between the phenol loading on the modified adsorbents NaOH-ACDK, NH₃-ACDK and the liquid

phase concentration of phenol at 28 °C. The Langmuir equation is written by the linear equation [40]:

$$Q_e = Q_m \times \frac{K_L \times C_e}{1 + K_L \times C_e} \quad (6)$$

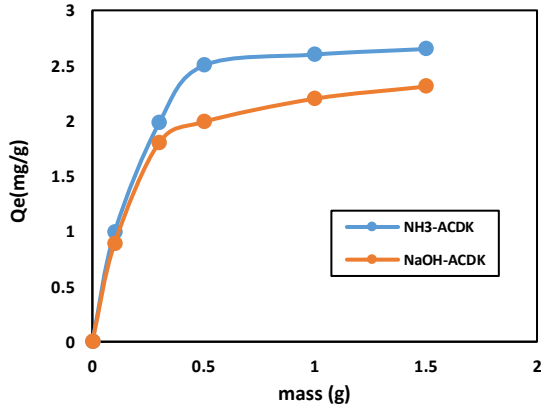


Fig. 5: Effect of the mass on phenol adsorption by modified adsorbents.

Q_m (mg/g) is the theoretical maximum monolayer adsorption capacity and K_L (l/mg) is the Langmuir constant associated with the energy of adsorption. The dimensionless separation parameter R_L contributes a notion of the favorability of the adsorption process.

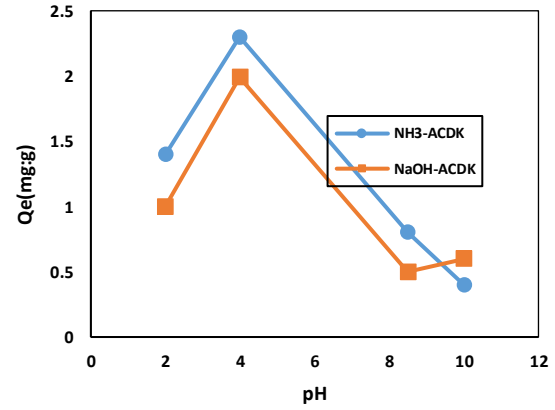


Fig. 6: Effect of pH on phenol adsorption by modified adsorbents.

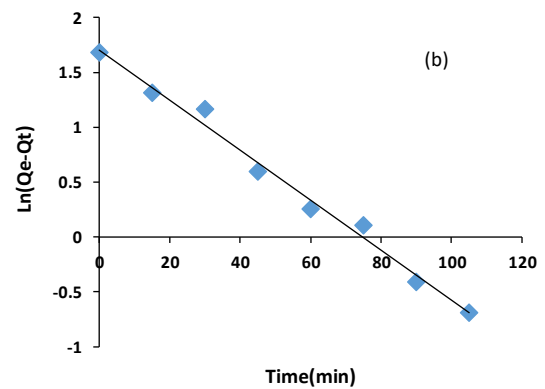
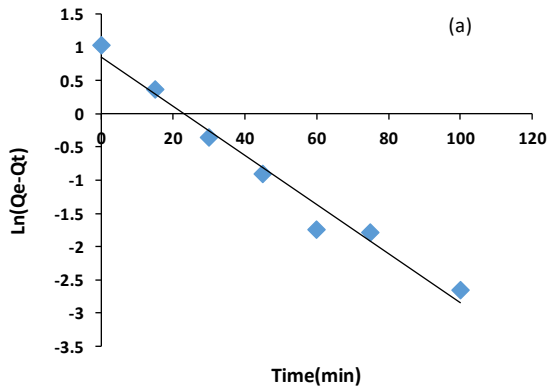


Fig. 7: Pseudo-first-order kinetic plot for the adsorption of phenol removal from aqueous solution using mineral adsorbents (a) NH₃-ACDK, (b) NaOH-ACDK (T = 28°C, pH = 4, dosage = 0.5 g/100 mL and C₀ = 30 mg/L).

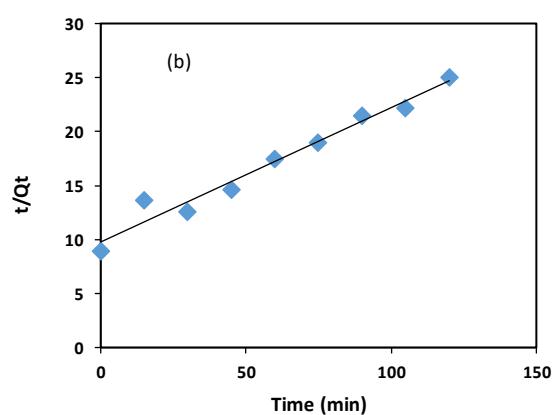
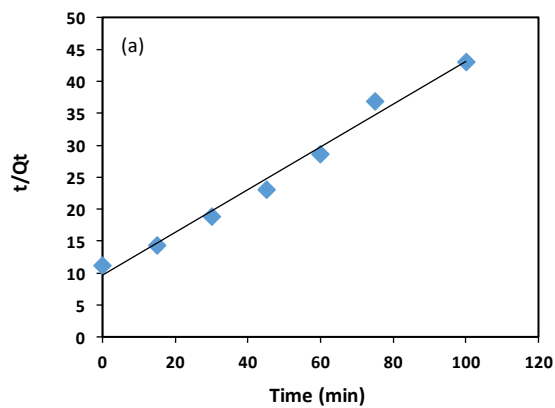


Fig. 8: Pseudo-second-order kinetic plot for the adsorption of phenol removal from aqueous solution using modified adsorbents (a) $\text{NH}_3\text{-ACDK}$, (b) NaOH-ACDK ($T = 28^\circ\text{C}$, $\text{pH} = 4$, dosage = 0.5 g/100 mL and $C_0 = 30$ mg/L).

According to R_L value, the shape of Langmuir isotherm is estimated to be favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), irreversible ($R_L = 0$) or linear adsorption ($R_L = 1$) [41].

The lesser R_L value designates highly favorable adsorption. R_L values are determined using the following equation [16,17]:

Table 1: The parameters of the pseudo-second-order kinetic model for modified adsorbents ($T = 28^\circ\text{C}$, $\text{pH} = 4$, dosage = 0.5 g/100 mL and $C_0 = 30$ mg/L).

Modified adsorbents	Pseudo-first order			Pseudo-second-order kinetic		
	K_1	Q_e	R^2	K_2	Q_e	R^2
NaOH-ACDK	0,022	5,479	0,943	0,0015	8,064	0,980
$\text{NH}_3\text{-ACDK}$	0,036	11,686	0,974	0,011	14,970	0,985

Table 2: Langmuir and Freundlich parameters for the adsorption of phenol onto modified adsorbents ($T = 28^\circ\text{C}$, $\text{pH} = 4$, dosage = 0.5 g/100 mL, with various initial concentrations of 5–50 mg/L).

Modified adsorbents	Langmuir isotherm				Freundlich isotherm		
	Q_m (mg/g)	K_L (l/mg)	R_L	R^2	K_F (mg/g)	1/n	R^2
NaOH-ACDK	5.988	2.4752	0,0575	0.957	1.6703	0.315	0.999
$\text{NH}_3\text{-ACDK}$	13.698	16.129	0,0116	0.989	10.859	0.3842	0.998

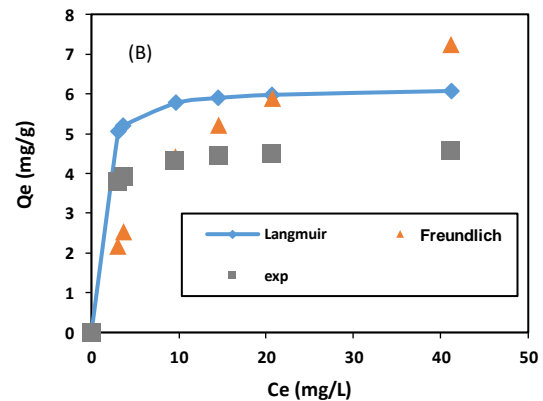
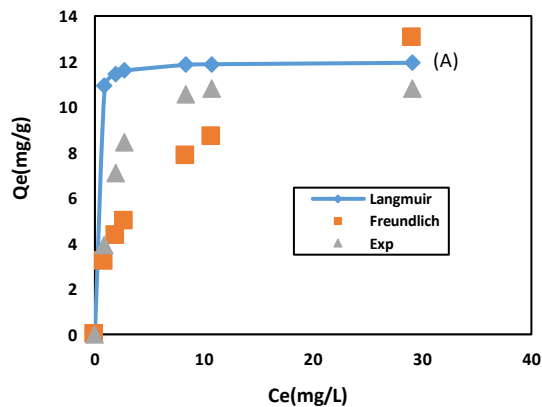


Fig. 9: Modeling of adsorption isotherms of phenol onto $\text{NH}_3\text{-ACDK}$ (A), NaOH-ACDK (B); ($T = 28^\circ\text{C}$, $\text{pH} = 4$, dosage = 0.5 g/100 mL, with various initial concentrations 5–50 mg/L).

$$R_L = \frac{1}{1 + K_L \times C_0} \quad (7)$$

The Freundlich model is an empirical equation assuming a heterogeneous adsorbent surface. It is expressed as follows [42]:

$$Q_e = K_F \times C_e^{1/n} \quad (8)$$

Where K_F and n are Freundlich constants representing the unit capacity factor related to the adsorbent capacity

and an empirical parameter of the heterogeneity of site energies, respectively [19,43].

The isotherms for phenol adsorption on the modified samples ($\text{NH}_3\text{-ACDK}$, NaOH-ACDK) were obtained experimentally for different initial concentrations of phenol from (5–50 mg/L). The similar forms of the isotherms Q_e versus C_e , according to the non-linear form of the Langmuir and Freundlich models, belong to the L type according to the Giles classification [43] are shown in Fig. 9 (A), (B). The obtained parameters for the adsorption

of phenol onto modified adsorbents are calculated by non-linear regression analysis according to isotherms curves, the results of the Langmuir and Freundlich parameters are presented in (Table 2). Results indicate a high affinity and mean that at low concentrations of phenol. The maximal phenol adsorption capacity determined in the table of the isotherms (Langmuir, Freundlich) is 13,698 mg/g and

Table 3: Comparison of removal percentage of phenol by some modified adsorbents with mineral elements described in the literature.

Precursor Biochar	modifying agents	pH	Temperature (C°)	Removal percentage (R%)	Reference
Date kernel	NH ₃	4	28	97.6	This work
Date kernel	NaOH	4	28	70.3	This work
Sugarcan bagasse	H ₂ O	4	25	69.7	[46]
Rice husk	KOH, DTA-4Na-	5	30	81	[19]
coconut shell	Cu(copper ion)	8	30	71.43	[47]
Sea-buckthorn stones	Co(Cobalt ion)	5-7	25-34	91.7	[48]
Corn husk	FeCl ₃	6-8	25	96.5	[49]

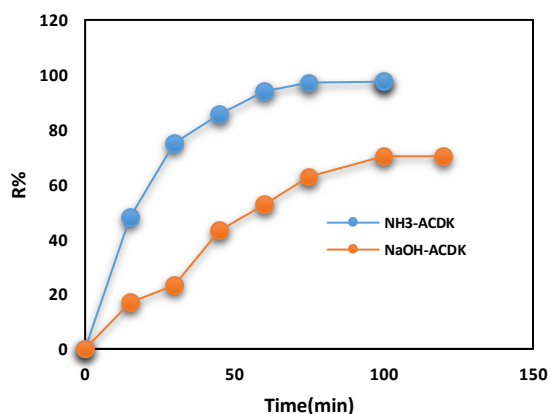


Fig. 10: Removal percentage (R%) of phenol onto modified adsorbents (NH₃-ACDK, NaOH-ACDK) (T = 28°C, pH = 4, dosage = 0.5 g/100 mL and C₀ = 30 mg/L).

that becomes multilayer adsorption and more effective. Moreover, the 1/n value of 0.3842 indicates a strong interaction between NH₃-ACDK and phenol, as well as good adsorption. The maximal phenol adsorption capacity is determined at the ring of 5,988 mg.g⁻¹. The value of the (R²) is higher for the Langmuir model than for the Freundlich model. This means that the Langmuir isotherm equation well signifies the process of adsorption of phenol on mineral adsorbent NaOH-ACDK, Phenol is attached to the site, no more adsorption takes place, showing that it is

10,859 mg/g respectively in the case of mineral sample NH₃-ACDK. However, the Freundlich model has a higher R² value (R²=0.998) for the mineral adsorbent NH₃-ACDK. Therefore, the adsorption belongs to a multilayer process [16], which means that the modification treatments with ammonia probably create the adsorption of phenol

a monolayer type of adsorption. This is probably due to the assumption of a homogeneous adsorbent surface [44].

The removal percentage of phenol on NH₃-ACDK is clearly good compared to other NaOH-ACDK as shown in Fig. 8 It shows the variation of R% as a function of the initial concentration of 30 mg.L⁻¹ of phenol at pH 4 for our samples. The percentage of phenol removal reaches a maximum for the NH₃-ACDK adsorbent. In fact, the removal percentage of phenol is 97.6%-70.3% were obtained respectively, with the modified adsorbents: NH₃-ACDK, NaOH-ACDK at equilibrium time of 60 min and 100min respectively.

CONCLUSIONS

In this investigation, ACDK was used as the base sample for the synthesis of modified adsorbents by a wetness impregnation process with mineral solutions: an ammonia solution and sodium hydroxide solution to modify activated carbon surface functional groups and prepare two modified adsorbents: NH₃-ACDK, NaOH-ACDK. The obtained modified adsorbents were characterized by SEM, FT-IR and DRX and TGA-DSC. These new materials were developed to recover their adsorption properties with the optimum conditions for phenol adsorption solution volume = 100 mL,

adsorbents mass = 0,5g, at pH 4, the solution's temperature was 28°C.

The equilibrium data for NaOH-ACDK were best represented by the Langmuir isotherm, the adsorption capacity for phenol on NaOH-ACDK was 5.988 mg/g with (R%=70.3%) at a contact time of 100 min. For the adsorption capacity of phenol by NH₃-ACDK, the results were determined by the Langmuir and Freundlich isotherm

models, which fit the experimental equilibrium data, Q_m =13,698 mg/g and 10,859 mg/g respectively with (R%=97.6%) at a contact time of 60 min, this was due to the basic surface functional groups generated by nitrogen integration in the particles of carbon ACDK [24]. The same for NaOH-ACDK is that the impregnation with sodium hydroxide solution is due to creating hydroxide ions incorporated on the surface of ACDK [44, 45].

Table 4: abbreviation and symbols.

Abbreviation/Symbols	Indication
ACDK	Activated carbon prepared from date Kernel
ACDK-NH ₃	Activated carbon prepared from date Kernel modified by ammonia solution at 10 per cent
ACDK-NaOH	Activated carbon prepared from date Kernel modified by Sodium Hydroxide solution at 10 per cent
TGA-DSC	Thermogravimetric analysis TGA/derivative differential scanning calorimeter (DSC)
XRD	Powder X-ray diffraction analysis
R ²	Correlation coefficient
R%	Removal percentage of phenol
PFO	pseudo-First-order model
PSO	pseudo-second-order model

The modified adsorbents: NH₃-ACDK, NaOH-ACDK can be used effectively for eliminate phenol one of industrial wastewater pollutants. So, as perspectives we recommend trying heavy metals removal by modified adsorbents.

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