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Medicinal product (Paracetamol) removal by adsorption in aqueous solution; Investigation of kinetic parameters, equilibrium and mass transfer

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ABSTRACT/RESUME

Abstract: *The adsorption behavior of the medicinal* product, *paracetamol, using commercial activated carbon in aqueous solution was investigated. In this work, the study of equilibrium, kinetics as well as the identification of the mass transfer stages that occur in adsorption were carried out.It was found that the appropriate isotherm model for the equilibrium process was the Langmuir, and the monolayer adsorption capacity was found to be 104.17mg.g^{-1} at 298 K. The result of the adsorption kinetics shows that the adsorption maximum was reached at 60 min and follows the linear form of the pseudo second order kinetics with R^2 = 0.99 for the three studied concentrations. Two mathematical models were tested in order to determine the limiting step of the mass transfer of the paracetamol adsorption process onto activated carbon. The results showed that the adsorption process was governed by external diffusion*

I. Introduction

Contamination of water and soils with pharmaceutical residues is an emerging environmental concern. Indeed, the presence of pharmaceutical residues, even at low concentrations in waste water, causes in recent years, a risk to aquatic and human life [1]. Several drugs are extensively used as antibiotics, antiseptics, anti-inflammatory and disinfectants [2]. These compounds are unfortunately released in urban waste water, spread through the water cycle, due to their low removal by sewage treatment plants. Paracetamol is an analgesic and anti-inflammatory agent commonly used for humans and animals [3, 4]. Clinical research shows that overdoses of paracetamol may be toxic and result in severe side effects, such as kidney injury and liver failure [5]. During therapeutic use of paracetamol, approximately 58-68% of the dose may not be used by the body [6]. Thus, it is directly released into the environment as the primary form or metaboline. It is the most important pharmaceutical compound in wastewater and river water [7]. Conventional waste water treatments for pharmaceuticals are ineffective in eliminating and/or degrading most of these compounds. Therefore, residual quantities remain in the treated water and, they are found to accumulate in drinking water [8, 9]. Indeed, the elimination of some emerging contaminants in waste water by conventional treatment is rather low due to the fact that most of them are resistant to biological degradation. Consequently sewage effluents are one of the main sources of these compounds and their metabolites, which can potentially end up in finished drinking water [10]. The presence of traces of pharmaceuticals in drinking water has a toxic effect on human and animal health. To preserve water quality and protect human health , water contaminated with emerging pollutants should be effectively treated using an appropriate technique, Various processes such as photocatalytic degradation [11] advanced oxidation [12] , biological treatment [13] and adsorption [14] are some of possible ways which could be employed in the removal of several pharmaceuticals.

In this work, adsorption of paracetamol (N-acetyl-aminophenol), a water emerging contaminant, onto commercial activated carbon is studied. Despite its high cost, commercial activated carbon can be regenerated. In addition, paracetamol being an emerging pollutant, we decided that it would be more interesting to have the maximum results on its adsorption on a commercial activated carbon before using low cost natural adsorbents.The influence of various experimental parameters including: pH, adsorbent dosage, contact time, and initial concentration were studied in order to obtain the optimum conditions for the maximum adsorption efficiency. Four sorption kinetic models (Pseudo-first order, Pseudo second order, Fractional power, Elovich) and four isotherms (Langmuir, Freundlich, Temkin, and Redlich-Peterson), were tested in order to describe observed sorption phenomena. To identify mass transfer limiting steps during adsorption, the models of Boyd and intraparticle diffusion were studied.

II. Experimental

II.1. Materials

Paracetamol [(N-acetyl-4-aminophenol), ATP], an Analgesic/anti-inflammatory compound commonly called acetaminophen was bought by Anqiu Lu'An Pharmaceutical Co., LTD (Standard BP2013). The paracetamol, molecular formula, molecular weight, $\lambda_{\max}$, pKa, molar volume and molecular volume are, respectively, , $C_8H_9NO_2$, 151.17 g/mol, $\lambda_{\max}$ = 244 nm (measured value), 9.5, 120.9 cm^3/mol and 8.85x4.21x2.3 L x l x e $(Å)^3$. Paracetamol molecule is shown in Figure 1. Stock ATP solution (1000 mg L^{-1}) was prepared by dissolving 1 g of ATP in 1 L of double distilled water. ATP solution of desired concentration was prepared by further dilution of the stock solution with suitable volume of double distilled water. A commercial activated carbon (Biochem Chemopharma, CAS 7440_44.OC) was used. The specific area, granulometry, porous volume and density were, respectively, 915 m^2/g, 1.25 – 3.15 mm, 0.4 cm^3/g and 230 kg/m^3.

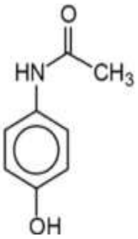

Figure1. *Chemical structure of paracetamol*

II.2. Determination pH of the point of zero charge pH$_{PZC}$

The zero point of charge pH$_{pzc}$ of adsorbent was determined according to [15].

II.3. Batch Adsorption Experiments

Adsorption experiments were conducted using the batch method with the influence of solution pH, adsorbent dosage, time and initial dye concentration. Adsorption was performed by agitating a given dose of the adsorbent with 50 ml of ATP solution of desired concentration at 20ºC in different shaker flasks. The shaking speed was maintained at 200 rpm throughout the study. After centrifugation, ATP concentration was determined by **a** Perkin Elmer Lambda 25 UV-VIS spectrophotometer**,** using a calibration curve based on absorbance at $\lambda_{\max}$=244 nm versus ATP concentration.

The experiments were conducted in duplicate and were found reproducible. The effect of pH was performed by examining the adsorption of ATP over the pH range of 1.32 to 12. The pH of dye solution was adjusted with NaOH and HCl solution. The amount of paracetamol adsorbed (mg.g^{-1}) at time (t) was calculated according to equation (1).

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

Where, C_0 (mg.L^{-1}) is the initial ATP concentration, C_t (mg.L^{-1}) is the concentration at any time t, V (L) is the volume of the solution and m denotes weight of dry adsorbent in (g).

The amount of ATP adsorbed at equilibrium, q_e (mg .g^{-1}) was calculated according to equation (2).

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

Where C_e (mg/l) is the concentration at equilibrium time

ATP removal percentage can be calculated by equation (3).

$$R(\%)_t = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (3)$$

Apart from the correlation coefficient (R^2), the residual root mean square error (RMSE) were also used to measure the goodness-of-fit. RMSE is defined by equation (4).

III. Results and discussion

III.1. Determination of pH_{PZC} adsorbent

The pH_{pzc} is the point where the curve of final pH - initial pH (pHi-pHf) crosses the line at initial pH (pHi). The used activated carbon adsorbent has a pH_{ZPC} of 6.5.

III.2. Batch Adsorption Study

III.2.1. Effect of initial ATP concentration and contact time

The uptake ($mg.g^{-1}$) of ATP removal versus time curves is single, smooth and continuous leading to saturation (Fig.2). A very rapid adsorption was found during the first 45 minutes due to the availability of a large number of vacant surface sites. However, the amount of ATP adsorbed increased with time and reached a constant value after 60 minutes. After the equilibrium time, the amount of ATP adsorbed did not alter with time. Similar results were reported [17].

Figure 2 also shows that the amount of ATP adsorbed increased with the increase in initial ATP concentration which is due to the increase in the driving force of the concentration gradient [18].

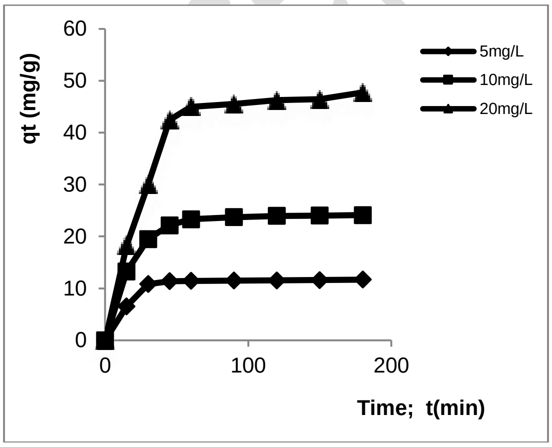

Figure 2. *kinetics of ATP removal (pH=6.68, [adsorbent]=0.4gL*$^{-1}$*).*

$$RMSE = \sqrt{\frac{1}{m-2}\sum_{i=1}^{m}(q_i - q_{ie})^2} \quad (4)$$

Where the observation from the batch experiment is q_i, q_{ie} is the estimate from the isotherm for corresponding and *m* is the number of observations in the experimental isotherm. The smaller RMSE value indicates the better curve fitting [16].

III.2.2 Effect of pH

pH strongly influences the adsorption because it affects the properties of both adsorbent and adsorbate. The adsorption behavior of ATP using activated carbons, in acidic and basic solutions was investigated. The effect of pH on the removal of ATP is shown in Figure 3. From the data, it is obvious the adsorption capacity of ATP on the activated carbon does not change significantly when the pH of the solution increased from 1.32 to 10. However, the adsorption capacity decreased sharply when the pH of the solution is increased from 10 to 12. This variation of the adsorption capacity can be attributed to the charge of the surface of activated carbon which is linked its pH of zero charge (pH_{ZPC}).

When the pH of the solution is lower than the pH_{ZPC}, the surface of the adsorbent is positively charged. When the pH of the medium is greater than pH_{ZPC} the surface of the adsorbent is negatively charged. The negativly charged ATP and the surface negativly of the adsorbent encumbered the adsorption process through the electrostatic repulsion, which, in turn reduced the removal of ATP by adsorbent. Similar trends were reported for adsorption of ATP using activated carbon of dende and babassu coconut mesocarp [19].

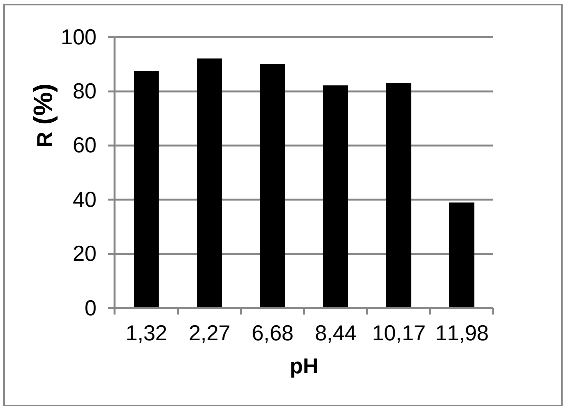

Figure 3. *Effect of the solution pH on the adsorption of ATP ([adsorbent] =0.4gL*$^{-1}$*, t=60 min)*

In this work it was found that adsorption decreases in basic solutions. The ATP molecule is a weak acid with pKa value between 9.5 and 9.9 [20]. For the solutions of pH <9, ATP molecules are neutral. When the pH is around 9.5, ATP is in its zwitter ionic form while in solutions of pH > 10, the anionic form predominates.
Figure 4 illustrates the optimized structure and electrostatic potential maps for both forms of the ATP molecule; neutral (a) obtained at pH 2 and anionic (b) at pH 11.

At pH 12 the dissociation of hydrogen of the phenolic group creates a high electron density region; ATP is therefore negatively charged which results in increasing repulsion with the activated carbon surface, which explains the decrease of the adsorption capacity.
The observed differences between the results obtained at acidic and neutral pH are due to the influence of the pH in the ionization state of weak electrolyte of ATP (pKa ~ 9.5) and the charges that may appear on the carbon surface. At pH 11, ATP molecule was repealed by the negatively charged carbon surface**.** At pH_{PZC} and pH 2, the neutral ATP molecules were absorbed by the equally neutral and positively charged adsorbent surface.

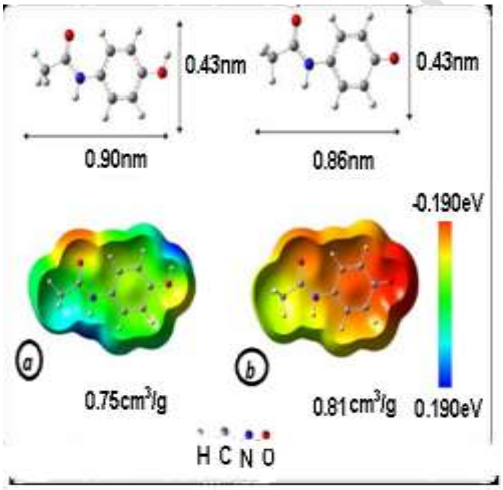

Figure 4. *Optimized structure and potential Electrostatic map for the - a) Neutral (pH 2) b -) Anionic (pH 11) forms ATP [19]*

III.2.3 Effect of adsorbent dosage

Figure 5 shows the effect of adsorbent dosage on the amount of ATP adsorbed by contacting 50 ml of ATP solution with an initial concentration of 20 mg/l for 1 h at pH=6.68.
The amount of ATP adsorbed per unit mass of adsorbent decreases with increasing the quantity of adsorbent.

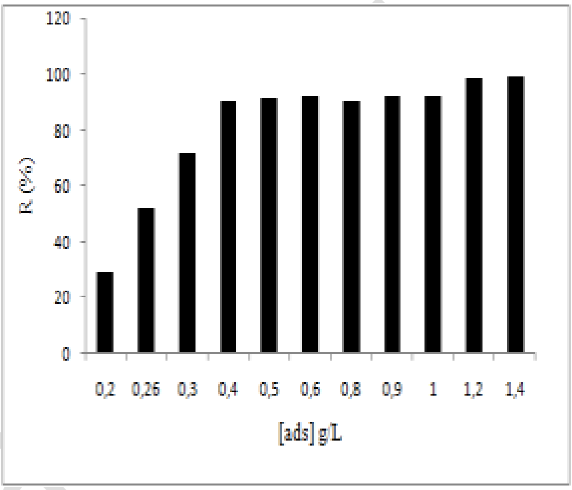

Figure 5. *Influence of adsorbent loadings on amount of ATP adsorbed (pH=6.68, t=60min)*

By increasing the quantity of adsorbent from 0.2 to 1.4 $g.L^{-1}$, removal rate increases from 29.37 to 98.97 %. After that, the increase in the dose of activated charcoal did not remarkably affect the efficiency of the process. A similar phenomenon was observed [21].

III.2.4 Adsorption kinetics

Table 1 shows some of the most important kinetic models which were employed in this work.

Table 1. *Kinetic models and their linear forms*

Kinetic model	Equation	Linear form	Plot
Fractional power	$q_t = k\,t^{\nu}$	$\ln q_t = \ln k + \nu \ln t$	$\ln q_t$ *vs.* $\ln t$
Pseudo first order	$q_t = q_e[1-\exp(-k_1 t)]$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t)$ *vs.* t
Elovich	$q_t = \ln(a_E \beta_E t)^{1/\beta_E}$	$q_t = \frac{\ln a_E \beta_E}{\beta_E} + \frac{1}{\beta_E}\ln t$	q_t *vs.* $\ln t$
Pseudo second order	$q_t = \frac{k_2 q_e^2 t}{(1+k_2 q_e t)}$	$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe}$	$\frac{t}{q_t}$ *vs.* $\frac{1}{t}$

Where k_1 is the constant rate of pseudo-first-order adsorption (min^{-1}), k_2 is the constant rate of pseudo-second-order adsorption ($g\ mg^{-1}\ min^{-1}$), ν the rate constant of power function (min^{-1}), a_E is the initial sorption rate (mg/g min), and the parameter β_E is related to the extent of surface coverage and activation energy for chemisorption (g/mg).

In order to describe the adsorption of ATP onto actived carbon, the four kinetic models (Table 1) were fitted. The analogy between experimental data and the model predicted values was expressed by the R^2. A high R^2 value indicates that the model successfully describes the kinetics of adsorption. From Table 2, the data followed the power function model as the value of v was less than 1 [22].

However, the kinetic data fitted poorly fractional power model as the value of R^2 is low. As shown in Table 2, the data were in disagreement with pseudo-first-order model, as very low value of R^2 was observed.

The Elovich model fits the kinetic data with acceptable correlation coefficient. The kinetic data were observed to fit well the pseudo-second-order model. The correlation coefficient (R^2) was observed to be close to 1. Thus the equilibrium adsorption capacities calculated by this model are very close to the experimental values. The initial rapid adsorption is attributable to surface adsorption. When the surface sites reach their saturation, the molecule begins to diffuse into the pores of the activated carbon and adsorbs on its internal walls. The low values of k_2 (0.0043 and 0.0009) confirm the slow diffusion of the molecules.

III.2.5 Equilibrium Isotherms

In this study, various adsorption isotherms Freundlich [23], Langmuir [24], Temkin [25], and Dubinin-Radushkevich (D-R) [26] were used to interpret the obtained experimental data.

The Freundlich adsorption isotherm is commonly used to describe adsorption characteristics for a heterogeneous surface. The empirical equation proposed by Freundlich is given by equation 5.

$$q_e = K_f C_e^{\frac{1}{n}} \quad (5)$$

Where K_f Freundlich isotherm constant (lg^{-1}), n adsorption intensity;

The Langmuir adsorption isotherm describes quantitatively the formation of a monolayer on the outer surface of the adsorbent, which contains a finite number of identical sites. The model assumes uniform adsorption energies on the surface

On the basis of these assumptions, Langmuir proposed equation (6).

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (6)$$

Where $q_{\max}$ Maximum monolayer coverage capacity ($mg.g^{-1}$), b Langmuir isotherm constant ($l.mg^{-1}$)

Temkin's model assumes that the heat of the adsorption of all the molecules in the layer would decrease linearly rather than logarithmically with cover. This model is given by equation (7).

$$q_e = \frac{RT}{b_T} \ln K_T C_e \quad (7)$$

K_T Temkin isotherm equilibrium binding constant ($l.mg^{-1}$)

b_T Temkin isotherm constant

B_T Constant related to heat of sorption ($J.mol^{-1}$)

$$B_T = \frac{RT}{b_T}$$

Table2. *Kinetic model parameters for ATP adsorption onto active carbon*

Models Parameters	Value		
	5 mg/l	10mg/l	20mg/l
Fractional power			
ν (min^{-1})	0.1782	0.2106	0.3485
k ($mg\ g^{-1}$)	5.0526	8.8543	8.9621
R^2	0.5909	0.7615	0.7806
Pseudo-first-order			
k_1 (min^{-1})	0.0283	0.0379	0.0248
q_e (cal) ($mg\ g^{-1}$)	3.59	14.84	28.93
R^2	0.7459	0.9629	0.8529
Elovich			
a_E ($mg\ g^{-1}\ min^{-1}$)	20.5763	14.6088	-20.2698
β_E ($g.mg^{-1}$)	0.6230	0.2526	0.0895
R^2	0.6184	0.8065	0.8269
Pseudo-second-order			
k_2 ($g\ mg^{-1}\ min^{-1}$)	0.0134	0.0043	0.0009
q_e (cal) ($mg\ g^{-1}$)	12.20	25.64	55.56
R^2	0.9972	0.9981	0.9895

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. This model is represented by equation (8).

$$q_e = q_{DR} \exp(-K_{DR}\varepsilon^2) (8)$$

$$\varepsilon = RT \ln(1+\frac{1}{Ce}) (9)$$

R is the gas constant (8.314 J mol^{-1} K^{-1} and T is the absolute temperature (K).

q_{DR} Theoretical isotherm saturation capacity ($mg.g^{-1}$),

K_{DR} Dubinin–Radushkevich isotherm constant (mol^2Kj^{-2})

ε Polanyi potential

The value of K_{DR} is related to the adsorption free energy that can be calculated from equation (10).

$$E = \frac{1}{\sqrt{2K_{DR}}} (10)$$

The value of free energy determines the type of adsorption mechanism. If E value lies between 8 and 16 kJ mol^{-1}, the adsorption process proceeds chemisorption mechanism, and if E is less than 8 kJ mol^{-1}, the adsorption process mechanism is physical [21].

Table 3 reports isotherm models and their linear forms.

The isotherm of adsorption of ATP onto actived carbon were performed, using the following experimental conditions, pH 6.68, contact time of 180 min, and temperature fixed at 25 °C. The plot of qe versus Ce for the adsorption of ATP onto actived carbon (Figure.6) was drawn and fitted to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm models.

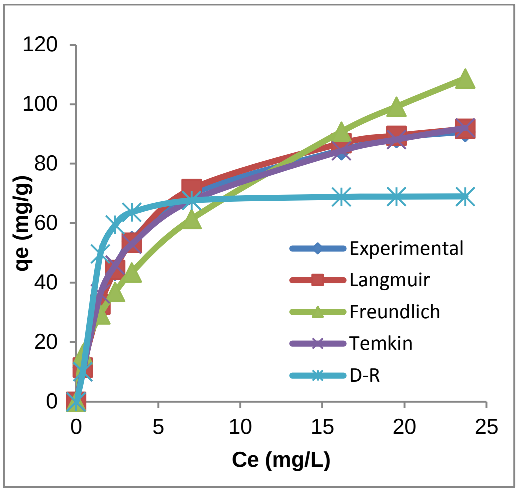

***Figure 6.** Equilibrium isotherm of ATP and fitted isotherm models (Adsorbent dosage: 0.4 g/l, contact time: 3 h, temperature: 298 K and pH = 6.68)*

From Table 3, it can be observed that the calculated isotherm parameters and their corresponding RMSE values vary for the four models.
Since the value of the linear regression analysis R^2 nearer to 1 and the smallest value of the RMSE indicate that the respective equation better fits the experimental data. The correlation coefficient for Langmuir isotherm was the highest in comparison to the Temkin, Freundlich and Dubinin–Radushkevich isotherms. Langmuir isotherm showed better fit followed by Temkin isotherm. The Langmuir isotherm was found to be the best fitting.
The result also suggested that the surface of adsorbent had nearly homogeneous sites for ATP
K_f and n are parameters characteristic of the sorbent-sorbate system, which have been widely applied to correlate sorption data where 1/n is a heterogeneity parameter, values of n > 1 represent favorable adsorption condition [27]. From the data in table 3, that value of n= 2.14 indicating that the sorption of ATP - actived carbon is favourable and the R^2 value is 0.9201
The adsorption process of ATP by actived carbon was also characterized by separation factor (R_L) associated with the Langmuir isotherm [28].

$$R_L = \frac{1}{1+bC_0} \quad (11)$$

Where; Co is initial concentration (mg/L).
The value of R_L indicates the shape of the isotherms to be either unfavourable (R_L>1), linear (R_L= 1), favourable (0<R_L<1) or irreversible (R_L = 0). It was observed that the value of R_L was in the range of 0-1 confirmed the favourable uptake of the process. Higher values at lower ATP concentrations showed that adsorption was more favourable at lower concentration.
Sorption energy value (K_{DR}), mean free energy (E) and heat of sorption (B_T) were estimated as 0.2 mol^2Kj^{-2}, 1.58 $kJmol^{-1}$, and 20.08 $Jmol^{-1}$ respectively. The found values indicate that physisorption dominates chemisorption and ion exchange [21, 29].
The maximum adsorption capacity of ATP wais compared with other adsorbents reported in the literature and listed in Table 4. The adsorption capacity of the activated carbon used is not among the highest capacities.

III.3 Mass transfer mechanism

Tow mathematical models were tested in order to determine the limiting step of the mass transfer of the ATP adsorption process onto activated carbon.

III.3.1 The intra-particle diffusion model

The intra-particle diffusion model based on the theory proposed by Weber and Morris [31] is described by equation (12).

$$q_t = k_{id}.t^{1/2} + C (12)$$

Where k_{int} is the intraparticle diffusion rate constant and C is parameter of the Weber and Morris equation (mg/g) which gives the idea on the thickness of the boundary layer. According to this model, the plot q_t versus $t^{0.5}$ should be linear and pass through the origin. When the plot does not pass through origin then intraparticle diffusion is not the rate limiting step. The plot q_t versus $t^{0.5}$ (Figure.7) shows multi-linearity for all concentrations of ATP, and each portion represents a distinct mass transfer step. The first portion or the initial zone of higher slope could correspond to the binding of the ATP in the external surface of adsorbent (film diffusion). The second portion would be related to the diffusion of ATP inside the particle (intraparticle diffusion). This indicates that more than one process is affecting the adsorption. Similar results were obtained by investigating the adsorption of ATP from aqueous solution on activated carbons; three-step curves in ATP sorption were observed [17].

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Table 3. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of ATP – Activated carbon

Models Parameters	Value	Equation
Freundlich		
R^2	0.9201	
K_f (lg^{-1})	24.5521	$q_e = 24.55C^{0.47}$
n	2.1386	
RMSE	11.1500	
Langmuir		
R^2	0.9997	
$q_{\max}$ (mg.g^{-1})	104.17	$q_e = \dfrac{32.47C_e}{1+0.3117C_e}$
b (l.mg^{-1})	0.3117	
RMSE	1.3896	
Temkin		
R^2	0.9966	
B_T (J.mol^{-1})	20.0779	
K_T (l.mg^{-1})	4.1307	$q_e = 20.08\ln 4.13C_e$
b_T	123.3980	
RMSE	1.8006	
Dubinin-Radushkevich		
R^2	0.8641	
q_{DR} (mg.g^{-1})	69.1581	$q_e = 69.16\exp(-0.2\varepsilon^2)$
$K_{DR}(mol^2/kj^2)$	2.10^{-1}	
$E(Kj/mol)$	1.58	
RMSE	16.8208	

Table 4. *Comparison of adsorption capacity with other adsorbent Of the ATP*

Adsorbent	Adsorption capacity (mg.g^{-1})	Reference
NaX nanozeolites	350.3	(Roshanfekr Rad, Irani, & Barzegar, 2015).
Activated carbon	105	(Boudrahem et al., 2017)
F400	261.04	(Lladó et al., 2015)
NPK	150.08	(Lladó et al., 2015)
SBC	53.75	(Lladó et al., 2015)
Pi/1:1/800/2	270.3	(Galhetas, et al., 2014) [30]
Pi/1:3/800/2	434.8	(Galhetas, et al., 2014) [30]
NS	267.7	(Galhetas, et al., 2014) [30]
VP	169.5	(Galhetas, et al., 2014) [30]
Activated carbon	104.17	This study

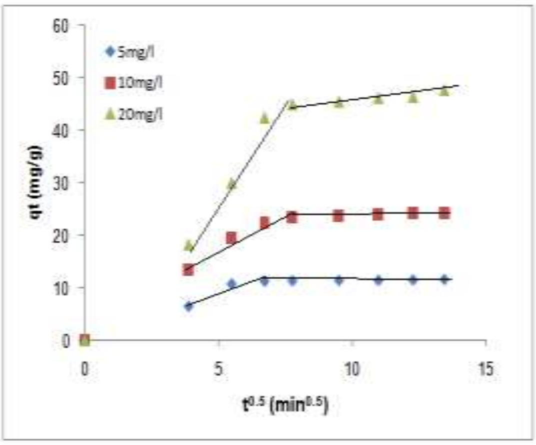

Figure 7. *Amount of ATP adsorbed* q_t *vs.*$t^{0.5}$ *for intraparticle diffusion at different initial ATP concentrations.*

The rate constants of intraparticle transport are estimated from the slope of the linear portion of the plot of amount adsorbed (mg/g) against square root of time. The adsorption rate constants of the intrapartical diffusion model are listed in table n°5.

Table 5. *Comparaison of the Adsorption rate constants of the intraparticle diffusion model*

Concentration (mg/L)	k_{id1} (mg/g min$^{0.5}$)	k_{id2} (mg/g min$^{0.5}$)
5	1,26	0,04
10	1,30	0,14
20	6,90	0,48

III.3.2 The Boyd model

Boyd model can be represented by Eqs. (13, 14, 15) [32]:

$$F = 1 - \frac{6}{\pi^2}\exp(-B_b t) \quad (13)$$

Where B_b is a constant and F is the fractional attainment of equilibrium at time t given by

$$F = \frac{q_t}{q_e} (14)$$

The equation (14) can be expressed in the form [32]:

$$B_b t = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) (15)$$

The Boyd kinetic equation was applied to identify the rate-limiting step of the adsorption process. The plot of $B_b t$ against time was used to distinguish between intraparticle diffusion and film diffusion. If the plots are linear and passes through the origin, then pore diffusion is the slowest step; otherwise they are governed by external mass transport or film diffusion [32]. Figure 8 shows that the curves of Boyd's model give straight lines; they fail to pass through the origin which indicates that external mass transport is the rate-limiting step. Similar tendencies were also recognized in pollutants adsorption by diverse adsorbents [32, 33, 34].

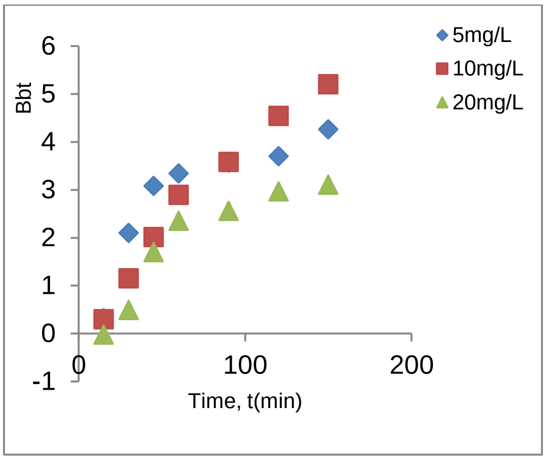

Figure 8. *Boyd plot for the adsorption of ATP onto activated carbon*

The elimination of paracetamol is greatly favored in acidic and neutral pH which could probably be explained by the attraction between the positively charged surface of the adsorbent and the highest electronic charges of the neutral paracetamol molecule located on the carbonyl group C = O. Then, chemisorption may have some contribution [19].

At zero point charge pH, the carbon surface is neutral and the charges of paracetamol may be weakly attracted to certain surface groups. The elimination of paracetamol showed a slight decrease in pH load from zero point. In this case, the carbonyl groups may induce chemisorption although physisorption should have the greatest contribution, mainly in the micropores, where the molecule can be better retained [19].

On the other hand, for basic pH, paracetamol molecules having much more negative charge are repelled by negative charges from the surface of the adsorbent. In such case, physisorption may be more significant.

Behavior as a function of pH could be explained by electrostatic attraction in acidic or electrostatic solutions repellency in base solutions. This is in accordance with the fact that in pseudo-second order kinetics, chemisorption involves valence forces [35].

IV. Conclusion

This study shows that the adsorption process can be successfully utilized for the removal of paracetamol from aqueous solution. The adsorption of paracetamol onto activated carbon was found to decrease quickly in the first 45 min and reach equilibrium within 3 h. The removal of paracetamol depends on the solution pH, adsorbent dose, contact time, and initial concentration. The Langmuir model best fits the equilibrium adsorption data and maximum adsorption capacity was 104.17 mg/ g of adsorbent. The adsorption kinetics followed the pseudo-second-order model at all-time intervals. Adsorption mechanism was found to be controlled by external mass transfer.

V. References

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