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Kinetics, Thermodynamics and Adsorption of BTX Removal From Aqueous Solution via Date-Palm Pits Carbonization Using SPME/GC-MS.

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Abstract

Benzene, toluene and xylene(BTX) compounds are toxic organic compounds that appear in underground water resources as results of leakage from underground fuel tanks and also improper waste discharge of oil and petrochemical industries. In this work, Palm date pits (Majhool) were used as the precursor in the preparation of activated carbon. The palm pits were activated and impregnated using different chemicals to achieve the best surface area. Adsorption of BTX compounds from water using activated carbon and impregnated by $FeCl_3$ was investigated in terms of contact time, adsorbent dose, temperature, *p*H and BTX concentration. Results indicated that the adsorption effectiveness was increased with increasing the *p*H, dose amount and the contact time. On the other hand, the adsorption efficiency was found to increase with decreasing the temperature. The equilibrium adsorption isotherm was explained using Langmuir and Freundlich models. BTX adsorption was better represented by Langmuir model. The kinetic of adsorption was studied using pseudo-first order, pseudo-second order and intraparticle diffusion. It was found that the adsorption followed pseudo-second order. Adsorption thermodynamic parameters for BTX adsorption such as standard enthalpy $\Delta H°$, standard entropy $\Delta S°$ and standard free energy $\Delta G°$ were calculated. The shape, size and surface area of the samples were determined using SEM, iodine number and BET. The effect of activating agent on the adsorption efficiency of BTX was also studied.

Keywords: BTX, adsorption, contamination, GC/MS, isotherm, kinetics parameter.

1. Introduction

Water is one of the most valuable resources on planet earth. It is the lifeline of almost all living things on earth. Although this fact is widely recognized, pollution of water resources is a common occurrence. During the last few decades, the rise of world population as well as industrial revolution has caused serious environmental pollution [1]. This has attracted a great deal of scientific, political, and media attention. Several dramatic accidents such as oil spills happened in the 1970s and latest in 2010 (British petroleum oil spillage in the Gulf of Mexico) encourage a lot of scientists to do research in cleaning those contaminants and spills from water. Water pollution occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds [2].Water pollution caused by inorganic and organic contaminants has

steadily increased in parallel with world population, industrialization, and urbanization especially in developing countries [3].Benzene, toluene and xylene (BTX) isomers are monocyclic aromatic hydrocarbons, which have a moderate solubility in water (benzene: 1600 mg/L; toluene: 500 mg/L and xylenes: 160 mg/L). These compounds are the major water-soluble constituents of petroleum derivatives (gasoline) [4]. In USA, it was found that the maximum level of benzene, toluene and xylene in drinking water to be 0.005, 1 and 10 mg/L respectively [5], while in Palestine, there is no study in this regard yet.

BTX compounds are toxic organic compounds that appear in underground water resources as results of leakage from underground fuel tanks, cracked pipelines, and also improper waste discharge of oil and petrochemical industries [5, 6, 7].

These pollutants have been found to cause many serious health side effects to humans (e.g. skin and sensory irritation, central nervous system depression, respiratory problems, leukemia, cancer, as well as disturbance of kidney, liver and blood systems) and therefore their removal from groundwater and surface water is essential [8]. Several processes have been examined for removal of BTX compounds from aqueous environment including oxidation, bioremediation and adsorption [9].Activated carbon has been the most widely used adsorbent, which is a versatile adsorbent due to its large area, polymodal porous structure, high adsorption capacity and variable surface chemical composition [9].

Date palm wastes have been used by different researchers as adsorbents for removing of water pollutants such as heavy metals and dyes. Al-Ghouti et al. investigated the adsorption mechanism of removing heavy metal ions (Cu^{2+} and Cd^{2+}) from aqueous solution using date pits as adsorbent [10]. While, El-Hendawy studied the adsorption of Pb^{2+} and Cd^{2+} ions onto date pits activated carbons [11].

Ashour studied the kinetics and equilibrium adsorption of methylene blue and remazol dyes onto the steam processed activated carbons developed from date pits [12]. In the other hand, activated carbon has been used for removal of phenolic and pesticides pollutants. For example, the potential of raw date stone powder for phenol adsorption from aqueous solution was studied by Okasha and Ibrahim [13].

Danish et al., reported the kinetics for the removal of paraquat dichloride from aqueous solution by calcium oxide activated date stone carbon [14].

This study is focused on studying the impact of water pollution by BTX. During this study we found the best method for carbonization date to be used for removal BTX from wastewater. Also, we studied both the isothermal and kinetics adsorption models. To understand the mechanism of adsorption both the thermodynamics and other variables like pH, temperature, concentration and contact time have been studied.

2. Materials and methods.

2.1 Precursor

Palm date pits (Majhool) were used as the precursor in the preparation of activated carbon. The date pitswere first washed with water to get rid of impurities, dried at 110 °C for 24 hrs, crushed using stainless steel mill, and sieved.

2.2 Chemicals and Reagent

All chemicals such as hydrochloric acid, sodium thiosulfate, iodine and sodium hydroxide were analytical grades with very high purity and purchased from Sigma-Aldrich (U.S.A). $FeCl_3$, $AgNO_3$ and $CuSO_4 \cdot 5H_2O$are used as chemical reagents for activation of date pits and were supplied locally from the chemical storage room at An-Najah National University. Benzene, toluene and xylene were used as adsorbate.

2.3 Preparation of Activated Carbon

A50 g of crushed stones were well mixed with 500 mL of $FeCl_3$,$AgNO_3$ or $CuSO_4 \cdot 5H_2O$solution at an impregnation ratio of 2 (weight of activating agent to weight of dried stone) for 24 hr at room temperature. The impregnated samples were next dried at 110^0C until completely dried and stored in desiccators. A stainless steel reactor was used for the carbonization of dried impregnated sample. This reactor was closed at one end and the other end had a removable cover with two holes, one

for inter the nitrogen and the other for escape of the pyrolyzed gases. The reactor was placed in a tube furnace and heated to reach an activation temperature (700°C) for 30 min; until no gas rising. At the end of activation time the carbonized sample was withdrawn from the furnace and allowed to cool. For removal of residual activated agent, the sample was soaked with 0.1M HCl solution such that the liquid to solid ratio is 10mL/g. The mixture was left overnight at room temperature and then filtered and washed with distilled water until the pH of filtrate reached 6.5-7 and to wash HCl out and making it neutral [15].

After that, the sample was dried at 110°C for 24 hrs and subsequently, was weighed to determine the yield of activated carbon product. Finally, it was stored in closed bottles. The flow diagram for activation process is summarized in Fig.1.

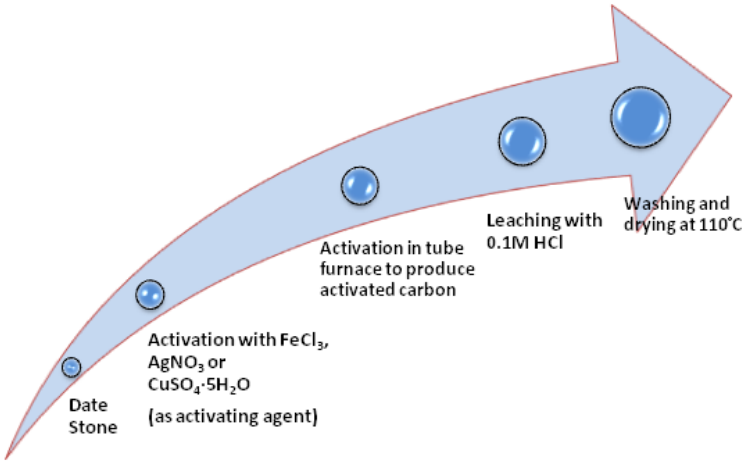

Fig. 1. The flow diagram for activation process.

The yield of the activated carbon was estimated from the following Equation:

$$\text{yield of activated carbon}\,(\%) = \frac{\text{weight of activated carbon}}{\text{weight of waste date stones}} \text{x}\,100\% \qquad \textbf{(1)}$$

2.4 Gas Chromatography Mass spectrometry (GC/MS)

In this work, the GC-MS coupled with SPME was used to determine the effect of contact time, dosage, temperature, pH, adsorption isotherm and kinetics of the adsorption by measuring the peak area at equilibrium using solid phase micro extraction (SPME). The analysis of BTX in water samples was conducted using solid phase microextraction (SPME) and GC/MS using the Clarus SQ 8S Mass Spectrometer from Perkin Elmer(U.S.A). The DB-5 column (60 m × 0.53 mm × 0.5 µm) was used. The experimental conditions are presented in Table 1 and the retention time with peak area was shown in Fig. 2.

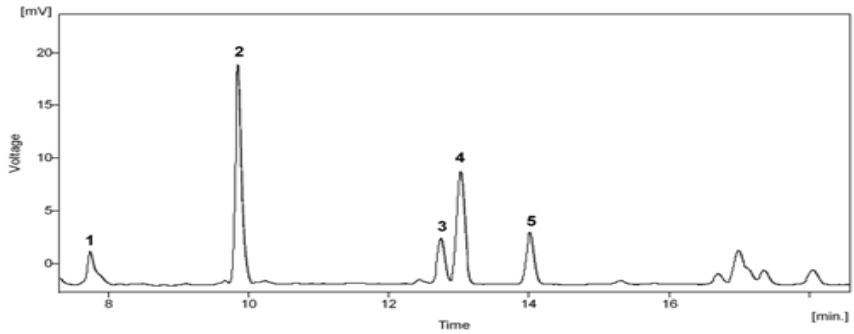

Fig.2. The chromatogram of water sample contaminated with 1.0 mg/L BTEX using SPME. 1– benzene; 2 – toluene; 3 – ethylbenzene; 4 – *p*-, *m*-xylene; 5 – *o*-xylene

Table 1. Experimental conditions for SPME and GC/MS.

SPME Conditions.

Sample Temperature	80 ˚C
Needle Temperature	110 ˚C
Transfer Line Temperature	120 ˚C
SPME Low/ SPME High	35 ˚C to 260 ˚C
Equilibration Time	8 min

Gas Chromatograph Conditions.

GC/MS	Clarus SQ 8S
Column	DB-5 (60 m x 0.53 mm x 0.5 μm)
Oven	40 ˚C for 0.5 min, then 35 ˚C/ min to 185 ˚C
Injector (PSS)	Temp Programmable Split/Splitless at 180 ˚C
Carrier Program (He)	1 mL/ min for 0.4 min, then 0.7 mL/ min

Mass Spectrometer Conditions.

Ionization Mode	Electron Impact
Acquisition	Full Scan
Filament Delay	1.5 min
Scan Speed	0.15 sec
Interscan Delay	0.04 sec
Run Time	4 min
Ion Source Temperature	200 ˚C
Transfer Line Temperature	200 ˚C

The values of limits of quantification (LOQ) and detection (LOD) for large volume direct aqueous injection method.

Analyte	LOD ($\mu g.l^{-1}$)	LOQ ($\mu g.l^{-1}$)
Benzene	0,8	3.5
Toluene	1.4	5.6
Ethylbenzene	2.1	5.2
p-Xylene	1.8	5.7
o-Xylene	2.2	5.9

2.5 Adsorption Efficiency

Several factors could affect the adsorption efficiency using activated carbon produced from date stone with $FeCl_3$ as activating agent.

2.5.1 Effect of contact time

To study the effect of contact time, 1.0 g of activated carbon was added to 50 mLBTX solution (50 mg/L) by volume at pH 10 and 25°C. These steps were repeated for different time intervals.

2.5.2 Effect of Dosage

Different weights were added to 50 mL (50 mg/L) BTX solutions at 25°C and pH 10 for 180 min to study the effect of dosage on adsorption.

2.5.3 Effect of Temperature

This effect was studied by adding 0.25 g of activated carbon to 50 mL (50 mg/L) BTX solutions at *p*H 10 for 180 min at different temperatures.

2.5.4 Effect of pH

This effect was studied using 0.25 g of activated carbon which was added to 50 mL (50 mg/L) BTX solutions for 180 min at 25°C and different *p*H (2 - 10).

2.5.5 Effect of concentration

To study the effect of concentration; 0.25 g of activated carbon was added to 50 mL of 10, 20, 30 and 40 mg/L solutions at *p*H 10 and 25°C for 180 min. The initial and final concentrations of BTX were measured.

The amount of adsorption at equilibrium, q_e, was calculated using the following equation:

$$q_e(mg/g) = \frac{(C_\circ - C_e)\cdot v}{m} \qquad (2)$$

Where $C_\circ$ and C_e (mg/L) are the liquid-phase concentration of BTX initially and at equilibrium, respectively. v is the volume of the solution (L) and m is the mass of dry adsorbent used (g). The data were fitted to Langmuir and Freundlich isotherms to evaluate the adsorption parameters.

The amount of removal percentage of BTX by AC was calculated using the following equation:

$$\mathrm{PR}\,(\%) = \frac{C_o - C_e}{C_o} \times 100\,\% \qquad (3)$$

Where PR is the removal percentage (%), C_o and C_e are the initial and equilibrium concentration of BTX solution (mg/L), respectively.

2.5.6. Kinetic study

For determining at what time the adsorption equilibrium is reached, 1 g of activated carbon was put into 50 mL of BTX at different concentrations.

The flask containing both carbon and BTX solutions was kept in a thermostatic bath at 20 ^{0}C with constant agitation (250 rpm). For the determination of equilibrium time, the aqueous samples taken at preset time intervals, and the concentration C_e (mol/L) of BTX remaining in the aqueous remaining solution was measured by SPME- GC/MS.

2.5.7 Adsorption isotherms

Adsorption experiments were carried out in the batch, at 20 ^{O}C, by adding 0.1 g of adsorbent to 100 mL of various BTX solutions at different concentrations. The mixtures were continuously stirred (250 rpm) for 180 min. This equilibrium time (t_e) has been previously determined from kinetic experiments. After such agitation, samples of 5 mL were taken for analysis using SPME - GC/MS to determine the concentration of BTX remaining in the aqueous phase. The adsorption capacity at time t, q_t (mol/g), were calculated using equations in the manuscript.

3.0 Results and Discussions

3.1 Carbon Characterization

The characteristics of date stones activated carbon and surface areas were studied and calculated. The pore structure characteristics of their sulting activated carbons were determined by nitrogen adsorption at 77.35K using an automatic micromeritics ASAP-2010 volumetric sorptionanalyzer. Priorto gas adsorption measurements, the carbon was degassed at 300^{0}C in vacuum condition for a period ofatleast 24hrs. Nitrogen adsorption isotherms were measured over a relative pressure (P/P_o) range from approximately 10^{-5} to 0.995.

The BET surface area (S_{BET}) and micropore surface area (S_{micro}) of the activated carbons were determined by application of the Brunauer–Emmett–Teller (BET) and Dubinin–Asthakov (DA) analysis software available with the instrument, respectively. The BET surface area was determined by means of the standard BET equation applied in the relative pressure range from 0.06 to 0.3 [16]. The data are summarized in Table 2.

Table 2. The characteristics and surface area of date stones activated carbon.

Sample code	Yeild	Iodine number (IN) mg/g	Surface area from IN; m^2/g	Surface area from BET m^2/g
AC/ $FeCl_3$	39.8%	739.775	694.149	893.780
AC/ $AgNO_3$	37.4%	676.275	635.519	818.289
AC/ $CuSO_4 \cdot 5H_2O$	42.3%	708.025	664.834	796.028

The results showed that at higher surface area which means that the use of date stones as activated carbon for removal of BTX from aqueous solutions was successful. On the other hand, the surface area was measured using iodine number and the high iodine number indicates that the date stone has a good capability to remove most of BTX which have molecular sizes in the range of microporescontent [16].

3.2 SEM Analysis of the activated carbon

SEM has been used to investigate the surface morphology of the prepared date stone activated carbon. Fig. 3. shows that many large pores were clearly found on the surface of the activated carbon. This shows that $FeCl_3$ was effective in developing pores on the surface of the precursor.

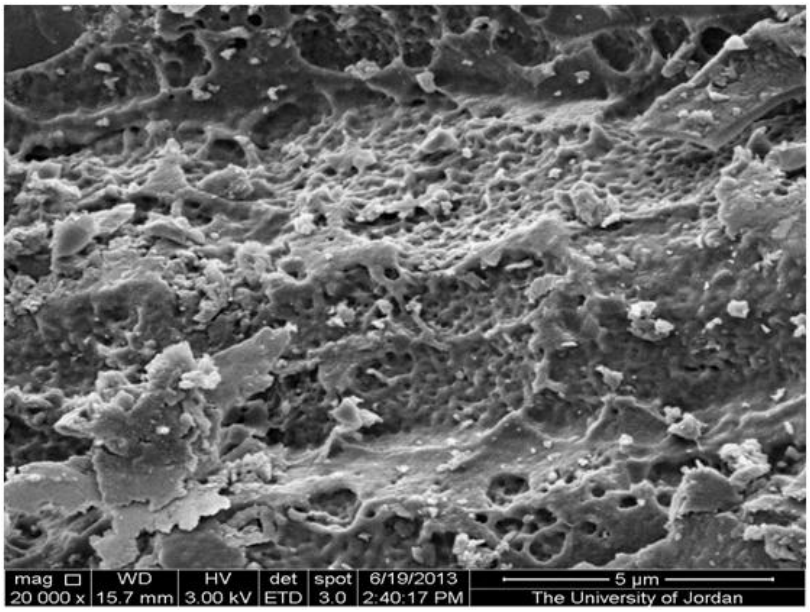

Fig. 3. SEM micrographs of AC/ $FeCl_3$.

3.3 Adsorption Efficiency of AC

3.3.1 Calibration curves for BTX

Different BTX standard solutions with different concentrations were prepared. The samples were analyzed using SPME - GC/MS. Calibration curves were constructed by plotting the value of area under the peak vs. concentration of standard BTX as shown in Fig. 4. A straight lines was obtained with a correlation factor (R^2)of 0.995, 0.999 and 0.991 for benzene, toluene and xylene respectively.

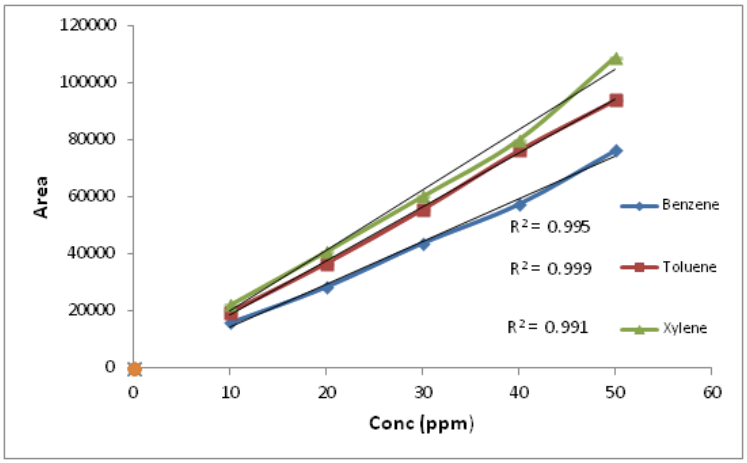

Fig. 4 Calibration curve for BTX standard solutions at 25 ºC.

***3**.3.2. Effect of the extraction time*

Extraction was performed from 5 to 80 min to determine the effect of extraction time. Fig. 5 shows the peak area versus extraction time profiles for the analyst. It can be seen that equilibrium is attained after 45 min. However, the increase on the peak areas for these analytes after 50 min extraction can be considered as not significant, but the results shows that there is degeneration on the method precision for longer extraction times. Therefore, the extraction time was fixed in 45 min.

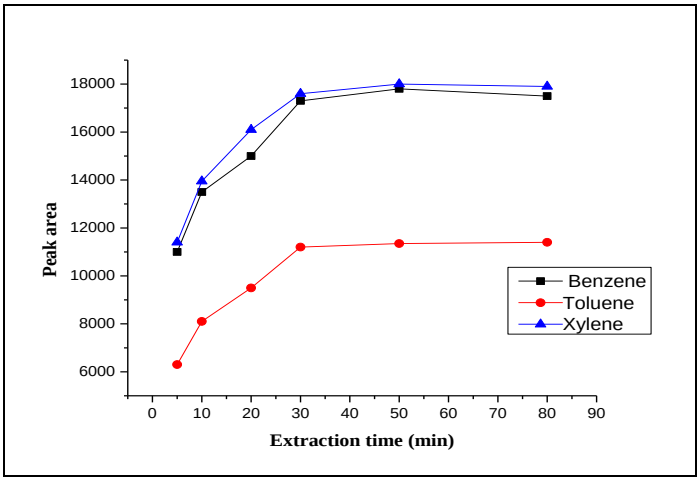

Fig. 5. The effect of extraction time on the extraction efficiency of BTX compounds when using SPME with methanol as the desorption solvent. Other extraction conditions: analyst concentration 10 g/L; stirring rate 600 rpm; heating temperature 55 ^{0}C.

3.3.3 Effect of contact time

The effect of contact time on the adsorption of BTX by date stones with $FeCl_3$ activating agent was studied in the range of 5-1440 min. The results are shown in Fig.6b. The Figure shows that BTX adsorption has been rapidly increased for the first 180min.Then the adsorption capacity increases slowly until it reached equilibrium.The fast adsorption at the initial stage may be due to the higher driving force making fast transfer of BTX ions to the surface of date stone particles and the availability of the uncovered surface area and the remaining active sites on the adsorbent [17].

The order of the sorption capacity of the modified adsorbent is B < T < X. This order may be due to the water solubility [18]. Many previous studies have confirmed that the sorption of BTX from aqueous solutions with various adsorbents follows a similar order as above [19].

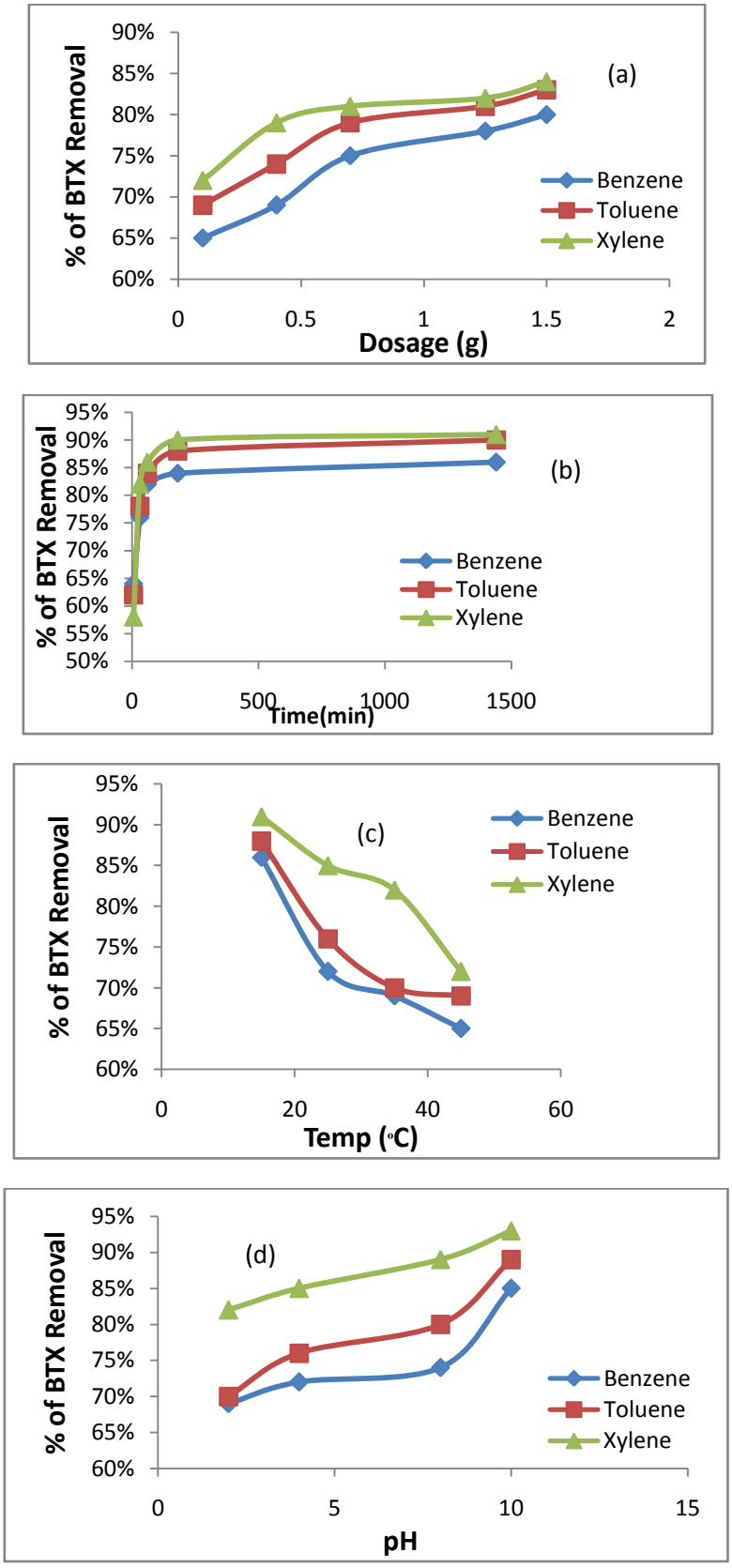

Fig. 6. The behavior of adsorption of BTX as (a) Effect of AC dosage (b) time (c) temperature and (d) pH

3.3.3 Effect of Dosage

The range of activated carbon dose which was used is 0.1-1.5 g. The effects of dosage are shown in Fig. 6a.The amount of BTX removal was increased rapidly until 0.7g of AC and then it increased slowly from 0.8 to 1.5 g.
In the first part, as the amount of AC increased at constant BTX concentration, the adsorption of pollutant increased because it provided more adsorption sites (i.e. more surface area)**.** But in the second part, the adsorptioneffectiveness was slowed down because most of BTX was adsorbed [20].

3.3.4 Effect of Temperature

This effect was studied at 15-45°C by adding activated carbon to 50 mg/L BTX solutions at pH 10 for 180 min. The results are summarized in Fig. 8. It can be seen from Fig. 6c.that, as the activation temperature increases, the adsorption effectiveness for BTX decreases. This is due to the loss of the volatile materialsandactive sites for adsorption at higher temperatures [21].
Generally, as temperature increases, the adsorption capacity decreases due to the following reasons:
1. Energy Content: As the temperature raises, the energy content increases, therefore, the adsorbent requires more energy to remain in a liquid state, thus directly affecting the adsorption balance.
2. Saturated vapour pressure: As the temperature rises, the vapour pressure increases making it more difficult to keep the adsorbent in its liquid state [22].

3.3.5 Effect of pH

The amount of BTX removal under the influence of *p*H was investigated in the range 2-10 and shown in Fig. 6d. From the Figure it can be noticed that the amount of BTX removals directly proportional to the degree of pH, and the adsorption value at *p*H 10 increases up to (85, 89 and 93%) for (benzene, toluene and xylene) respectively.
As we see in Fig. 6d, the addition of NaOH leads to decrease the solubility of all organic material because NaOH is more soluble in water, which means increases the adsorption of benzene, toluene and xylene, due to the salting out effect [19].

3.4 Adsorption Isotherm

Adsorption isotherm is the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature [23].
Langmuirequation used for the molecules that are in contact with a solid surface at a fixed temperature. The Langmuir Isotherm developed by Irving Langmuir between 1909-1916.It assumes a monolayer adsorption onto a uniform adsorbent surface with energetically identical sorption sites [24]. The linear form of Langmuir isotherm Equation is described by the following Equation (eq. 4):

$$C_e/q_e = (1/q_{max})C_e + 1/q_{max}\ 1/K_L \qquad (4)$$

where $C_e$is the solution centration ate equilibrium (mgL^{-1}), q_e is the amount of BTX that is adsorbed at equilibrium (mg. g^{-1}), $q_{máx}$is the monolayer capacity of the adsorbent (mg. g^{-1}), and K_L is the Langmuir adsorption constant, which is related to the energy of adsorption (Lmg^{-1}). The graph C_e/q_e versus C_e is linear; its slope is $1/q_{máx}$ and the intersection with the C_e/q_e axis is $1/q_{máx}K_L$.
In 1909, Freundlich gave an empirical expression representing a relationship between the concentrations of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid.It describes equilibrium on heterogeneous surfaces and hence does not assume mono layer capacity [24 - 25]. The logarithmic form of the Freundlich isotherm is given by the following Equation (Eq. 5):

$$\log q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e \qquad (5)$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate per unit mass of adsorbent (mg/g), K_f and n are Freundlich constants.

The study of adsorption isotherm is important to determine the adsorption capacity of BTX by date stone activated carbon.

In order to achieve this, the data were fitted to Langmuir and Freundlich isotherms which describe the relationship between the amounts of BTX adsorbed and its equilibrium concentration in solution.

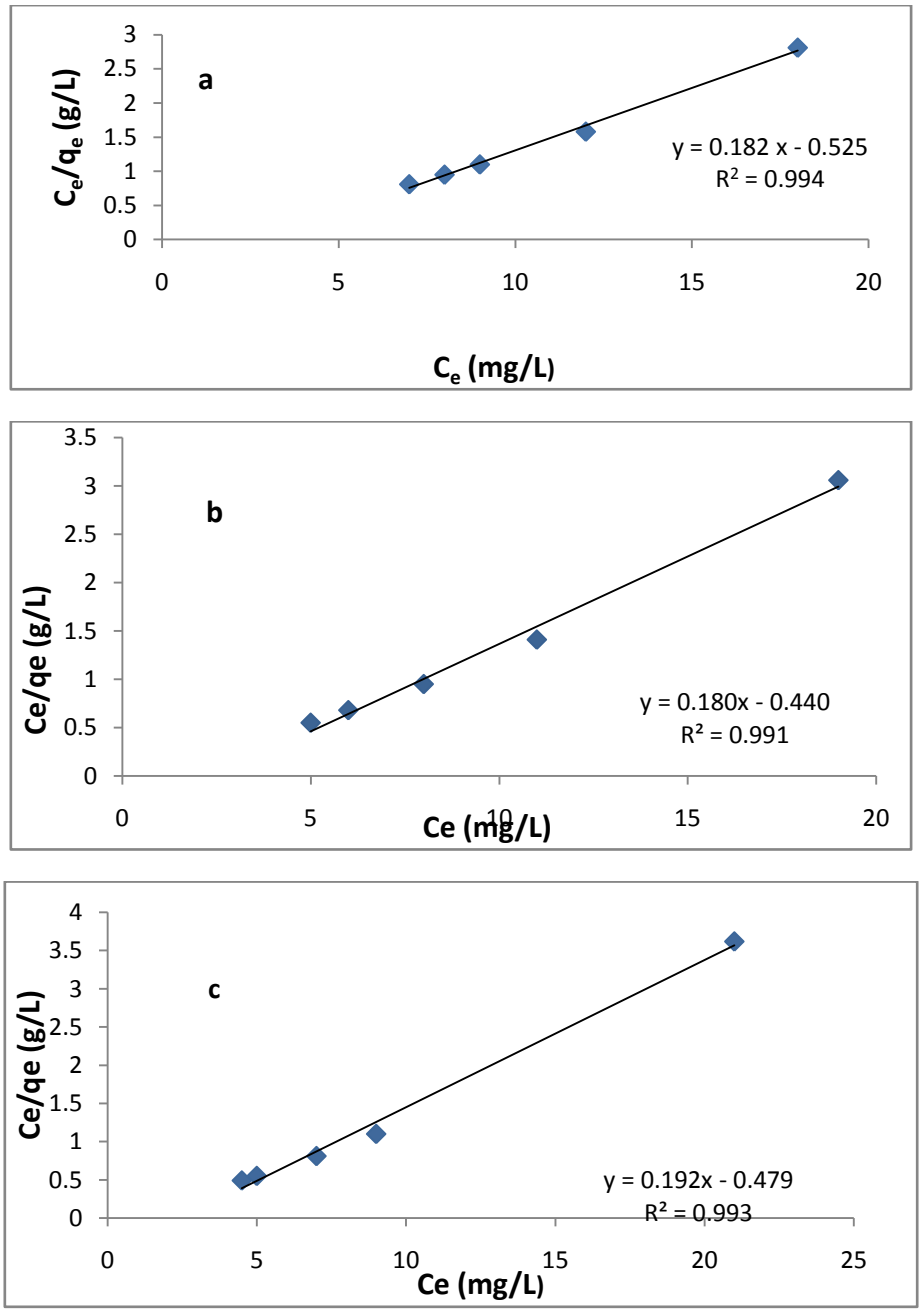

Fig. 7. Langmuir plot for (a) benzene (b) toluene and (c) xylene adsorption onto AC/$FeCl_3$ at temperature: 25ºC, pH: 10 and solid/liquid ratio 0.25 g/50 mL.

The adsorption parameterswere investigated by plotting C_e/q_e vs. C_e for Langmuir (Eq.4) and log $q_e$vs.logC_e for Freundlich(Eq.5) as shown in (Fig.10.a, b,c) and (Fig.11.a,b,c) respectively.

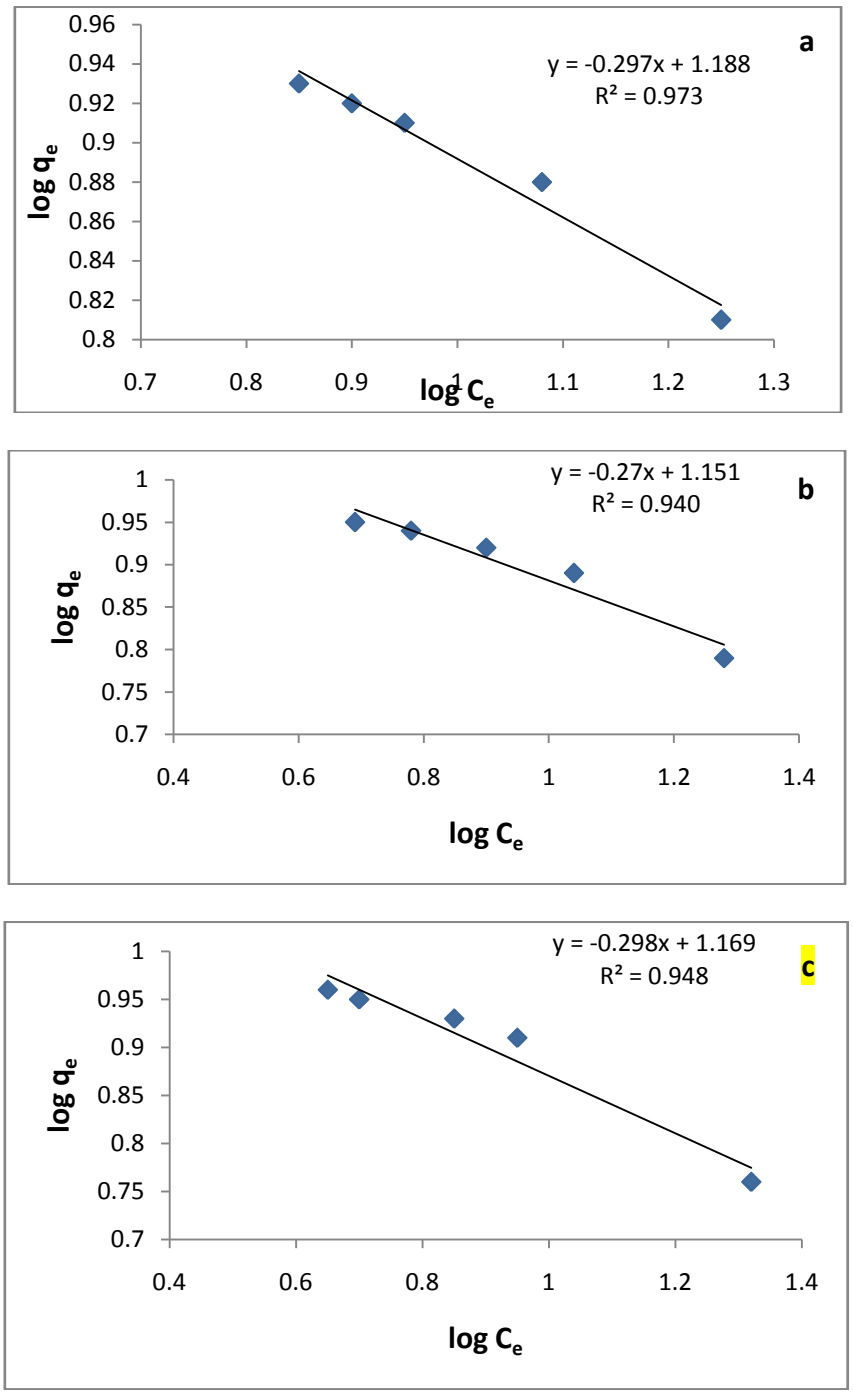

Fig. 8. Freundlich plot for (a) benzene (b) toluene and (c) xylene adsorption onto AC/$FeCl_3$ at temperature: 25 ºC, pH: 10 and solid/liquid ratio 0.25 g/50 mL).

The adsorption isotherm parameters and correlation coefficients which were found from the slopes and intercepts are summarized in Table 3.
As shown in Table 3, the correlation coefficients in Langmuir adsorption isotherm are very high and closer to one than in Freundlich.

Table 3. Langmuir and Freundlich isotherm parameters and correlation coefficient of BTX adsorption onto AC/$FeCl_3$.

Isotherm	**Langmuir**			**Freundlich**		
Adsorbate	**Parameters**			**Parameters**		
	q_o(mg/g)	**b** (L/mg)	**R^2**	**K_f** ((mg/g)(L/mg)1/n)	**n**	**R^2**
Benzene	5.47	-0.35	0.995	15.44	-3.37	0.973
Toluene	5.53	-0.41	0.992	14.16	-3.70	0.940
Xylene	5.19	-0.40	0.993	14.76	-3.35	0.948

In Freundlich isotherm, n valuegiving an indication of how the adsorption process issuitable.Adsorption process is considers as beneficial when nvalue is between 1 and 10, which means stronger interaction between the adsorbent and the adsorbate [26]. A value for (n) below one indicates a normal Langmuir isotherm, while (n) above one is indicative of efficient adsorption [26].In this study, the calculated n value as shown in Table 3.were below than 1 for all BTX compounds. Other thing as a conclusion, the adsorption of BTX follows Langmuir isotherm in this study.

3.5 Kinetics of adsorption

The process of removal BTX can be explained by using several kinetics models. In this study we used the first-pseudo, second-pseudo order and intraparticle models [27].

3.5.1 Pseudo-First Order Kinetics Model

Is a second order reaction, in which one of the reactants is present in such great amounts that its effect is not seen and the reaction thus behaves as first order.The simple form of first order model, is shown in (Eq. 6) [28].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (6)$$

Where k_1 is the rate constant, q_e is the equilibrium concentration (mg/g); q_t (mg/g) is the amount of adsorbed at any time t (min).

3.5.2 Pseudo -Second Order Model

The general form of the model is given in (Eq. 7) [29].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (7)$$

In which, k_2 is the equilibrium rate constant (g/mg.min) of pseudo-second order. q_e is the amount of adsorption sorbed at equilibrium (mg. g^{-1}), q_t is the amount of adsorbatesorbed at t (min). The straight line plots of (t/q_t) vs t have been tested to obtain rate parameters [30].

3.5.3 Intraparticle Model

Intraparticle diffusion model can be expressedby Weber and Morris [31], as the (Eq. 8)

$$q_t = k_i t^{0.5} + A \qquad (8)$$

Where k_i is the intraparticle diffusion constant and q_t(mg/g) is the amounts of adsorbate per unit mass of adsorbent at time t (min), the intercept A reflects the effects of the boundary layer thickness.
The experimental kinetics data for BTX adsorption on date stones are fitted with pseudo-firstorder, pseudo-second order and intraparticle diffusion models, (Eqs.6-8), to investigate the mechanism of BTX adsorption process.
The kinetics parameters and correlation coefficients at 50 mg/L initial adsorbate concentration have been calculated from the linear plots of log (q_e-q_t) versus t and t/q_t versus t, Figs 9 and 10a respectively, and the results are presented in Table 4.

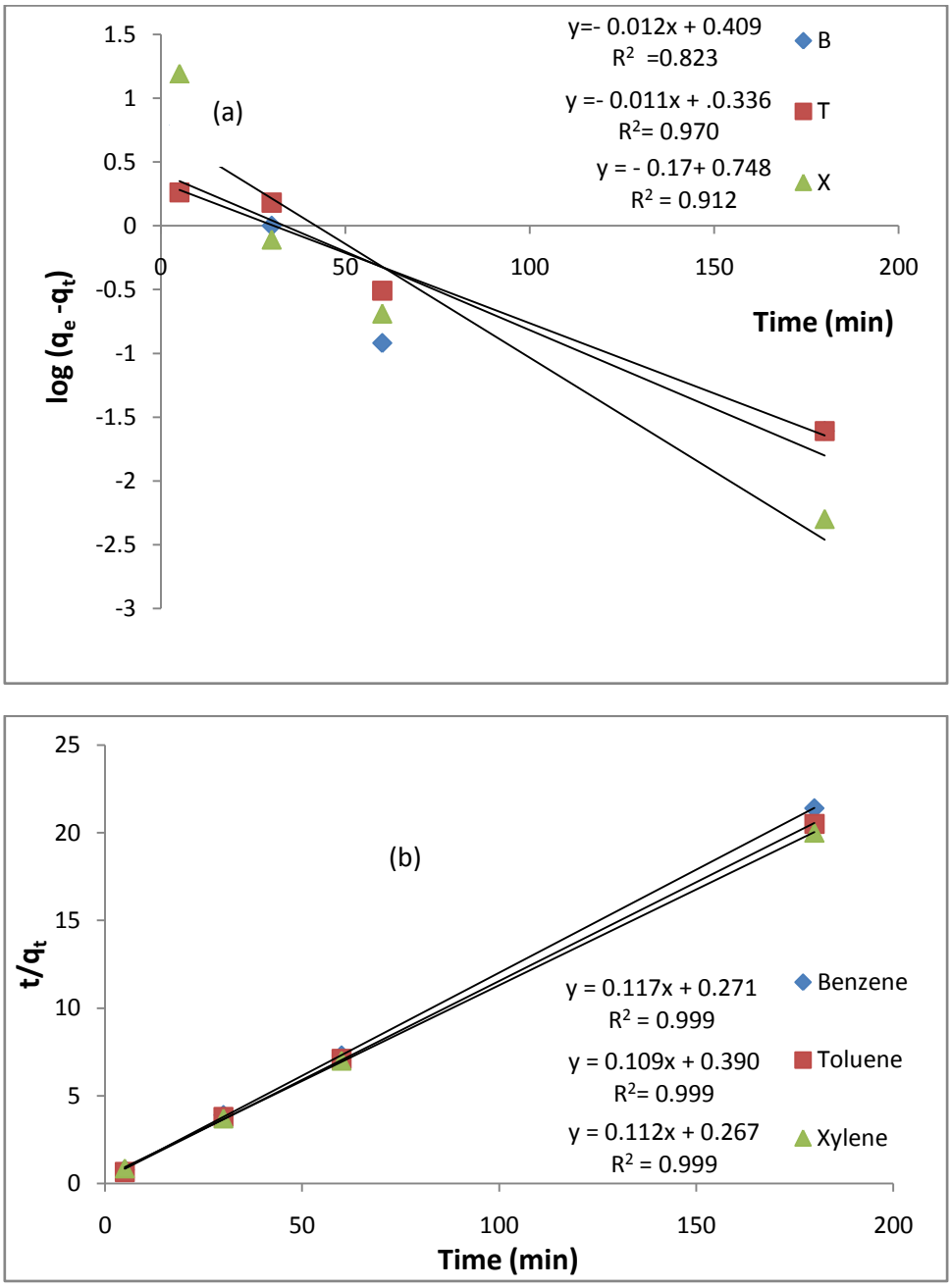

Fig. 9. Kinetics of BTX removal according to the (a) pseudo-first-order and (b) pseudo-second-order model by AC/$FeCl_3$ at temperature: 25 ºC, pH: 10 and solid/liquid ratio 0.25 g/50 mL).

The data shows large difference between the experimental and calculated adsorption capacity (q_e) for BTX on the pseudo-first order model and good agreement based on the pseudo-second order model. On the other hand, the agreement coefficient of the pseudo-second order model was larger than for pseudo-first order model, indicating a poor pseudo-first order to fit the experimental data. Seifi et al.(2010) studied the adsorption kinetics of BTEX onto natural zeolite nanoparticles that were modified with surfactant and also found that the pseudo-second-order model best described the experimental data [31].

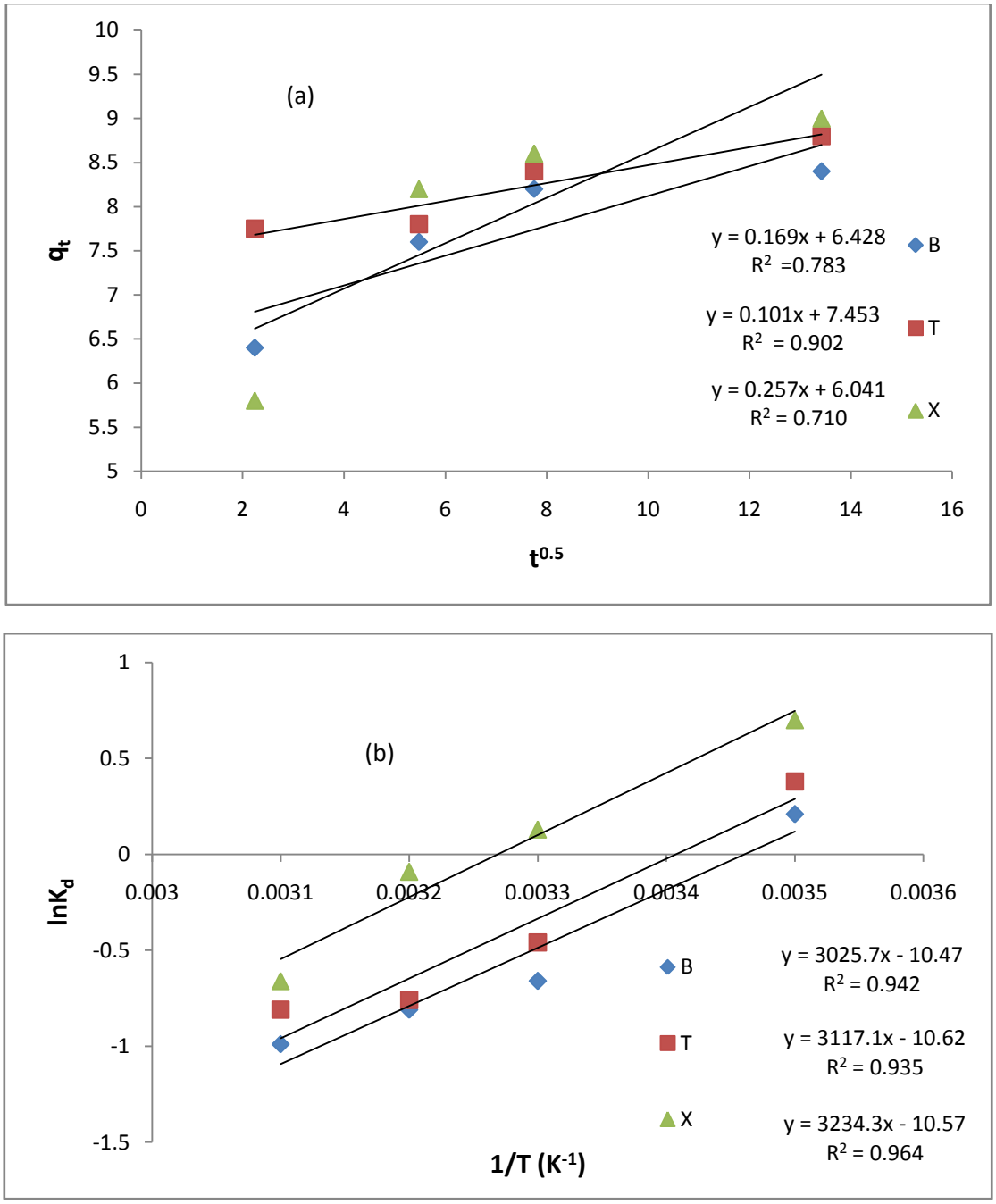

Fig. 10. (a) Kinetics of BTX removal according to the intra-particle diffusion model by AC/$FeCl_3$ and (b) Plot of lnKd versus 1/T for BTX adsorption on AC/ $FeCl_3$ at temperature: 25ºC, pH: 10 and solid/liquid ratio 0.25 g/50 mL).

Table 4. Pseudo-first-order and pseudo-second-order kinetic model parameters for BTX adsorption by AC/ $FeCl_3$.

Adsorbent	q_e (exp) (mg/g)	Pseudo-first order kinetic model		R^2	Pseudo-second order kinetic model		R^2
		k_1 (min-1)	q_e(calc) (mg/g)		k_2 (g/mg.min)	q_e (calc) (mg/g)	
Benzene	8.6	0.0123	1.51	0.8231	0.0507	8.52	0.9999
Toluene	9.0	0.0110	1.40	0.9704	0.0305	9.17	0.9999
Xylene	9.1	0.0178	2.11	0.9127	0.0475	8.87	0.9997

This suggests that the pseudo-second order is better to describe the mechanism of BTX adsorption process by date stone activated carbon which means was chemisorption between adsorbentsurfaceandadsorbate [31].

Table 5. Intra-particle diffusion kinetic model parameters for BTX adsorption by AC/ $FeCl_3$.

Adsorbent	K_i (mg/g $min^{1/2}$)	A	R^2
Benzene	0.1691	6.728	0.7831
Toluene	0.1016	7.4535	0.9021
Xylene	0.2574	6.0412	0.7109

For the intraparticle diffusion model (Eq. 8), the q_t values are calculated using the Eq. 6. The values of K_i and A are found from the slope and the intercept of the linear plot of q_t versus $t^{0.5}$.The results are shown in Fig. 10a, Table 5.

The intraparticle diffusion model is used to describe the diffusion mechanism. If the straight lines did not pass through the origin, this indicates that the rate is limited by mass transfer across the boundary layer and the mechanism of removal is complex [32]. While the value of A give an information about the thickness of the boundary layer. In our study the line did not pass through the origin, hinting that pore diffusion may not be the only rate-controlling step in the removal of the adsorbates, especially for the early stages of adsorption[33].The controlling step rate is believed to be the surface-adsorbate interaction due to the high abundance of the adsorbing sites on the external surface which becomes the pre-dominant effect [34]. The data are shown in Fig. 10a. Considering K_i(Eq. 8),the intraparticle diffusion rate constants listed in Table 5, an irregular trend appears for the BTEX components relative to each compound; this may be due to the small fractions sorbed per unit time.

3.6 Adsorption Thermodynamics

Thermodynamic considerations of the adsorption process of BTX on date stones are necessary to conclude whether the process is favorable or not.

This behavior was evaluated by the thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) (Eq. 9).

$$\ln k_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R}\frac{1}{T} \qquad (9)$$

Where T (K) is the absolute solution temperature, R (8.314 J/mol K) is the universal gas constant and K_d is the distribution coefficient which can be calculated as(Eq. 10):

$$K_d = C_{Ae}/C_e \qquad (10)$$

Where C_{Ae} (mg/L) is the amount adsorbed on solid at equilibrium and C_e (mg/L) is the equilibrium concentration. ΔG° can be calculated as below (Eq. 11):

$$\Delta G^{\circ} = -RT \ln K_d \qquad (11)$$

According to (Eq. 9), the ΔH°, ΔS° parameters for BTX can be calculated from the slope and intercepts of the plot of In K_d versus 1/T respectively (Fig. 10b), and ΔG° values are obtained from the (Eq. 11). While the values of $K_d$calculatedby using (Eq. 10). The obtained values of ΔH°, ΔS° and ΔG° are listed in Table 6.

Table 6. The values of the thermodynamic of adsorption at various temperatures and various adsorbents.

Adsorbent	ΔH° (kJ/mol)	ΔS° (J/mol K)	ΔG° (kJ/mol)			
			288 K	298 K	308 K	318 K
Benzene	-25.16	-87.06	-0.50	1.58	1.94	2.37
Toluene	-25.91	-88.30	-0.90	1.14	1.95	2.14
Xylene	-26.89	-87.89	-1.68	-3.22	0.23	1.74

The negative values of enthalpy (ΔH°) indicate that the nature of the adsorption is exothermic and its magnitude gives information on the type of adsorption, which can be either physical or chemical adsorption.
Furthermore, the negative values of entropy (ΔS°) show that the decrease in the randomness at sorbate-solution interface during the adsorption process.
A negative ΔG° value means the reaction is favorable. Increase in the value of ΔG° with rise in temperature show that the adsorption is more favorable at lower temperature.

Conclusion

The results that have been obtained in this work can be summarized in the following points:

1. Using of activated carbon produced from date stones to remove the BTX from water is good and efficiency method.
2. Date stones have high surface area which means that the use of it for the removal of BTX from aqueous solutions is successfully.
3. The values of surface area showed that the using $FeCl_3$ as activating agent for date stones is better than $CuSO_4.5H_2O$ and $AgNO_3$.
4. The results showed that the adsorption of BTX by date stones activated carbon increase by increasing time, dosage and pH.
5. The results indicate that the adsorption effectiveness was increased with decreasing temperature.
6. Adsorption of BTX by AC/$FeCl_3$ followed Langmuir isotherm.
7. Experimental data showed that BTX adsorption can be represented by pseudo- second order model.
8. Intraparticle model which describe the diffusion mechanism showed that the mass transfer happen across the boundary layer.
9. The results of ΔH°, ΔS° and ΔG° show that the adsorption of BTX by AC/ $FeCl_3$ is exothermic and favorable process.
10. The adsorption of BTX by $FeCl_3$ is physical adsorption.

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