Chemical Science International Journal

Volume 33, Issue 3, Page 1-21, 2024; Article no.CSIJ.114205
ISSN: 2456-706X
(Past name: American Chemical Science Journal, Past ISSN: 2249-0205)

Toward Cleaner Ecosystems; Elimination of Paracetamol Drug via Mesoporous Activated Carbon Date Pits

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Authors' contributions

This work was carried out in collaboration among all authors. Authors FAAA and MMF were the supervisors of the work, they established the core idea, brought the necessary requirements for the work. Author LNA was the master student who did the experimental work, and deduce the results and author LNA wrote the manuscript. Authors FAAA and MMF both edited and put the final touches of the manuscript. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CSJI/2024/v33i3890

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/114205

Original Research Article

Received: 07/01/2024
Accepted: 12/03/2024
Published: 16/03/2024

ABSTRACT

The purpose of this study is to remove pharmaceuticals drugs from water due to high potential impact on human health. Specifically, non-prescriptive drugs like paracetamol drug, which cause infections to various human organs like liver, kidneys and immunity system. Activated carbon (AC) was synthesized from date pits via thermal and chemical carbon activation using air at high

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temperature and phosphoric acid respectively, three ratios of (AC:Acid) were prepared to adsorb the most commonly used antipyretic and analgesic drug "Paracetamol" from aqueous solutions. The experiments were done in the department of Chemical Engineering and department of Chemistry, between September 2018 and August 2019. Characterization of the activated carbon (AC) was carried out through surface area analysis (BET), X-ray diffraction (XRD), spectroscopic Fourier Transform Infrared (FTIR), thermal (Thermogravimetric analysis TGA) and derivative thermogravimetry (DTG), and microscopic (scanning electron microscopy SEM) techniques. Several parameters for Paracetamol adsorption from aqueous solutions were tested, and the optimum parameters were as follow: contact time= 150 min, pH= 7.0, temperature= 25ºC, (AC:Acid) ratio = 1:1. The equilibrium data were fitted to different adsorption isotherms, the two-step Langmuir isotherm gave the best fit to the data, and the pseudo-second-order model represented the adsorption process as dynamic studies illustrated. Thermodynamic parameters showed the process was exothermic (-15.7 kJ/mol) and physisorption. The results of the experiments showed the removal efficiency using AC (1:1) ratio was 92.9%, and the entire removal was attained using 16 g/L. The maximum paracetamol uptake at equilibrium was 165 mg/g. The used carbon in the adsorption process can be cleaned and reused again (regeneration), the regeneration efficiencies were 60% for hot water method and 68% for methanol method. This clearly helps toward cleaner ecosystems.

Keywords: Date pits; activated carbon; drug removal; mesoporous; paracetamol; clean ecology.

1. INTRODUCTION

Water pollution is an historical phenomenon that has existed since human existence. Pollutants evolved with the development of human life. Therefore, wastewater is now classified as domestic, commercial, industrial [1]. Recently, industries have dramatically increased, resulting in increased production of industrial wastewater filled with various types of organic and inorganic pollutants, inorganics such as heavy metal (mercury, cadmium, arsenic, chromium, thallium, and lead) are poisonous at low concentrations and metal salts can cause hardness in water and affect the aquatic life [2]. There are different types of organic pollutants in water as (hydrocarbons, pesticides, phenols, plasticizers, fertilizers, oils, detergents and pharmaceuticals), water pollution by organic pollutants is considered very dangerous due to their various side effects and carcinogenic nature [3,4]. Pharmaceuticals have been neglected as potential environmental pollutants for a long time compared to other pollutants such as pesticides and heavy metals. Pharmaceuticals existed in soil and aquatic mediums by sewage or treated sewage sludge due to their high solubility in aqueous media at ordinary temperature and pressure, and they are detected in wastewaters at ng L^{-1} (nanogram per liter) to µg L^{-1}(microgram per liter) levels [5]. In the 1970s the concern of pharmaceuticals as environmental pollutants has been started, while lately the treatment of these pollutants' effects was started [6–8]. Many institutions have paid great attention to the issue of drug water pollution; due to the impact of this problem on the environment and people. For example, the most important institution of the drug administration is the American Food and Drug Administration (FDA), which requested each pharmaceutical company producing a new drug product to evaluate the effects of this drug concentration on the environment if the expected concentration is higher than 1 µg.L^{-1} [9]. These pharmaceutical compounds enter the body either directly by taking therapeutic doses or indirectly via drinking water or eating plants and fish containing amounts of them [10]. Increasing drugs concentrations in the human body may cause many diseases. One of the main effects of this accumulation in the body is an increase in human immune resistance for such drugs and hence stop their effect for the cure [11]. Painkillers and antipyretics drugs are the most commonly used drugs around the world [12,13]. High doses of these contaminants on the long term exposure cause damage of liver and kidneys for humans and animals, diseases of nerves, blood, tissues and hormones and increase incidences of cancer [14]. The existence of the pharmaceuticals in wastewater wasn't only proven in the western world, but also Arabic countries (yes,middle east). many drugs were found in Jordan and Al-Madina Almunwarah-Saudi Arabia's wastewater [15,16]. Paracetamol (acetaminophen) drug is one of the most important drugs used to treat fever and relieve pain if it is used in accordance with therapeutic doses, but leads to serious diseases and sometimes to fatal liver poisoning if used in

Table 1. Paracetamol maximum uptake using different adsorbents.

ADSORBENT	MAXIMUM UPTAKE (MG/G)	REFERENCE
AC FROM PEAT	150	[47]
AC FROM TEA WASTE	99.4	[36]
AC FROM DENDE COCONUT	70.6	[37]
AC FROM OAK	45.45	[48]
MAGNESIUM OXIDE	4.34	[49]
HORSERADISH PEROXIDASE IMMOBILIZED ON NANOFIBROUS MEMBRANES	343	[50]

high doses [17]. It was discovered at the end of the 19th century in Germany. More than 20 million prescriptions of paracetamol were released in 2017 according to U.S. government data [18]. Paracetamol was detected in deferent wastewater samples around the world with concentrations (ng/L to µg/L) [19–24]. The risk quotient (RQ) of paracetamol was classified as a high risk to the aqueous medium and the environment [25,26]. Paracetamol is one of the pharmaceuticals that readily is biodegradable in the environment by 57%- 99% in a month, but it stays in the environment due to its continuous discharging [27,28]. The chemical formula is $C_8H_9NO_2$, and the chemical structure is shown in (Fig. 2B). Galus found that a mixture of four pharmaceuticals (paracetamol, venlafaxine, gemfibrozil and carbamazepine) in water with specific concentration for each (500 $ng.L^{-1}$) causes a clear change in the production of embryos, the development of oocyte and fertility in zebrafish female [12].

Several methods have been used to treat wastewater, such as activated sludge [29] , reverse osmosis [30] anaerobic oxidation [31] ozonation and [32] membrane filtration [33,34]. Although these methods are effective in pharmaceutical removal from wastewater, they can not be used in all cases because they are expensive, not eco-friendly and usually dependent on the concentration of the waste[35]. Adsorption using activated carbon is an effective method, cheap, uncomplicated process and obtainable, which can be derived from various plants in nature such as coconut mesocarp, olive waste cake, wood and tea waste [13,36,37]. Activated carbon (AC) has many shapes: powdered, granular, pellets (cylindrical and spherical), fibers, and coke [38]. AC specifications vary -even if it is from one source- according to the preparation, manufacturing and carbonation methods. The most important feature of activated carbon that makes it suitable for adsorption is porosity and thus a large internal surface area, which is described as a sponge or honeycomb. Pores are produced through the carbonization process of an organic matter via chemical and thermal activation stages [39–41]. In this work chemical activation was done by using phosphoric acid (85%) and thermal process was done by using a tubular furnace. Activated carbon has been found to be much efficient in removing organic matters than removing inorganic materials [42]. The main advantage of using activated carbon to remove pharmaceutical contaminants is that it doesn't produce toxic substances and has shown high drug adsorption capacity [43–46]. Table 1 shows the maximum uptake of paracetamol using different adsorbents, we can notice that the capacity of the activated carbon depends on its source.

In this work, new powdered ACs were synthesized from date pits to remove the paracetamol drug completely from aqueous solutions. Characterizations of ACs were determined by many techniques such as; FTIR, XRD, TGA and SEM tests. Optimal conditions, adsorption isotherms, kinetics and thermodynamics for paracetamol removal were also studied.

2. MATERIALS AND METHODS

2.1 Materials

Paracetamol drug high purity (Assay >99%) was purchased from Cayman company, USA, Date pits were collected locally, Jordan. Distilled and deionized water. Methanol (HPLC grade). Acids used: Phosphoric Acid H_3PO_4 (85%) (Riedel-de Haën) and Hydrochloric Acid HCl 37% (Sigma-Aldrich company).

2.1.1 Synthesis of AC

The date pits were washed with deionized water and dried in the oven to remove peels and moisture to ensure easy grinding. They were

finely ground with a coffee mill to get the powder form.

Powdered DP was mixed with 85% phosphoric acid (H_3PO_4) in different weight ratios (DP: Acid) of (1:1), (1:2) and (1:3). Each solution was diluted 5 times with deionized water (without dissolved mineral particles) in a 1L beaker then heated and boiled for few hours on a magnetic stirrer until all liquid was evaporated and a black paste was formed at approximately 160°C. The air was entered into the paste at constant flowrate using a glass tube for 15 minutes, with continuous stirring and a gradually rising in temperature from 160 to 215°C. The produced activated carbon (blake paste) was put in a suitable dish that was placed in a tubular furnace and activated for 30 min at a temperature between 300 to 500°C with constant airflow during the activation process. Then the sample was removed from the oven and left a few minutes to cool. After the activation process, the resulting activated carbon was washed with deionized water by boiling with 20 g/L carbon concentration. then filtered and rinsed with deionized water. To ensure the acid was completely removed from the activated carbon it was washed with deionized water using the Soxhlet extractor method for 48 hours. Then the carbon was boiled with deionized water and filtered, after cooling the water pH value was measured to ensure neutrality. The carbon was dried for 12 hours at 100 °C in a vacuum oven, cooled in a desiccator, ground, placed in a container, and stored in the desiccator according to Abu Al-rub's method [29].

2.2 Methods

2.2.1 Charaterization techniques

Fourier Transform Infrared Spectroscopic Analysis (FTIR) is used to investigate carbon's functional groups after the oxidation and activation processes. The range of recorded spectra were between 4000 - 400 cm^{-1} using KBr pellets. Thermogravimetric analysis (TGA), was used to study the thermal stability of raw date pits (DP) and produced activated carbons (AC). The decomposition temperatures of these materials were determined by using the derivative thermogravimetry (DTG) technique. Samples were exposed to heat ranging from room temperature to 900°C with a heating rate of 10 ^oC /min under the inert nitrogen gas flow. X-ray powder diffraction (XRD) is a rapid analytical technique, was used to determine the crystalline structure of DP and ACs before and after the oxidation process. The scanning rate was 2°/min, from 5 to 80°. The materials must be a homogeneous fine powder and the measurement was carried using Cu-K_α radiation. The surface structure of porous ACs as surface area, micropore volume and pore size distribution were determined using Surface area analysis technique (BET) (Brunauer-Emmet-Teller) by adsorption of nitrogen at 77°K using a Micromeritics ASAP 2010 gas adsorption surface area analyzer. Scanning electron microscopy (SEM) is a major test in any microstructural analysis, it was used to study the topological changes of DP and manufactured ACs after activation and oxidation processes. All images were determined and tuned by the instrument's software programs. Concentrations of paracetamol were detected using a UV-vis spectrophotometer (Hach Lange DR5000) at several time intervals in the range of 200-400 nm. The (λ_{max}) maximum wavelength was 243 nm, then the calibration curve of paracetamol was established.

2.2.2 Paracetamol removal

The ACs were placed in paracetamol drug solutions of different concentrations and shaken in a thermal water bath shaker for different periods to determine the equilibrium time. The uptake of paracetamol drug by the activated carbons was calculated from the following equation

$$q_e = \frac{(C_o - C_e)\, V}{W} \qquad (1)$$

where (q_e) is the equilibrium drug uptake (mg/g), (C_o and C_e) are the initial and equilibrium drug concentration (mg/L) respectively, (V) is the volume of the solution (L), and (W) is the mass of the AC (g). Adsorption experiments were carried out to investigate the optimum adsorption conditions. To define the equilibrium contact time, 50 mg of AC was added into paracetamol solutions with a concentration of 50 ppm for several time intervals between 0.5 and 24 h while keeping the rest of the parameters constant during the experiments as follows: pH= 7.0, temperature=25°C and solution volume= 50 ml. To determine the optimum solution pH value, various values of pH in the range 3-9 were tested at equilibrium contact time = 150 min, AC mass= 50 mg, solution conc.= 50 mg/L, solution volume=50 ml and temperature= 25°C. To determine the maximum uptake (q_{max}) of

paracetamol drug by AC, many solution concentrations were tested at equilibrium contact time = 150 min, pH=7, AC mass= 50 mg, solution volume= 50 ml and temperature= 25°C. To determine the optimum mass of AC to 100% drug removal, different masses in the range of 0.05−1 g were tested at contact time= 150 min, pH= 7.0, solution volume= 50 ml, solution concentration=50 ppm and temperature= 25°C. Finally, the optimum temperature was determined to achieve the best adsorption, three different temperatures of the adsorption process were tested (25, 35 and 45℃) at pH= 7.0, contact time= 150 min, solution volume= 50 ml, AC mass= 50 mg and solution concentration= 50ppm. All of these experiments were repeated using the three manufactured ACs (DP: Acid) ratios to determine which ratio is the best in the adsorption process.

2.2.3 Desorption process

The desorption process is a very useful step to determine if the spent adsorbent can be reused again in the adsorption process, that allows the reuse of activated carbons many times to remove the paracetamol drug from aqueous solutions. Two desorption methods were tested; thermal using hot water and chemical by methanol to determine the more efficient desorption way. Desorption of AC by thermal technique was done by adding 0.5 g of used AC to 50 ml of hot distilled water at 85°C and the beaker was placed inside the thermal water shaker with 150 rpm for 3 hours; then AC was filtered, washed with distilled water, dried in the oven, and stored inside the desiccator for reuse again. The desorption percentage equaled 73%.[51] The same procedure was repeated for the chemical method using methanol at 25°C. Methanol was chosen due to the high solubility of paracetamol in it. The desorption percentage was 81% [51].

3. RESULTS AND DISCUSSION

3.1 Properties of Activated Carbon and Date Pits

3.1.1 Structural composition

The functional groups of date pits and activated carbon were monitored and specified using Fourier transform infrared spectroscopic analysis (FTIR). The FTIR spectra of date pits (DP) and activated carbon (AC) were showed in Fig. 1. While the characteristic FTIR vibrational assignments with their wavenumbers and transmittance(%) were illustrated in (Table 2). The increase in the formation of asymmetric and symmetric carboxylate groups (COO–), carbonyl group (C=O) and (C-O) bonds at 1563 cm^{-1}, 1344 cm^{-1}, 1691 cm^{-1} and 1150 cm^{-1} respectively is proof of the success of the carbon oxidation process. Moreover, the unchanged (C-C) stretching value at 1518 cm^{-1} confirmed that the oxidation process was completed without destroying the carbon structure. On the other hand, the epoxy groups (COC) were broken completely during the activation process. The phosphorous groups were used in the chemical activation process as an acid are not presented in the resulting activated carbon, in addition to the absence of amino acid that was present in the raw material (DP), which indicates that the acids have been completely removed from the activated carbon. It is an excellent result because their presence causing a change in the pH value of the solution and reduce the adsorption capacity due to the acid-filling of sites (Fig. 1).

3.1.2 Thermal stability

The thermal stability of the raw date pits and all manufactured activated carbon ratios were measured by thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) at temperatures ranging from room temperature to 900°C with a heating rate of 10°C /min under the inert nitrogen gas flow; to know the decomposition temperatures of these materials and study their thermal stability before and after oxidation processes. (Fig. 2). Illustrated (TG) and (DTG) analysis for our compounds. The raw material (DP) curve showed degradation temperature between about 250 and 400 °C, and the decomposition peak was at 293°C. This peak was attributed to the thermal degradation of cellulose and hemicellulose [52]. On the other hand, activated carbon (1:1) and (1:3) ratios didn't show any peaks or any degradation, and their weights loss were negligible, this indicated that they became very thermally stable after the activation process as shown in (Fig. 2). While the last sample activated carbon (1:2) ratio displayed gradually degradation and weight loss during the temperature elevation, it did not have a specific decomposition temperature, the sample was thermally stable but lower than other ratios [53].

3.1.3 Interlayer spacings

X-ray powder diffraction (XRD) is a rapid analytical technique, that determines the crystalline structure of a substance before and after the oxidation process, the material must be

a homogeneous fine powder. The distance between the crystal planes of date pits (DP) and activated carbons (ACs) was calculated using Bragg's equation as follows:

$$n\lambda = 2d\sin\theta \qquad (2)$$

Where n is an integer number referred to the order of diffraction and selected as 1, λ is the X-ray wavelength of the radiation used equals to 1.54056 A^o using Cu-K_α radiation, d is an inter-planer spacing Å (Angstroms), θ is Bragg's angel which is the small angle between an incident X-ray beam and the planes of crystal (degree). The raw date pits (DP) diffraction peaks at 2θ= 15.9°,18°, 20° and 32.9° with an inter-planer spacing d= 5.6Å, 4.9Å, 4.4Å and 2.7Å respectively. Such values correspond to the presence of hemicellulose, cellulose and xylene dehydrate [54] between date pits particles as shown in (Fig. 3). These peaks disappeared in the activated carbon curves due to the decomposition of hemicellulose and cellulose during the thermal activation process [55,56]. Also, the DP pattern has two peaks the first one at 2θ= 25° represented to the presence of carbon (C), and the other at 2θ= 43° with very low intensity indicated to the presence of graphite (G). The same peaks were found on the AC curves regardless of the ratio of DP to Acid with higher intensity values, which is evidence of the success oxidation process. The presence of peaks with the same degrees for DP and AC confirms that the crystal structure was not influenced by the oxidation process [55,57]. The higher intensity AC the higher the crystallinity structure, and thus the more packed and the lower adsorbance active surface as found in AC (1:2) sample.

3.1.4 Surface micro- and meso-porosity

Surface structure of a porous adsorbent, as surface area, micropore volume and pore size distribution was determined by surface area analysis (BET) using adsorption of nitrogen at 77°K technique [58]. (Fig. 4) is a plot that explains the relation between relative pressure in the sample vessel and the adsorbed volume of gas. From the plot, it was observed that AC (1:2) ratio has the least nitrogen adsorption ability, which indicates that it has the lowest surface area.

Pore diameter, micropore volume, and total pore volume are determined by Barrett-Joyner-Halenda (BJH) analysis [59]. The results of BET and BJH analysis were summarized in (Table 3). The surface properties of activated carbon change according to the concentration of phosphoric acid. As it was observed, the diameter of the pores increases with increasing acid concentration, while the microporous volume decrease.

Table 2. Characteristic FTIR vibrational assignments with their wavenumbers and transmittance

Material	Transmittance (%)	Wavenumber (cm^{-1})	Vibrational Assignment
Raw Date Pits	92.0	3470	N–H Stretching Of Amino Acids
	90.0	3355	O–H Stretching
	76.3	2921	Asymmetric C–H Stretching
	81.1	2885	Symmetric C–H Stretching
	82.0	1744	C=O Stretching
	95.7	1646	C=C Stretching
	94.5	1611	Asymmetric Coo^- Stretching
	96.7	1518	C–C Stretching
	92.9	1371	Symmetric Coo^- Stretching
	86.9	1150	C–O Stretching
	72.8	1010	Coc Stretching
Activated Carbon (Ac)	98.8	1691	C=O Stretching
	95.8	1563	Asymmetric Coo^- Stretching
	96.7	1518	C–C Stretching
	96.4	1344	Symmetric Coo^- Stretching
	94.3	1150	C–O Stretching

From (Table 3) it appears that the activated carbon (1:1) ratio has the highest surface area because it has the smallest pore diameter and the highest size of micropores and thus the largest number of pores. In the second activated carbon ratio (1:2), decreasing the total pore volume and the microporous volume to the half of (1:1) ratio values indicates that an increase in the acid concentration leads to an increase in crystallization and packing, thus closing part of the pores and reducing the surface area, and this was confirmed also by the XRD test. The total pore volume is almost the same for the activated carbon ratios (1:3) and (1:1), but the pore diameter in the ratio (1:3) is approximately 10 times greater than the pore diameter in the (1:1) ratio, due to the high acid concentration where it led to the expansion of the pores and damaged [60]. The new pores in this ratio are very large compared to the drug molecule dimensions as shown in (Fig. 5), which means one pore can adsorb many molecules, that lead to repulsion between them and the exit of some, thus decreasing the final uptake.

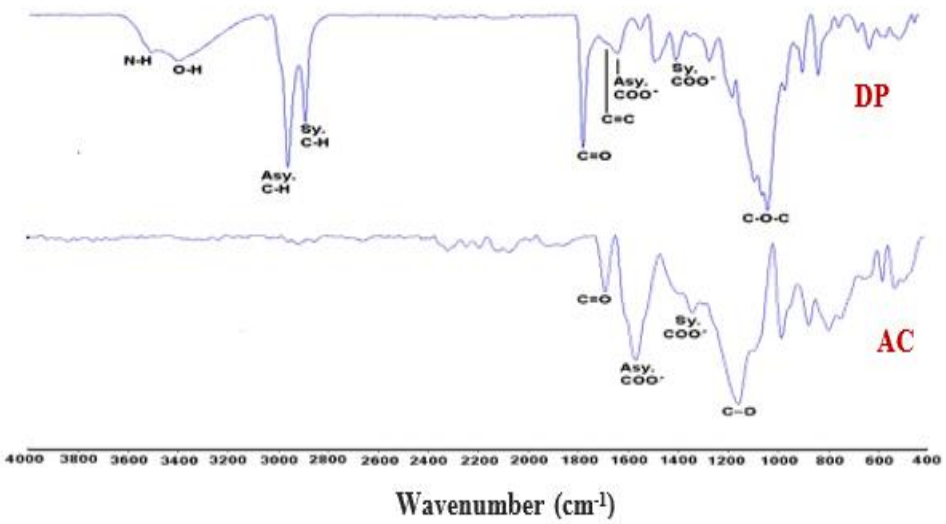

Fig. 1. FTIR spectra of date pits (DP) and activated carbon (AC)

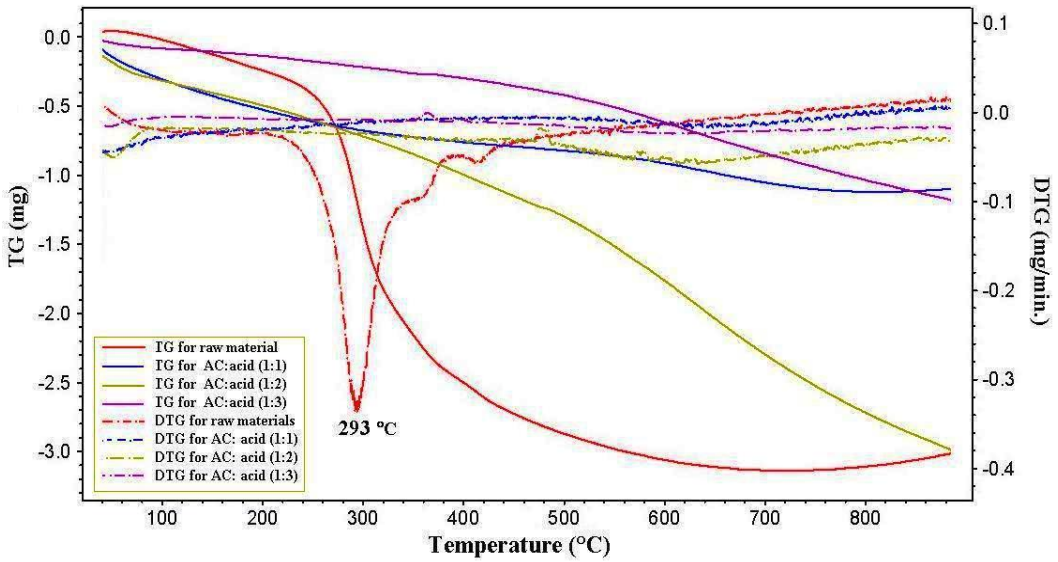

Fig. 2. TGA and DTG curves of raw date pits (DP) and the three ratios of produced activated carbon, DP: Acid (1:1, 1:2 and 1:3 ratios)

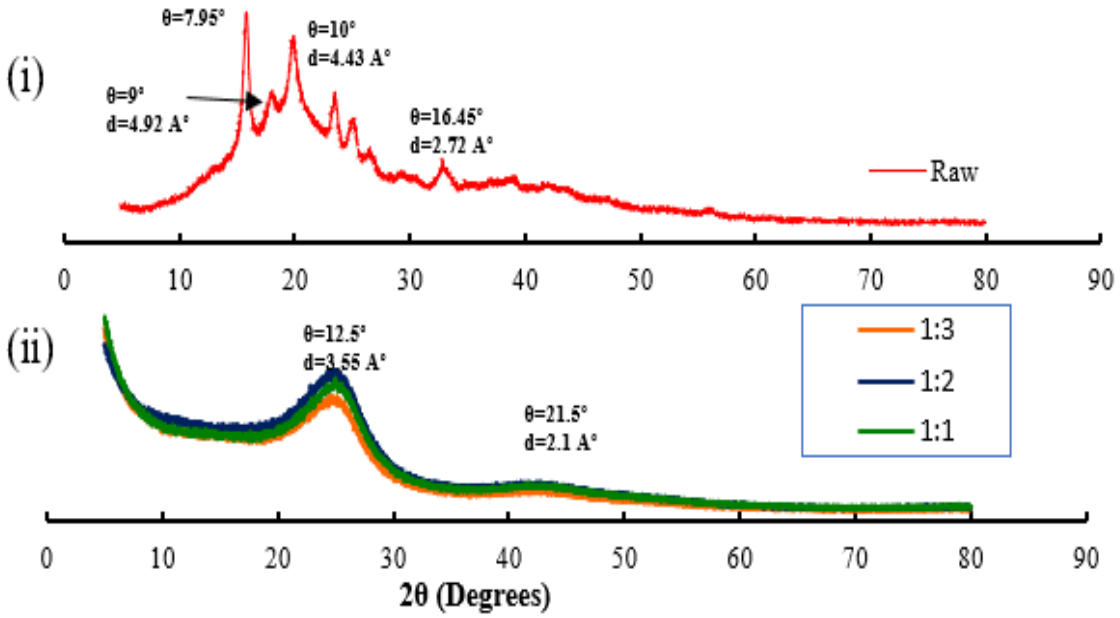

Fig. 3. XRD patterns of (i) raw date pits (DP) and (ii) activated carbon (AC) with different AC ratios

Table 3. Surface properties of produced activated carbon

SAMPLE ID	TOTAL PORE VOLUME (CM^3/G)	MICROPOROUS VOLUME (CM^3/G)	PORE DIAMETER (Å)	BET SURFACE AREA (M^2/G)
AC (1:1)	0.46324	0.223	26.9	838.4077
AC (1:2)	0.20679	0.107	29.4	372.2272
AC (1:3)	0.51565	0.0066	277.6	649.1893

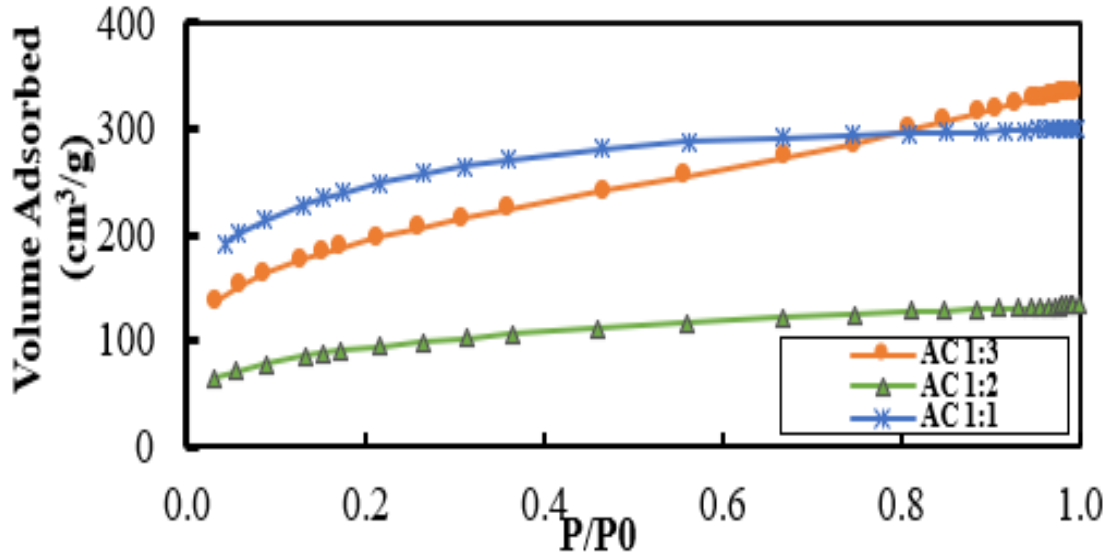

Fig. 4. The relationship between relative pressure and nitrogen adsorbed volume

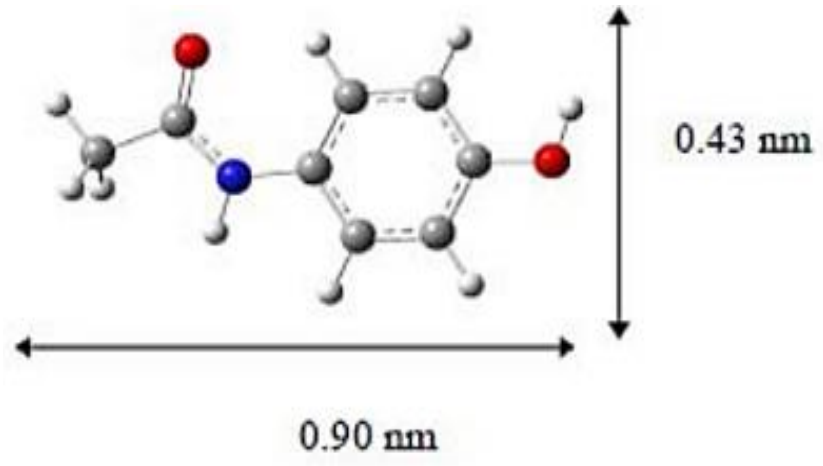

Fig. 5. Paracetamol molecule dimensions [61]

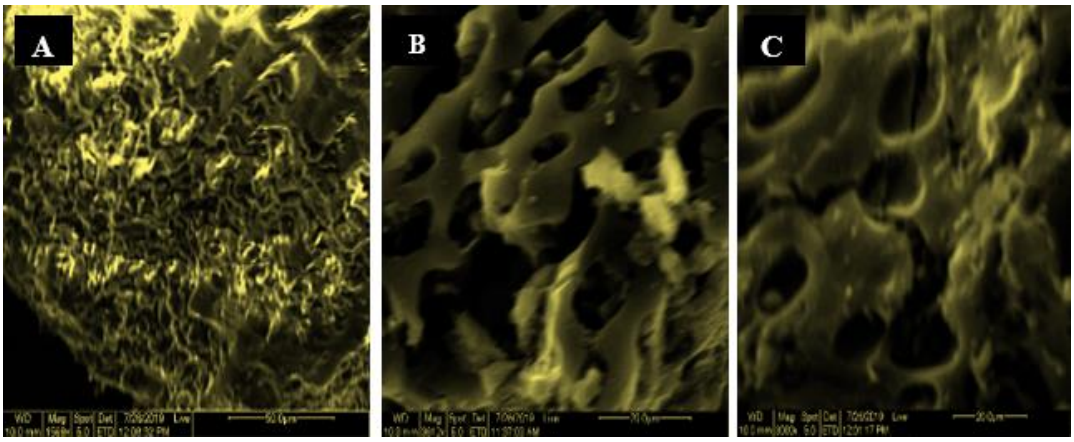

Fig. 6. Scanning electron microscopy images of (A) Raw DP, (B) AC (1:1), and (C) AC (1:3)

3.1.5 Surface topology

The scanning electron microscopy (SEM) technique provides data that links the topological structure, morphology, phase distribution, compositional differences, and crystal orientation. The SEM pictures of used adsorbent in the experiments DP and ACs (1:1 and 1:3) ratios were shown in (Fig. 6). Raw date pits image showed waves only and didn't show any pores, meaning that it can't adsorb (Fig. 6-A), while the pores appeared clearly in AC (1:1) image (Fig. 6-B) , which supported the results of previous tests for the ability of this compound to adsorb drug molecules. (Fig. 6-C), represents AC(1:3), showed larger pores and less number of pores than AC (1:1). This increases the chances of repulsion inside the pores, thus decreases adsorption uptake, while its remaining high in AC(1:1) due to the higher surface area and smaller pores.

3.2 Optimum Parameters

Various parameters and conditions were tested to verify optimal conditions for paracetamol removal from aqueous solutions. Batch adsorption experiments were processed, and the parameters studied were: contact time, solution pH, drug concentration in solution, adsorbent mass and temperature. These conditions were tested for all ratios of (DP: Acid) ACs to determine the most efficient adsorption ratio.

3.2.1 Contact time, solution pH, drug concentration

The effect of contact time, solution pH, and drug concentration in the solution was studied for paracetamol drug removal from aqueous solutions using all manufactured ACs (Fig. 7 A−C). Several time intervals were tested, the

time was increased until equilibrium adsorption was reached. The drug was adsorbed significantly during the first 30 minutes, and the adsorption continued slowly during the next 120 minutes, then the adsorption became constant over time, which means that it reached equilibrium. The occurrence of rapid adsorption in the first 30 minutes indicates that there are many empty sites in the adsorbent with no internal resistance diffusion [62]. Over time, the adsorption of the drug became slow due to the saturation of the sites with drug particles [63]. The equilibrium time was found as 150 min (Fig. 7 A).

Different values of solution pH in the range pH= 3-9 were tested (Fig. 7 B). It was observed that the adsorption was almost constant and was not affected by the change in pH, and the maximum adsorption was at pH= 7, so the rest of the experiments were done at this value. Adsorption of paracetamol on the surface of Activated carbon depends on the surface charge of the adsorbent (AC-H_3PO_4) and (pKa) dissociation constant of paracetamol. The paracetamol (acetaminophen) drug has a pKa value of 9.38 [64]. When pH < pKa, paracetamol drug particles will be protonated and carry a positive charge. The point zero charge pH determines the carbon surface charge (pHzpc), the pHzpc of (AC-H_3PO_4) is 2 [48].

At pH > pHzpc the surface of adsorbent is negatively charged. In the pH 3-9 range, the adsorbent surface charge is negative while the paracetamol charge is positive. Therefore, adsorption in this range is high due to the attraction between the drug and the adsorbent surface.

The effect of different initial drug concentrations (0-700) mg/l was studied on drug absorption (Fig. 7 C). Obviously, the increase in concentration leads to an increase in the drug uptake due to an increase in the driving force (difference between initial concentration of drug in the solution and intial concentration of drug in AC which is zero) which dominates the resistance of the drug molecules transfer to the adsorbent's active sites [48]. The maximum adsorption uptake of ratios (1:1, 1:2, 1:3) increased from zero to (165, 115, 151) mg/g, respectively. It was observed that adsorption by AC(1:2) ratio was the lowest, that due to its small surface area compared to the rest of the ratios, as shown by the BET test.

3.2.2 Adsorbent mass and temperature

Different ACs weights were tested in the range of 5-1000 mg to remove paracetamol drug from aqueous solutions, and the maximum adsorption capacity occurred at the minimum weight of the adsorbent (Fig. 7 D). Increasing the adsorbent mass may accumulate the adsorbent's particles over each other and covering some active sites, which decreasing the uptake of the drug [65,66]. Final parameter was the effect of temperature on the adsorption process. Temperatures in the range 25-45°C were tested, (Fig. 7 E) illustrated the drug adsorption uptake was decreasing along with the increasing temperature. This was due to the increase of the drug solubility in the solution as temperature rises, decreases the interactions between adsorbent and adsorbate, and this indicates that the adsorption process is physical and exothermic [36,65].

3.2.3 Entire removal of paracetamol from aqueous solutions

The entire removal of the drug from aqueous solutions is one of the most important parts of this study, due to the increase in the body's immunity to respond to the drug and sometimes death caused by its accumulation in the body [67]. To study the process of completely removing the drug, several masses of the three ratios (DP: Acid) ACs were used to remove the drug with an initial concentration of 50 ppm (Fig. 7 F). Clearly, The removal percentage (%) increased with increasing the activated carbon mass. The entire removal of the dissolved paracetamol from the solution was using 0.8 g of AC (1:1), 1 g of AC (1:2), and 0.9 g of AC (1:3) as shown in (Fig. 7 F). (Several masses of AC were used to determine the removal percentage for each mas and determine which case reaches 100% with the lowest amount of activated carbon).

3.3 Regeneration of Activated Carbon

The regeneration of spent activated carbon was studied for the best ratio used in these experiments, which was AC(1:1) ratio. Two methods were tested in this regeneration process: thermal (using hot water about 85°C) and chemical (using methanol). After the desorption-adsorption processes, desorption percentages were 73% and 81%, and the regeneration efficiencies were 60% and 68% for thermal and chemical regeneration methods respectively.

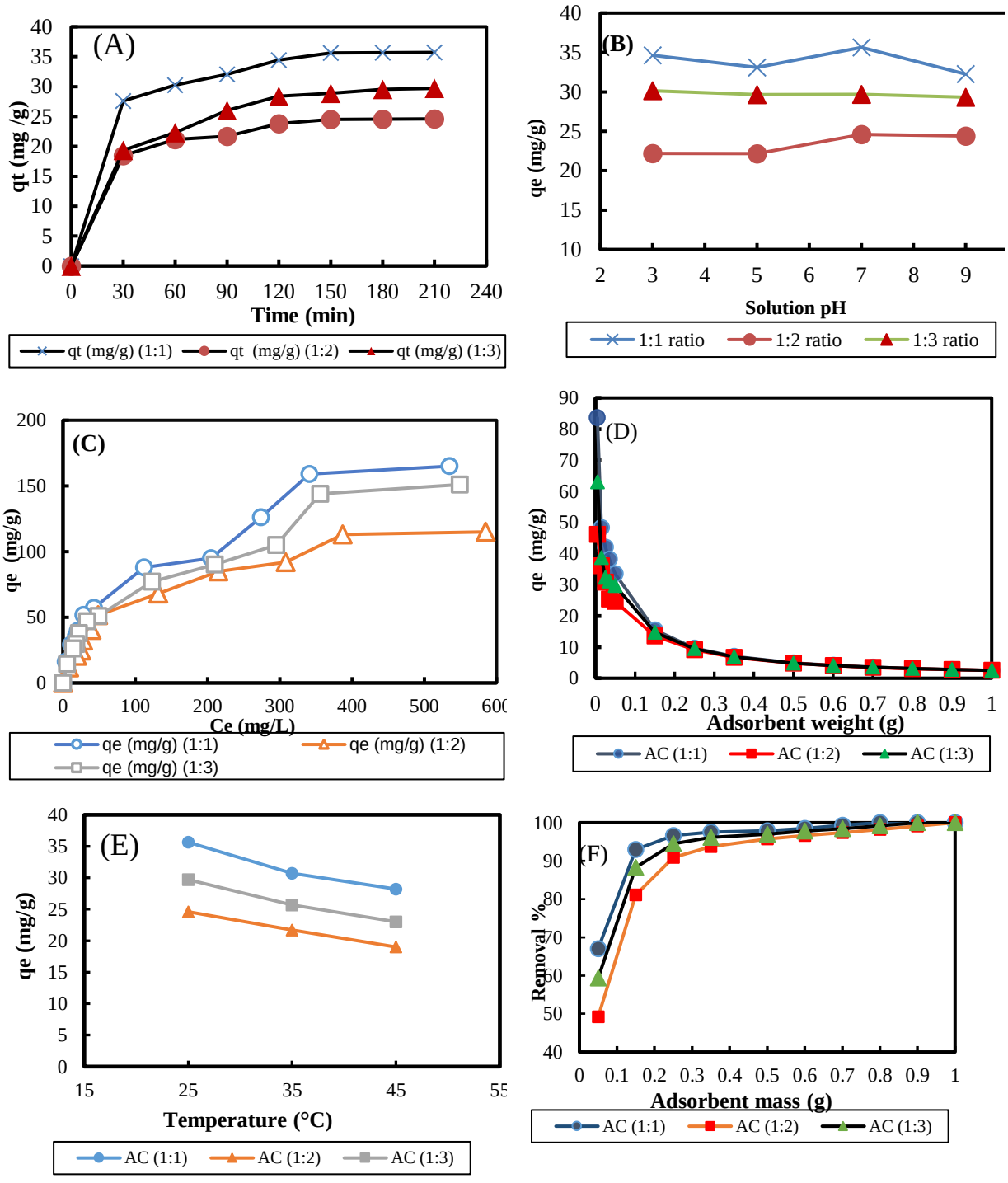

Fig. 7. Optimum conditions for paracetamol drug adsorption of on the surface of activated carbon DP/Acid

(A) Contact time (pH = 7.0, solution volume = 50 mL, AC mass = 50 mg, temperature = 25 °C, AC (DP:Acid) ratios are (1:1, 1:2,and 1:3) (B) solution pH (contact time = 150 min, solution volume = 50 mL, temperature = 25 °C, AC mass = 50 mg, (C) initial concentration (pH = 7.0, solution volume = 50 ml, contact time = 150 min, AC mass = 50 mg, temperature: 25 °C, AC (DP:Acid) ratios are (1:1, 1:2,and 1:3). (D) AC mass (pH = 7.0, solution volume = 50 mL, contact time = 150 min, temperature = 25 °C, , (E) temperature (pH = 7.0, solution volume = 50 mL, contact time = 150 min, AC mass = 50 mg, AC (DP:Acid) ratios = (1:1, 1:2,and 1:3), and (F) effect of adsorbent mass on the removal efficiency of paracetamol on ACs (pH: 7.0, solution volume: 50 ml, time: 150 min, initial solution concentration= 50ppm, temperature= 25 °C

3.4 Adsorption Kinetics

Two models for drug removal kinetics were tested, the pseudo-first order and pseudo-second order, and the drug uptake proved to be a pseudo-second-order model as shown in (Fig. 8 A), with the calculated uptake($q_{e\text{-}calc}$) very close to the experimental uptake and correlation coefficient value (R^2) exceeding 0.99. The second- order model equation is as follows

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2\, t \qquad (3)$$

Linear form for this equation is:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e^2\, k_2} \qquad (4)$$

where k2 is the rate constant of drug uptake (g/mg min), q_e is the equilibrium drug uptake (mg/g), q_t is the drug uptake at time t (mg/g), and t is the time (min) [68]. The equilibrium drug uptake (qe) and the rate constant of removal (k2) were determined by plotting t/qt against time t (Fig. 8 B). The calculated equilibrium uptake of the drug ($q_{e\text{-}calc}$) was very close to ($q_{e\text{-}exp}$) with a correlation coefficient (R^2) in the range (0.9905-0.9964). the intraparticle diffusion model was used to validate the mechanism of drug adsorption [69].

$$q_t = k_d t^{0.5} + C \qquad (5)$$

Where k_d is the rate of intraparticle diffusion constant (mg/g.min$^{0.5}$), and **C** is a constant related to the boundary layer (mg/g). C and K_d constants can be determined from intercept and slope of $\mathbf{q_t}$ vs. $\mathbf{t^{0.5}}$ plot respectively [70]. If there are multilinear plots then two or more steps affect the adsorption process (Fig. 8 C). in the first step, there is a clear change in uptake, which indicated an immediate adsorption resulting (from external surface diffusion). The second step showed slow adsorption, which indicated (pore diffusion) [29,71].

3.5 Adsorption Isotherms

Adsorption efficiency, the relationship between adsorbent and adsorbate, and some adsorption properties can be determined using isotherms models when equilibrium is reached at a constant temperature. Four adsorption isotherms were explained to the adsorption of the paracetamol drug on the surface of the ACs: Langmuir, Freundlich, Temkin, and two-step Langmuir isotherm. The adsorption isotherms presented as linear curves, the most suitable isotherm that fit's the process is the one that has the highest correlation coefficients (R^2) and the closest q_{max} to $q_{e\text{-}exp}$. Langmuir isotherm equation is as follows

$$q_e = \frac{q_{max}\, K_L C_e}{1 + K_L C_e} \qquad (6)$$

Where q_{max} is the maximum uptake at the given conditions at all sites (mg/g), q_e is the uptake at equilibrium (mg/g), K_L is the Langmuir constant (L/mg), represents the affinity between adsorbent and adsorbate and is related to the adsorption energy through Arrhenius equation, Ce is an adsorbate equilibrium concentration (mg/L). Constants K_L and q_{max} can be calculated from the linear curve of Ce/qe vs. Ce plot [72]. The Langmuir adsorption isotherm for the paracetamol drug at 25°C and different ACs is shown in (Fig. 9A). The maximum uptake of the drug decreased with temperature increase as shown in (Table 4). It is clear that the kinetic energy of the drug molecules and the adsorbent surface increases with the increase in temperature, which leads to a decrease in the drug adsorption on the hot surface of the adsorbent.

The second model was Freundlich, and its equation as follows

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (7)$$

Where K_f ((mg/g)*(L/mg)$^{1/n}$) is the Freundlich constant, 1/n is the degree of the surface's heterogeneity, when n >1, the adsorption is a physical process and Ce is the equilibrium concentration of the drug (mg/L) [73]. Constants K_F and 1/n can be calculated from The linear curve of ln qe versus ln C_e plot [74]. The Freundlich adsorption isotherm for the paracetamol drug at 25°C and different ACs is shown in (Fig. 9B). Freundlich parameters for different temperatures and adsorbents with correlation coefficients (R^2) were illustrated in (Table 4).

The third model was Temkin isotherm, its linear form is as follows

$$q_e = B \ln(K_T) + B \ln C_e \qquad (8)$$

Table 4. Adsorption Isotherm Parameters for Paracetamol Drug Removal at elevated temperatures

Isotherm	Adsorbent	Parameters	Temperature		
			298 K	308 K	318 K
Langmuir	AC (1:1)	q_{max} (mg/g)	196	182	172
		K_L (L/mg)	0.0079	0.0064	0.0053
		R^2	0.931	0.9514	0.9218
	AC (1:2)	q_{max} (mg/g)	137	138	135
		K_L (L/mg)	0.0087	0.0061	0.0048
		R^2	0.983	0.9854	0.9789
	AC (1:3)	q_{max} (mg/g)	185	182	161
		K_L (L/mg)	0.0066	0.005	0.0045
		R^2	0.9253	0.9417	0.9795
Freundlich	AC (1:1)	1/n	0.464	0.487	0.4754
		Kf ((mg/g)*(L/mg)1/n)	9.41	6.77	6.73
		R^2	0.9904	0.9869	0.978
	AC (1:2)	1/n	0.557	0.536	0.5881
		Kf ((mg/g)*(L/mg)1/n)	4.3	4.02	2.65
		R^2	0.96	0.974	0.977
	AC (1:3)	1/n	0.491	0.5514	0.5222
		Kf ((mg/g)*(L/mg)1/n)	7.13	4.44	4.54
		R^2	0.9861	0.9915	0.988
Temkin	AC (1:1)	KT(L/mg)	0.148	0.046	0.096
		bT	70.89	57.4	89.4
		BT(J/mol)	34.95	44.59	29.571
		R^2	0.9337	0.9481	0.9468
	AC (1:2)	KT(L/mg)	0.107	0.065	0.092
		bT	88.97	85.8	91
		BT(J/mol)	27.845	29.841	29.1
		R^2	0.9824	0.9733	0.9655
	AC (1:3)	KT(L/mg)	0.127	0.0612	0.0688
		bT	76.4	69.7	87
		BT(J/mol)	32.43	36.735	30.4
		R^2	0.93	0.934	0.9697

Where B = RT/b_T, b_T is a Temkin constant related to the heat of adsorption(J/mol), R is the gas constant (8.314 J/mol.K), T temperature in (K), K_T is a Temkin constant expressed maximum binding energy (L/mg), constants B and K_T can be determined from the intercept and slope of qe versus ln C_e plot (Fig. 9C) [75].Temkin parameters for different temperatures and adsorbents with correlation coefficients (R^2) were illustrated in (Table 4).

The last isotherm was Two-step Langmuir isotherm, This model is expressed by the following equation

$$qe = \frac{q_{max1} K_{L1} C_{e1}}{1 + K_{L1} C_{e1}} + \frac{q_{max2} K_{L2} (C_{e2} - C_2)}{1 + K_{L2} (C_{e2} - C_2)} \quad (9)$$

Where **C_2** is the critical concentration (mg/L) of the sorbate in the solution, all of the other variables were explained in the Langmuir model [76]. This isotherm was used because the adsorbent was porous and the pores were in the range (2-50 nm) as its conditions of use [77]. (Fig. 10 (A, B, and C)) illustrated its results' curves for three temperatures and three adsorbents, which showed the best fitting for the experimental data, and the parameters' values were listed in the (Table 5), where all of the R^2 values were high and almost equal to (1) also the

maximum adsorption uptakes were very close to that from experiments' results. This means that this model is the most appropriate one to fit the adsorption results.

3.6 Adsorption Thermodynamics

several properties of the adsorption process can be determined from thermodynamic parameters, such as endothermic or exothermic, spontaneous or not, entropy change and if the process is chemisorption or physisorption. The adsorption process is considered to be spontaneous if the Gibbs change ΔG° is negative. when values are high (-80 to – 400 kJ/mol) the process is chemisorption, and it is physisorption when the values are low (0 to-20 kJ/mol) [78]. The positive value of the enthalpy change ΔH° means that the adsorption is endothermic, and the negative indicates that it is exothermic, while the positive value of the entropy change ΔS° indicates increased randomness during the process. Thermodynamics parameters of paracetamol removal are presented in (Table 6). The parameters were determined using the following equation

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (10)$$

Where **R** is the gas constant, 8.314 J/mol.K, K_L is the equilibrium constant (L/mg); which is determined from Langmuir isotherm. The entropy change (ΔS°) and enthalpy change (ΔH°) can be found from the intercept and slope respectively of the plot ln K_L versus 1/T (Fig. 11). The Gibbs free energy (ΔG°) values are calculated from $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ [79] it was found that the adsorption was spontaneous, exothermic, physisorption, and its entropy increased [80].

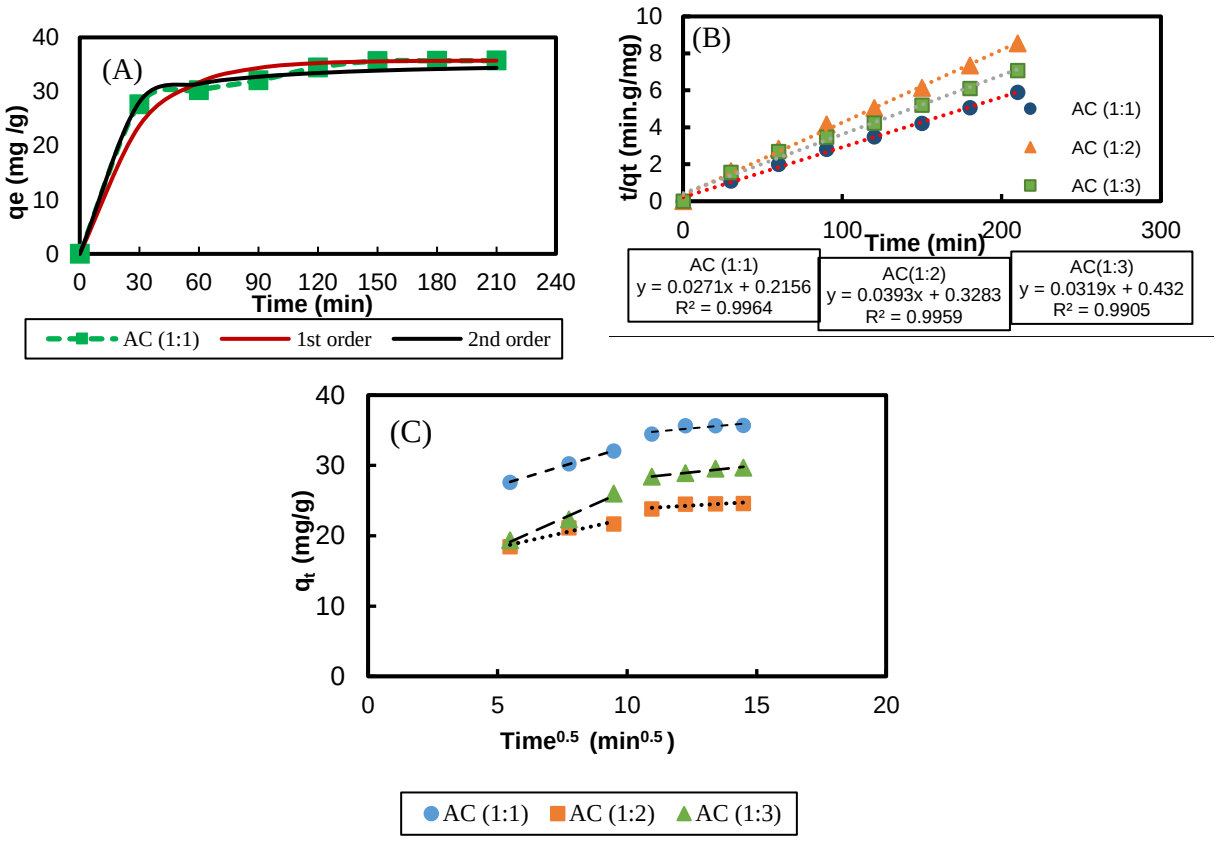

Fig. 8. (A) dynamic change of drug uptake pseudo-first order, pseudo-second order and experimental results for AC(1:1) ratio , (B) linear Pseudo-second order, (C) intraparticle diffusion curves for drug removal by ACs from aqueous solution

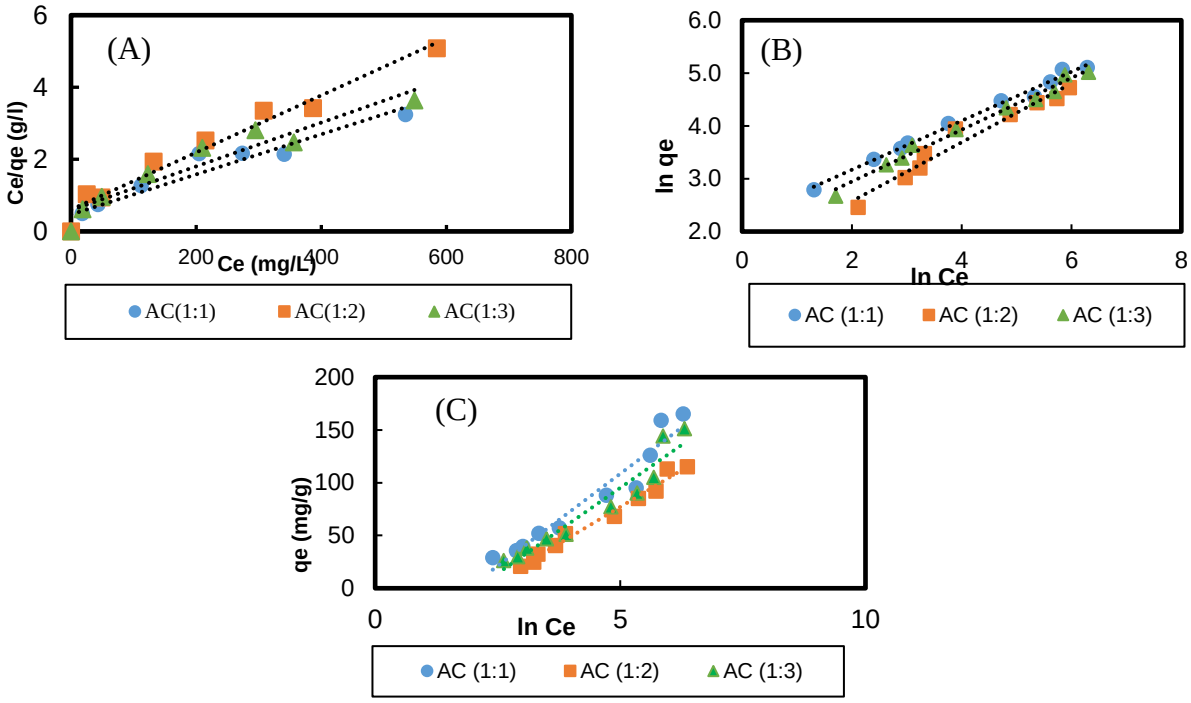

Fig. 9. (A) Linear form of Langmuir adsorption isotherms for Paracetamol removal with different adsorbents at 25°C, (B) Linear form of Freundlich adsorption isotherms for Paracetamol removal at 25°C, (C) Linear form of Timken adsorption isotherms for Paracetamol removal at 25°C

Table 5. The nonlinear two steps Langmuir isotherm parameters' values for paracetamol drug removal

T (ºC)	Sample	Step 1 $\left[Q_e = \frac{Q_{max1} b_1 C_e}{1 + b_1 C_e}\right]$				Step 2 $\left[Q_e = \frac{Q_{max2} b_2 (C_e - C_2)}{1 + b_2 (C_e - C_2)}\right]$			
		$q_{e\text{-}exp}$	Q_{max1} (mg/g)	b_1 (L/mg)	R^2	Q_{max2} (mg/g)	b_2 (l/mg)	C_2 (mg/L)	R^2
25	AC(1:1)	165	115	0.025	0.998	169.5	0.1	205	1.00
	AC (1:2)	115	115	0.0124	0.968	117.6	0.1	215	0.995
	AC (1:3)	151	113.6	0.0177	0.998	156.25	0.06	209.8	0.985
35	AC(1:1)	145	131.6	0.0126	0.983	147	0.245	292	1.00
	AC (1:2)	107	128	0.007	0.977	107.5	0.447	312.5	1.00
	AC (1:3)	137	133.3	0.0084	0.986	138.9	0.2	302	1.00
45	AC(1:1)	131	113.6	0.0135	0.991	131.6	0.93	308.5	1.00
	AC (1:2)	97	137	0.0046	0.950	98	0.45	319	1.00
	AC (1:3)	115	120.5	0.0085	0.991	117.6	0.156	310.5	1.00

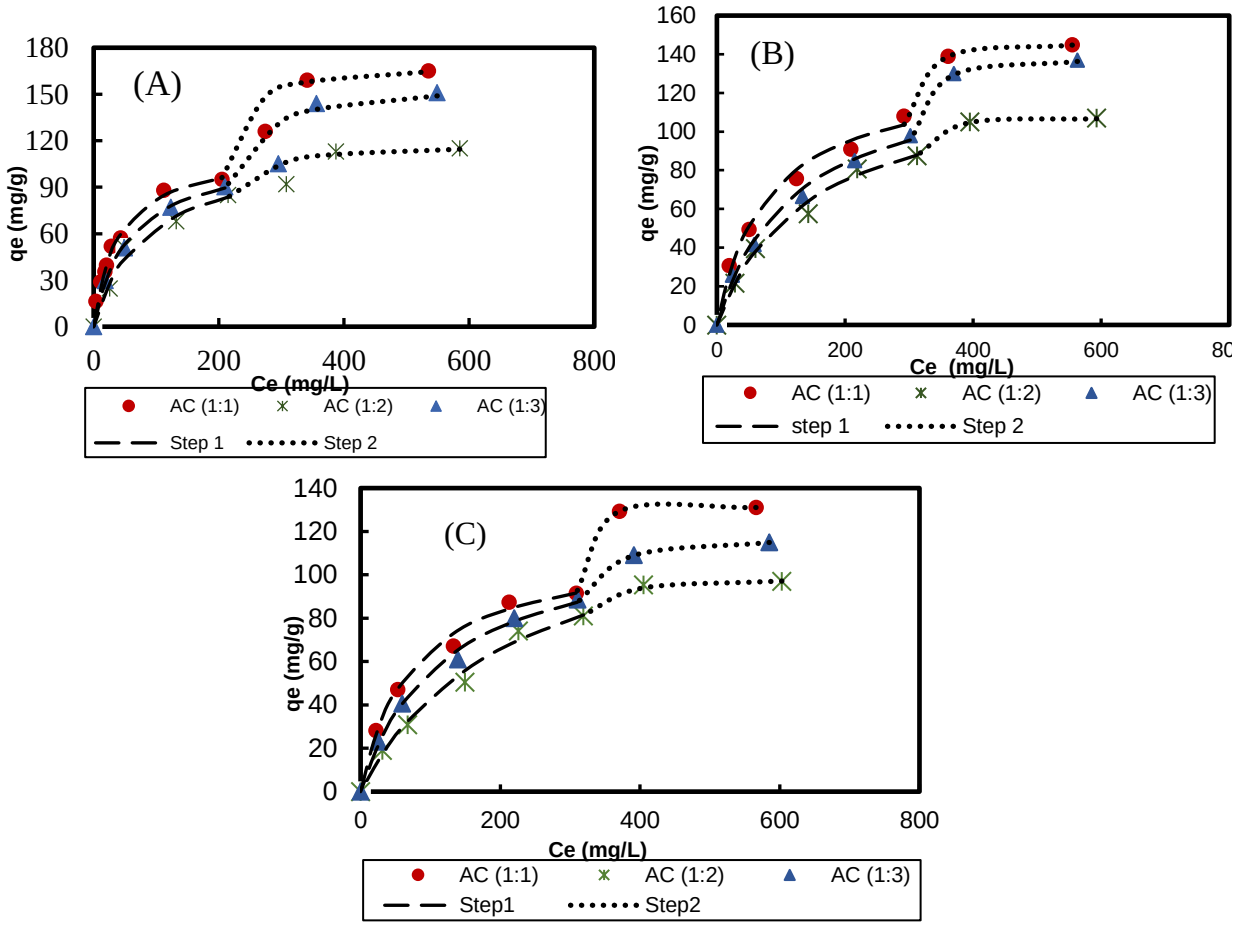

Fig. 10. Two steps Langmuir isotherm equation for Paracetamol removal using three adsorbents at (A) 25°C, (B) 35°C, and (C) 45°C

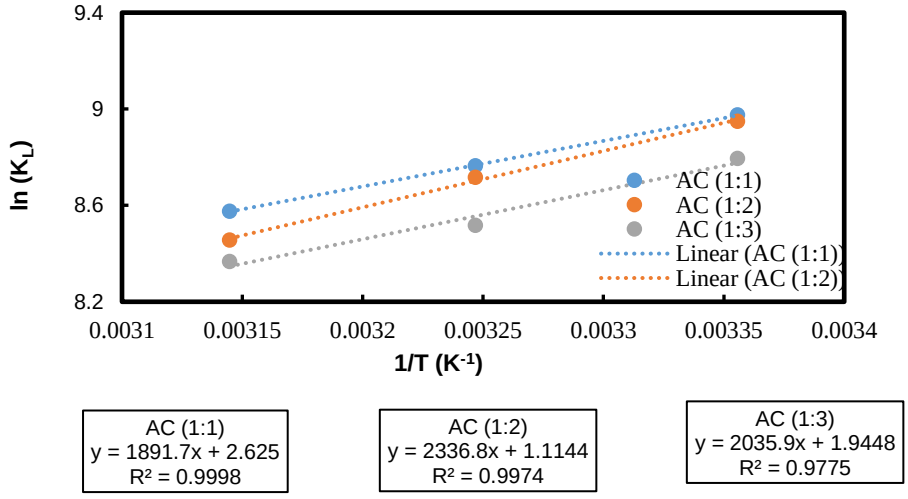

Fig. 11. Curve of thermodynamic parameters

Table 6. Thermodynamic Parameters for Paracetamol Removal

ACTIVATED CARBON	TEMPERATURE (K)	EQUILIBRIUM CONSTANT (K_L)	ΔG° (KJ/MOL)	ΔH° (KJ/MOL)	ΔS° (J/MOL.K)
	298	$7.9x10^3$	-22.23		
AC (1:1)	308	$6.4x10^3$	-22.44	-15.727	21.824
	318	$5.3x10^3$	-23.67		
	298	$7.7x10^3$	-22.187		
AC (1:2)	308	$6.1x10^3$	-22.28	-19.43	9.26
	318	$4.7x10^3$	-22.37		
	298	$6.6x10^3$	-21.79		
AC (1:3)	308	$5x10^3$	-21.96	-16.926	16.169
	318	$4.3x10^3$	-22.24		

4. CONCLUSION

In this paper, a new activated carbon was formulated for the entire removal of the paracetamol a painkiller from aqueous solutions. Manufactured ACs were validated to remove paracetamol from the aqueous solution. The optimal parameters were tested for the removal process such as contact time, solution pH, solution concentration, adsorbent weight, temperature, and AC(DP: Acid)ratio. The maximum uptakes were 165 mg/g, 115 mg/g and 151 mg/g for activated carbon ratios (1:1), (1:2) and (1:3), respectively. Paracetamol optimum adsorption conditions were 150 minutes of residence time at pH=7, 25 °C and the best ratio was (1:1). The entire removal of the dissolved paracetamol from the solution was occurred using 0.8 g of AC (1:1), 1 g of AC (1:2), and 0.9 g of AC (1:3). As adsorption kinetics and equilibrium isotherm models showed that pseudo-second order and two-step Langmuir models were very suitable for representing adsorption results.The process was exothermic, spontaneous as thermodynamic study illustrated. The physisorption process facilitated the regeneration process as it's efficiencies were 60% using hot water.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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