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Adsorptive removal of amoxicillin from wastewater using wheat grains: equilibrium, kinetic, thermodynamic studies and mass transfer

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ABSTRACT

Wheat grains are natural products which grow in the north of Algeria. In this study, they were used as adsorbent to remove amoxicillin antibiotic from wastewater. Adsorption isotherm of amoxicillin on both crude and modified wheat grains with 20% tartaric acid was investigated in batch tests. A model was developed regarding both the kinetic partitioning and the mechanism governing the forward transfer of amoxicillin. Results were interpreted in terms of a two-film theory for flat interface. The percentage of maximum adsorption capacity of amoxicillin was found to be 84% for the following optimal conditions: amoxicillin concentration of 4 mg/L, 5 min contact time, pH 7, temperature 25°C, and 0.24 g/L initial amoxicillin concentration and 150 μg particle size. The pseudo-first-order, pseudo-second-order kinetic models and the intraparticle diffusion model were used to describe the kinetic data, and the rate constants were evaluated. It was found that the pseudo-second-order model provides the most adequate correlation of experimental data. The rate parameters of the intraparticle diffusion model for adsorption were also evaluated and to identify the adsorption mechanisms. The adsorption constants were evaluated by using the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) adsorption isotherm models. The results showed that Temkin isotherm agrees with experimental data better than other adsorption models for the adsorption of amoxicillin. The thermodynamic parameters (ΔG, ΔH, and ΔS) showed that the process was feasible, spontaneous, and exothermic.

Keywords: Wastewater; Amoxicillin; Wheat grains; Adsorption; Kinetics; Mass transfer; Modeling

1. Introduction

Pharmaceuticals and personal care products have become the center of much current environmental research. These "emerging contaminants" have been known to be present in the environment for decades, from sources such as wastewater treatment plant effluent and confined animal feeding operation run-off [1–4]. Groundwater contamination by pharmaceutical ingredients (analgesic, antibiotics, antidepressants,

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antidiabetics, contraceptives, growth regulators, impotence drugs, painkillers, and tranquilizers) is an environmental problem of widespread concern [5,6]. Pharmaceutical ingredients are actually found as residues in water and have been recognized as part of the hazardous chemical substances able to alter the natural equilibrium system of the surrounding environment [7]. Recently, antibiotics were quantified in hospital sewage water and wastewater [8–11].

Antibiotics are the most successful family of drugs so far developed to improve human health. Besides this fundamental application, antibiotics have been used in veterinary and human medicine for preventing and treating animal and plants infection as well as for promoting growth in animal farming [12,13]. All of these applications cause antibiotic drugs to be released in large quantities to natural ecosystems. Yet these compounds when released into the environment have potential risks for aquatic and terrestrial organisms [14,15].

Amoxicillin is one of the most used commercial penicillin antibiotic due to its high bacterial resistance and large spectrum against a wide variety of microorganisms [16,17]. Its existence in wastewater from pharmaceutical industries and hospital effluents causes unpleasant odor, skin disorder, and microbial resistance among pathogen organisms or the death of microorganisms which are effective in wastewater treatment. The resistant bacteria may cause disease that cannot be treated by conventional antibiotics; therefore, amoxicillin wastes need to be treated before disposal to the environment [18–20].

The need to treat wastewaters charged with pharmaceutical ingredients is obvious. Remediation techniques were tested to remove pharmaceutical compounds including membrane adsorption, reverse osmosis, sand filtration and ozonation, activated carbon, nanofiltration membranes for antibiotics elimination, coagulation and granular activated carbon filtration for tetracyclines removal and amoxicillin [21–25], as well as biological processes, filtration, and coagulation/flocculation/sedimentation.

Among them, adsorption processes have been proved to be effective because of major advantages such as applicability over a large concentration range of sorbate, effective removal efficiency, low instrumentation cost, and the presence of many rate-controllable parameters [26–28]. Another important advantage of using activated carbon to remove pharmaceuticals is that toxic or pharmacologically active products are not generated. However, only few reports have been published on the removal of antibiotics from wastewater using alternative adsorbents [29–31].

Recently, adsorption of amoxicillin onto chitosan beads, bentonite, organobentonites, and activated carbon has been investigated. Also, clays and oxides have been exploited for the removal of antibiotic drugs using adsorption technology [32–34]. Adsorption of amoxicillin onto activated carbon plays an important role. However, the most used adsorbents in this process are activated carbons granular (GAC) and powdered (PAC) which are costly [35].

Snyder et al assessed the mechanisms underlying the adsorption of various pharmaceuticals on GAC and PAC and obtained removal percentages of around 90% for most of the pharmaceuticals studied [36].

However, in the majority of the studies involving sorptive removal of antibiotics, activated carbon has been employed as a potential sorbent material [26]. The relatively high production cost of activated carbon places a question mark on its large-scale application. Environmental chemists have therefore focused their attention on employing agricultural wastes as sorbents [37].

Cost is an important parameter for comparing sorbent materials. Hence, the usage of indigenous biodegradable resources for treating hazardous waste would be less expensive [38,39]. For this purpose, sun flower stalks, rice husk, almond husk, sawdust, and spent grain, etc. have been used. The cost of these biomaterials is negligible compared with the cost of activated carbon or ion-exchange resins [40].

Agricultural by-products consist of functional groups in the structure of lignin, cellulose, hemicellulose, ligno-humic, proteins, starch, and polysaccharides. Agricultural by-products are appropriate for an environmental purpose, because they are abundant in nature, readily available, and low cost. The use of agricultural by-products as low-cost adsorbents can be thereby advantageous.

Among such agricultural by-products, the bran of wheat is the shell of the wheat seed and contains many nutrients of wheat. This bran is usually removed during the processing of wheat into flour. It is environmentally friendly and is nutritious to the plants. Therefore, the use of wheat bran to eliminate pollution from water and wastewater is interesting [41]. X-ray diffraction and IR studies of wheat bran have proved that it contains various organic functional groups. The surface area of is 441 m^2/g and fixed carbon percentage is 31.78% [42]. Wheat bran contains various groups including aliphatic and phenolic hydroxyl groups, methoxyl and carbonyl groups that offer the capability to catch pollutant [40]. It has been successfully tested for the removal of metal ions from liquid waste [42,43]. It was therefore considered as a raw material for this study.

Citric, tartaric, and oxalic acids may be used as modifiers, allowing to establish carboxylic acid functional groups (–COOH) by esterification reactions, resulting in an increase of the adsorption capacity of agricultural by-products [42]. Chemical modification of agricultural by-products by citric acid, epichlorohydrin, and different modificators, was also shown to improve the exchange capacity and usability of them [44,45].

In order to make the overall process cost-effective and applicable at an industrial scale, the aim of this work focused therefore on the development of a new modified wheat grain as adsorbent available and cheap to remove amoxicillin antibiotic from wastewater. This study investigated the effects of experimental conditions such as contact time, temperature, particle size, initial amoxicillin concentration, and adsorbent quantity on the sorption of amoxicillin from wastewater. The corresponding kinetics, equilibrium, and thermodynamic parameters were also examined.

2. Materials and methods

2.1. Biosorbent preparation

The pre-treatment of wheat grains consisted of washing several times with distilled water before drying for 24 h in order to remove dirt and surface impurity; it was then baked at 50˚C for another 24 h. The clean biosorbent obtained was milled and sieved to get a powder of different particle sizes.

The chemical modification was realized by using tartaric acid as cited by Kaya et al. [46]. After washing, the purified biosorbent was mixed with 0.5 M tartaric acid at percentages of 10, 20, and 30%. Next, the slurry was stirred at 600 rpm for 30 min at 20˚C, placed in an air oven and dried at 50˚C for 24 h.

2.2. Chemicals and analysis

The antibiotic drug amoxicillin was kindly provided by the pharmaceutical company Saidal of Medea (Algeria) and used as a model adsorbate. Tartaric acid was purchased from FLUKA. The amoxicillin concentration in the solution was analyzed using a UV spectrophotometer (Shimadzu UV Mini-1240) by monitoring the absorbance changes at a wavelength of maximum absorbance of 232 nm.

2.3. Adsorption studies

To study the adsorption capacity of wheat grains, 2 g of adsorbent was placed in a 1,000 mL Erlenmeyer flask containing an aqueous solution of 0.24 g/L of amoxicillin (500 mL) and the solution was shaken at 350 rpm at 25˚C. Various experimental conditions, including contact time, agitation speed, temperature, and adsorbent dose were tested for their impact on amoxicillin adsorption. The amount of amoxicillin adsorbed onto wheat grains was calculated using the following relationship:

$$Q(\mathrm{mg/g}) = (C_0 - C_e) \times V/m \quad (1)$$

where C_0 and C_e are the initial and equilibrium amoxicillin concentrations (mg/L), respectively, V the volume of solution (L), and m the adsorbent dose (g).

All experiments were carried out in duplicate.

2.4. Mass transfer model development

The extraction of amoxicillin is governed by the transfer of antibiotic molecules from the aqueous to the organic phase. In fact, the two phases involved in this study are the aqueous phase (phase 1 with a volume V_1 and an amoxicillin concentration at time t of $C_1(t)$) and the organic phase (phase 2 with a constant volume V_2 and an amoxicillin concentration $C_2(t)$). At the start of the extraction experiments, all the effluent reside in the aqueous phase, and thus the concentration of amoxicillin in the two phases is $C_1(t) = C_1(0)$ and $C_2(t) = 0$. So the mass balance of amoxicillin in the system at any given time is:

$$V_1C_1(0) = V_1C_1(t) + V_2C_2(t) \quad (2)$$

At equilibrium, the relative amoxicillin concentration would be given by $C_1^* = mC_2^*$, where m is the equilibrium partition coefficient (assumed to be constant under given conditions). C_1^* and C_2^* are the equilibrium concentrations of amoxicillin in phases 1 and 2, respectively. Therefore, the value of equilibrium partition coefficient is given by:

$$m = \frac{C_1(\infty)}{C_2(\infty)} \quad (3)$$

Since a two-film model is used to describe solute transfer, the mass transfer rate is given by:

$$J = KA(C_1(t) - C_1^*) \quad (4)$$

where K is the overall mass transfer coefficient and A is the total interfacial area between the two phases and $C_1^* = mC_2(t)$. Thus:

$$V_1 \frac{dC_1}{dt} = -KA(C_1(t) - mC_2(t)) \quad (5)$$

In this study, the actual interfacial area between the two phases is unknown, and thus we can only obtain a combined mass transfer coefficient, KA, having units of m^3/s. Rearranging Eq. (2) in terms of $C_2(t)$ gives:

$$C_2(t) = \frac{1}{V_2}(V_1C_1(0) - V_1C_1(t)) \quad (6)$$

Then substituting $C_2(t)$ in Eq. (5) and rearranging gives:

$$\frac{dC_1}{dt} = -\frac{KA}{V_1}(1 + mV_r)\left[C_1(t) - \left(\frac{mV_r}{1 + mV_r}\right)C_1(0)\right] \quad (7)$$

where V_r is the phase volume ratio ($V_r = V_1/V_2$). Integrating Eq. (7) between the limits $C_1(0)$ and $C_1(t)$ and rearranging gives:

$$C_1(t) = C_0((1 - \beta)\exp(-\alpha t) + \beta) \quad (8)$$

where

$$\alpha = \frac{KA}{V_1}(1 + mV_r) \quad (9)$$

and,

$$\beta = \frac{mV_r}{1 + mV_r} \quad (10)$$

α and β are the two model parameters where each of them is a function of some physicochemical parameters (K, A, V_1, V_r, and m).

The overall resistance to antibiotics transfer, as represented by KA, can be described as the sum of the resistances of both aqueous and organic boundary films; and then the overall combined mass transfer coefficient can be represented as:

$$\frac{1}{KA} = \frac{1}{K_{aq}A} + \frac{m}{K_{org}A} \quad (11)$$

It should then be possible to estimate the individual aqueous phase and organic phase mass transfer coefficients, since a plot of $1/KA$ vs. m should yield a straight line of slope $1/K_{org}$ A and intercept $1/K_{aq}$ A.

3. Results and discussion

3.1. Effect of the contact time

The contact surface between the solid phase of the biosorbent and the liquid phase plays an important role in biosorption phenomena. The best particle size range corresponds to the optimal compromise between the biosorption capacity and the mechanical behavior.

A series of flasks containing each 0.24 g/L of amoxicillin was used to examine the effect of the contact time. Flasks were stirred at a speed of 350 rpm at home temperature and neutral pH. Samples were taken at various time intervals. From Fig. 1, it can be seen that maximum adsorbed amount for different particle size was obtained for a contact time of: 40 mn for 500 µm, 30 mn for 400 µm, and 20 mn for 150 µm.

The size of adsorbent particles affects significantly the accumulation speed and the necessary time to achieve biosorption equilibrium. The kinetics of amoxicillin biosorption became faster with the reduction of particle diameter (Fig. 1). This is explained by the increase of the external surface (the grain size reduction implies an increase of the flux crossing the external layer) and by an easier accessibility of sites by a reduction of the superficial diffusion stage [47].

The best kinetic of amoxicillin adsorption was observed for the finer particle sizes, leading to satisfactory results.

To improve the adsorption efficiency, treatment of the wheat grains was carried out for different percentages of tartaric acid. The optimal contact time was found to be 5 min with an optimal amount of tartaric

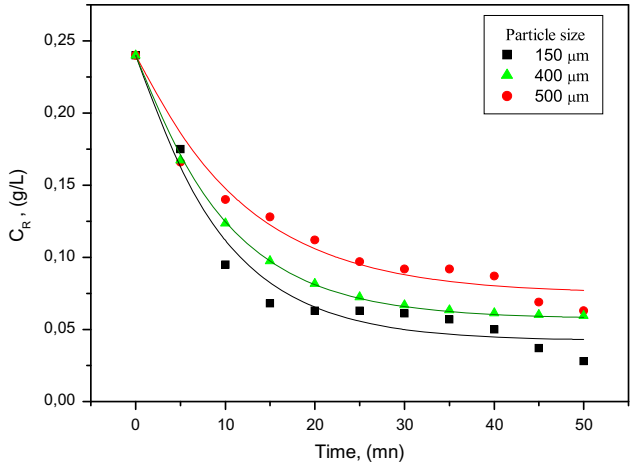

Fig. 1. Time-course of amoxicillin adsorption on crude wheat grain for different particle size (T = 25°C, C_0 = 0.24 g/L, m = 4 g, pH 7, ω = 350 rpm).

acid of 20% leading to a percentage removal of 84%. No remarkable changes were observed beyond this time it was therefore considered for the rest of the experiments (Fig. 2).

3.2. Effect of the agitation speed

The impact of the agitation speed on the adsorption efficiency was investigated as it affects the solute distribution. Agitation speeds ranging from 150 to 800 rpm were tested at the predetermined optimal contact time of 5 min; the corresponding results are displayed in Fig. 3. As can be seen from the figure, an agitation speed of 300 rpm appeared to be the most appropriate.

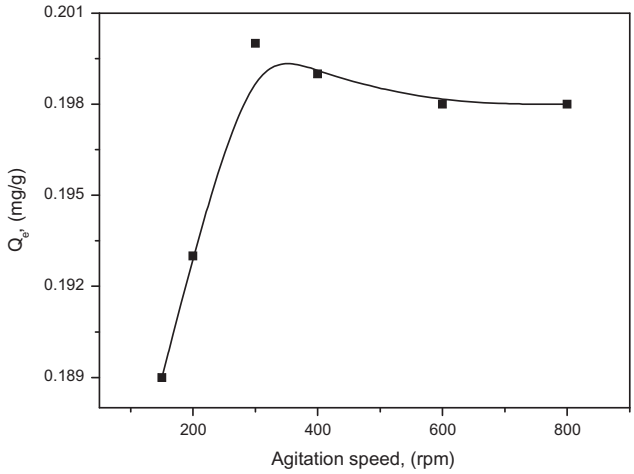

Fig. 3. Effect of agitation speed on amoxicillin adsorption onto modified wheat grains isotherm. Experiment condition: T = 25°C, pH 7, m = 4 g, C_0 = 0.24 g/L, particle size of 150 μm.

3.3. Effect of temperature

Temperature has a vital effect on the adsorption process as it can increase or decrease the amount of adsorption. Influence of temperature on the removal of amoxicillin from wastewater shows the feasibility of adsorption and its nature whether it is an exothermic or endothermic process as mentioned by Senthil kumaar et al. [48]. The adsorption capacity of amoxicillin onto modified wheat grains was therefore examined in the range from 20 to 50°C.

As shown in Fig. 4, the maximum removal was observed at 25°C. The equilibrium adsorption capacity of amoxicillin onto modified wheat grains was affected by the temperature and decreased from 0.22 to 0.13 mg/g with increasing temperature from 20 to 50°C, which indicates that the adsorption of amoxicillin was favored at lower temperatures and it is controlled by an exothermic process. This is probably due to the weakening of the sorptive forces between amoxicillin and the active sites on the adsorbent surface as a result of decreasing adsorption efficiency. This allows to conclude that the phenomenon is a physical adsorption.

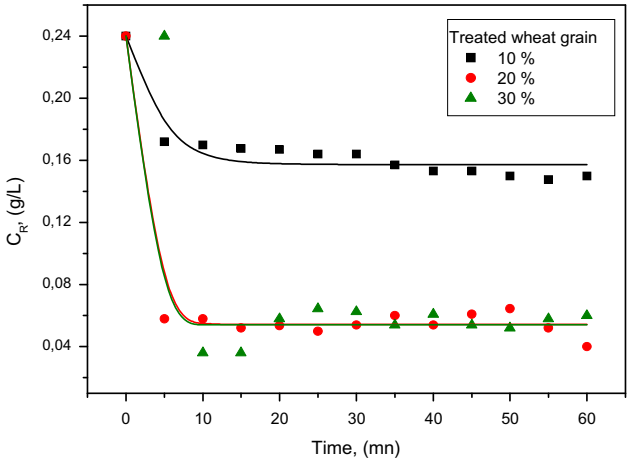

Fig. 2. Time-course of amoxicillin adsorption on treated wheat grain for different percentage of tartaric acid (T = 25°C, C_0 = 0.24 g/L, m = 4 g, pH 7, ω = 350 rpm, particle size of 150 μm).

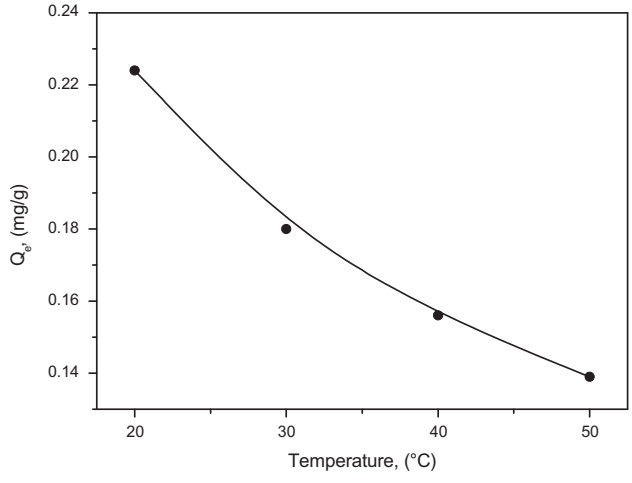

Fig. 4. Effect of the temperature on Amoxicillin adsorption onto modified wheat grains. Experimental conditions: pH 7, contact time 5 min, ω = 300 rpm, m = 4 g, C_0 = 0.24 g/L, particle size 150 μm.

3.4. Effect of adsorbent dosage

To study the effect of the adsorbent dose (g) on amoxicillin uptake, experiments were conducted at initial amoxicillin of 0.24 g/L, while the amount of adsorbent added was varied from 1 to 5 g. Fig. 5 shows the effect of the adsorbent dose on the amount adsorbed. Commonly, increasing adsorbent dosage improves adsorption efficiency. The increase in removal efficiency with increasing adsorbent dose is probably due to the greater adsorbent surface area and pore volume available at higher adsorbent dose, providing more active adsorption sites resulting in a higher removable percentage. Optimum adsorbent dosage was determined to be 4 g, since no improvement of the amount of amoxicillin adsorbed at equilibrium above this dosage. Similar results were reported by Ahmed et al. [49].

3.5. Mass transfer model development

In order to verify the model that described the amoxicillin transfer from the aqueous phase to the organic phase according to the two-film model, experimental results ($C_1(t)$ vs. t data) were modeled using a microcomputer program, written in MATLAB language and involving the "fminsearch" function to optimize the model coefficients according to the nonlinear least-squares method. The theoretical and experimental results are compared in Fig. 6 in which the solid line represents the result of the two-film model, while the symbols correspond to the experimental results [50]. It was found that the model fitted accurately experimental data with a correlation coefficient R^2 of 0.999.

The values of the model coefficients α and β given by the program were then inserted into Eqs. (6) and (7) to calculate the combined mass transfer coefficient (KA) as shown in Table 1.

Fig. 7 shows that the plot of $1/KA$ vs. k yielded a straight line, allowing to estimate the combined film mass transfer coefficients for both crude and treated wheat grains $K_C\ A$ and $K_T\ A$ which were 0.86×10^{-7}–1.56×10^{-6} m^3/s, respectively.

4. Adsorption isotherms

Equilibrium isotherms are widely used to represent the relationship between the adsorbed concentration in the adsorbent phase and the dissolved concentration at equilibrium. Such isotherms are a characteristic feature for a specific system at particular environmental conditions. Several isotherm equations are available for analyzing experimental sorption equilibrium parameters; the most usual ones were considered in this study, the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) models [51].

The Langmuir model assumes monolayer adsorption on adsorbents which have homogeneous energy distribution. The Freundlich isotherm is an empirical model suitable for heterogeneous surface adsorption. The Temkin model is a proper model for the chemical adsorption based on strong electrostatic interaction between positive and negative charges and the D–R isotherm model is valid for the adsorption of low concentration of contaminants onto both homogeneous and heterogeneous surfaces [52]. The adsorption

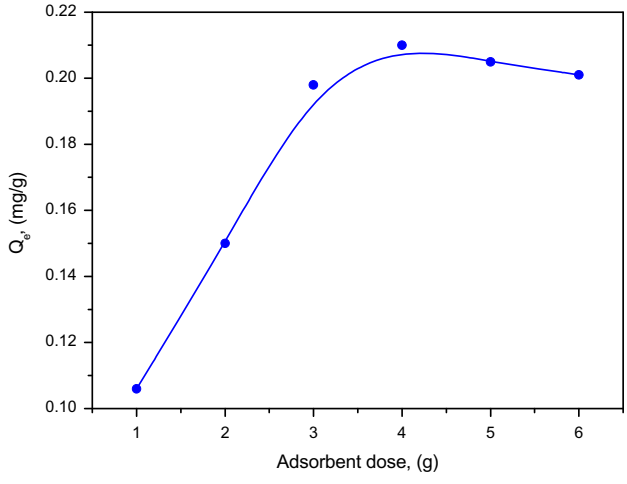

Fig. 5. Effect of adsorbent dose on adsorption of amoxicillin onto modified wheat grains (T = 25°C, C_0 = 0.24 g/L, pH 7, ω = 350 rpm, particle size of 150 μm).

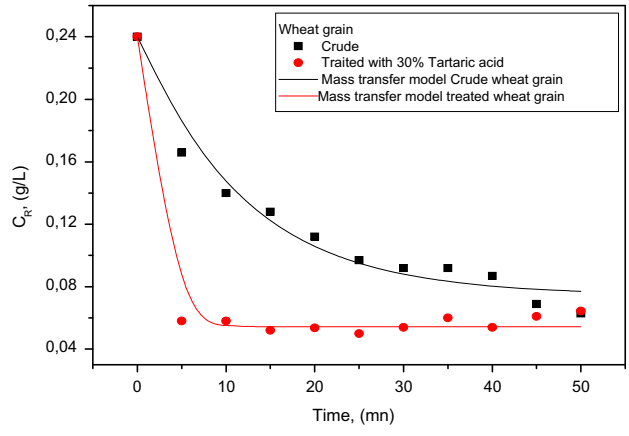

Fig. 6. Time-course of amoxicillin adsorption on wheat grain (C_0 = 0.24 g/L, m = 4 g, pH 7, ω = 300 rpm, T = 25°C, particle size of 150 μm).

Table 1
Values of model coefficients (α and β) and combined mass transfer coefficient (KA)

Parameters	α	β	KA (s/m^3)	R^2
Crude wheat grain	0.24	0.78	5.71×10^{-7}	0.992
Treated wheat grain 20% tartaric acid	0.57	0.229	2.94×10^{-6}	0.997

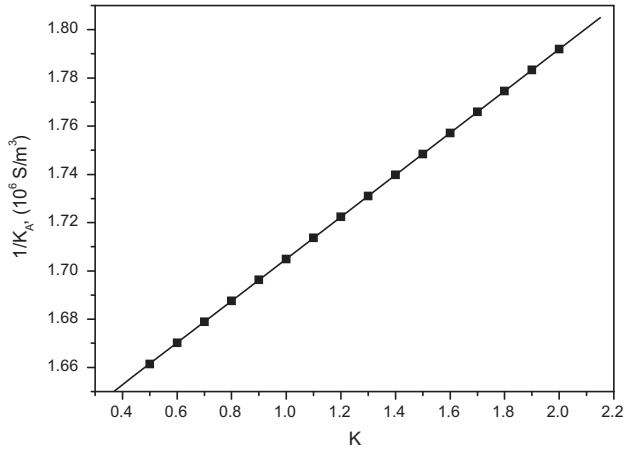

Fig. 7. Plot of the combined mass transfer coefficient ($1/KA$) against the equilibrium partition coefficient (k) for amoxicillin adsorption on wheat grains.

isotherm is characterized by certain constants which values express the surface properties and affinity of the adsorbent. It can also be used to find the adsorption capacity of the adsorbent [53].

The mathematical representations of the Langmuir (Eq. (12)), Freundlich (Eq. (14)) Temkin (Eq. (15)), and D–R (Eq. (17)) models are given below:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \tag{12}$$

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{13}$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{14}$$

$$Q_e = B \ln A + B \ln C_e \tag{15}$$

$$B = \frac{RT}{b} \tag{16}$$

$$\ln Q_e = \ln X_m - K' \varepsilon^2 \tag{17}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{18}$$

The value of adsorption energy (E_a) indicating the nature of adsorption can be determined through the equation below:

$$E_a = 1/\sqrt{2K'} \tag{19}$$

where Q_m is the theoretical maximum adsorption capacity per unit weight of the adsorbent (mg/g), C_0 = initial concentration (g/L), R_L value indicates the adsorption nature to be unfavorable if $R_L > 1$), linear if $R_L = 1$, favorable if $0 < R_L < 1$, and irreversible if $R_L = 0$.

K_L, K_F, B, and K are adsorption constants of Langmuir, Freundlich, Temkin, and D–R models, respectively, and $1/n$ is the Freundlich biosorption intensity. $1/n$ values indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$), and unfavorable ($1/n > 1$) [54].

The Langmuir (Q_m, K_L), Freundlich (K_F, $1/n$), Temkin (A, B), and D–R (X_m, K') constants were calculated at 25°C from the linear plots of (C_e/Q_e) vs. (C_e), ln Q_e vs. ln C_e, Q_e vs. ln C_e and ln Q_e vs. ε^2 (Fig. 8(a)–(d)). The linear regression coefficients were calculated by fitting the experimental equilibrium data; they are given in Table 2.

In Table 1, it can be seen that the obtained correlation coefficients are very close for the different models. Therefore, it can be concluded that the linear fits using the four equations were good for studying the adsorption of amoxicillin antibiotics onto modified wheat grains within the used concentration range. Also, we can conclude that the Temkin isotherm was the most appropriate followed by Langmuir, D–R, and Freundlich isotherms. Each model can give some useful information regarding the adsorption phenomenon.

The Temkin isotherm contains a factor taking into account interactions between amoxicillin and modified wheat grains regardless of the considered range of concentrations. The model assumes that heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage. Its derivation is characterized by a uniform distribution of binding energies [55].

From the Temkin plot shown in Fig. 8(c), the following values were estimated: $A = 113.57$ L/g, $B = 7.10$ J/mol which is an indication of the heat of sorption indicating a physical adsorption process with an R^2 value of 0.999.

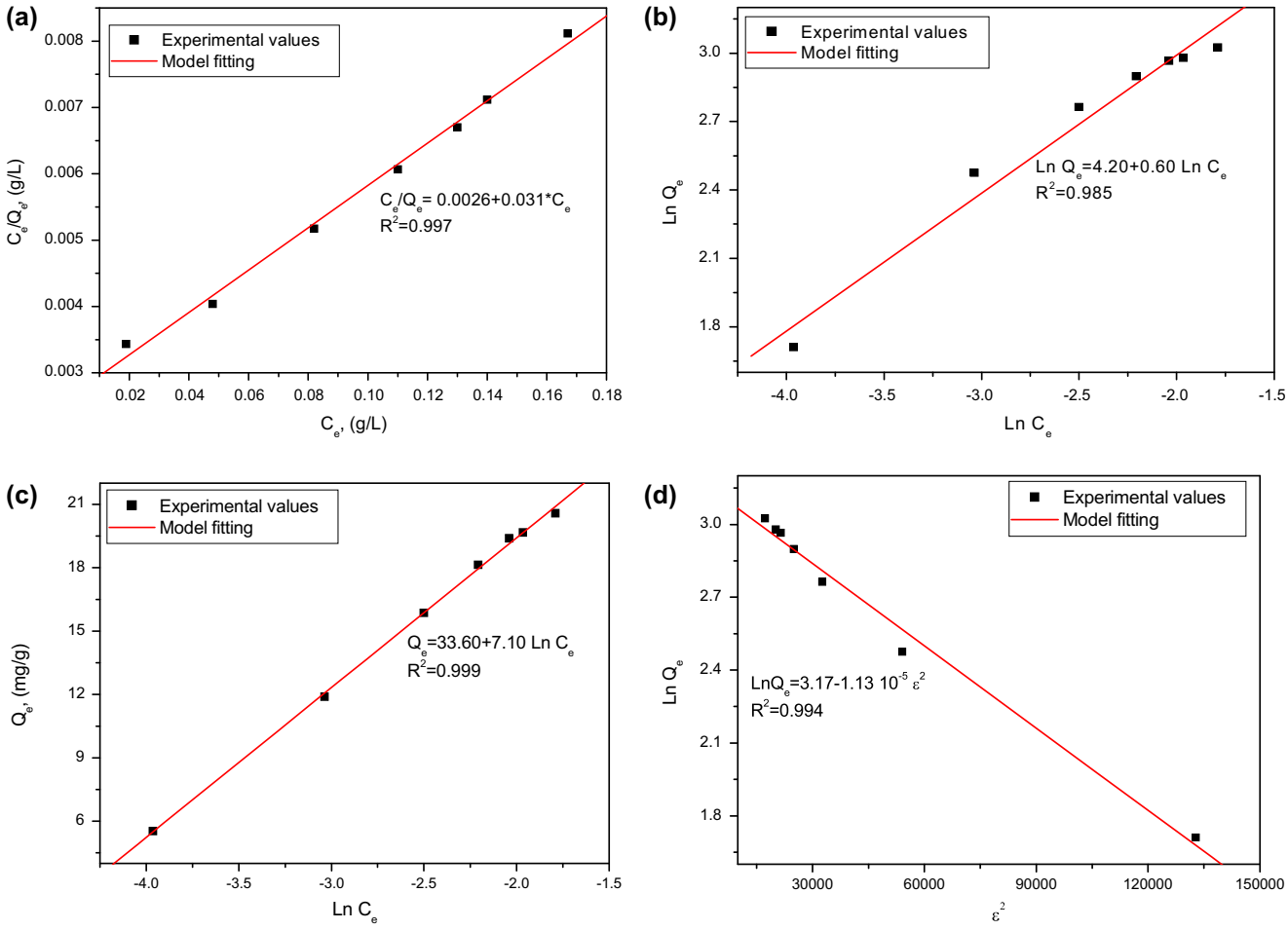

Fig. 8. Adsorption isotherms of amoxicillin onto modified wheat grains: (a) Langmuir, (b) Freundlich, (c) Temkin isotherm, and (d) D–R isotherm. Experiment condition: T = 25°C, pH 7, ω = 300 rpm, m = 4 g, C_0 = 0.24 g/L, particle size of 150 μm.

The Langmuir isotherm represents the equilibrium distribution of amoxicillin between the solid and liquid phases. The Langmuir isotherm is based on these assumptions: antibiotic is adsorbed at a fixed number of well defined sites; each site can hold only one ion; all sites are energetically equivalent and; there is no interaction between adsorbed molecules.

The essential characteristic of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor R_L. From the data calculated in Table 2, the R_L was less than unity indicating that Langmuir isotherm was favorable. The maximum monolayer coverage capacity (Q_m) was determined to be 31.25 mg/g, K_L was 0.60 L/mg, R_L was 0.25, and R^2 value is 0.997.

The D–R isotherm was chosen to estimate the characteristics porosity of the biomass and the apparent energy of adsorption. The Linear form of equation of D–R indicates a good fit of the isotherm of amoxicillin adsorption to the experimental data. The values of X_m and K' were calculated to be 23.80 mg/g and 1.13 10^{-5} mol^2/kJ^2, respectively. The approach was applied to give an idea about the type of adsorption of amoxicillin which is mainly physical or chemical. Indeed, low activation energies (5–40 kJ mol^{-1}) are characteristics for physiosorption and higher activation energies (40–800 kJ mol^{-1}) are characteristics for chemisorption [56]. The mean free energy, Ea was found to be 0.21 kJ mol^{-1} for the adsorption of amoxicillin onto modified wheat grains, indicating a physical adsorption.

The Freundlich isotherm plot for amoxicillin antibiotic onto modified wheat grains was found to be linear (Fig. 3(d)), with a correlation coefficient of 0.984 suggesting that the Freundlich model fit experimental data.

Freundlich constant (K_F) and the heterogeneity factor ($1/n$) calculated from the slope and the intercept of the linear plot were found to be 66.68 mg/L and 0.60, respectively. Therefore, the value of $1/n$ was less

Table 2
Adsorption isotherms for amoxicillin antibiotic adsorption on modified wheat grains: Equilibrium parameters (T = 25°C, ω = 300 rpm, m = 4 g, C_0 = 0.24 g/L, particle size of 150 μm)

Isotherm models	Estimated isotherm parameters
Langmuir isotherm	
Q_m/(mg/g)	31.25
K (L/mg)	12.30
R_L	0.25
R^2	0.997
Freundlich isotherm	
$1/n$	0.60
K_F (L/g)	66.68
R^2	0.985
Dubinin–Radushkevich isotherm	
X_m/(g g^{-1})	23.80
K/(mol^2/kJ^2)	1.13×10^{-5}
R^2	0.994
Temkin isotherm	
A (L/g)	113.57
B (J/mol)	7.10
R^2	0.999

than unity suggesting favourable adsorption, the high value of K_F confirms the high adsorption capacity.

5. Adsorption kinetics

In order to study the mechanism of adsorption and determining the rate controlling step, the kinetics data were analyzed by pseudo-first-order, pseudo-second-order, and intraparticle diffusion models [57,58]. The mathematical expressions of these models can be written as:

Pseudo-first-order equation of Lagergren:

$$\frac{1}{Q_t} = \frac{K_1}{C_e} \cdot \frac{1}{t} + \frac{1}{C_e} \tag{20}$$

Pseudo-second-order equation:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \tag{21}$$

Intraparticle diffusion model:

$$Q_t = K_{id}\, t^{1/2} + C \tag{22}$$

where Q_t (mg/g), Q_e (mg/g), C_e (g/L) are the amount of amoxicillin adsorbed per gram of sorbent at time t and at equilibrium and its concentration at equilibrium, respectively; K_1 (min^{-1}) and K_2 (g/mg min) are the rate constants of the pseudo-first-order and pseudo-second-order adsorption process.

K_{id} (mg/g $min^{1/2}$) is the intra-particle diffusion rate constant, and C (mg/g) is a constant that gives an idea about the thickness of the boundary layer.

The linear plots, obtained between, $1/Q_t$ vs. $1/t$ for the pseudo-first-order and t/Q_t vs. t for the pseudo-second-order reactions of the adsorption of amoxicillin are shown in Fig. 9(a)–(c).

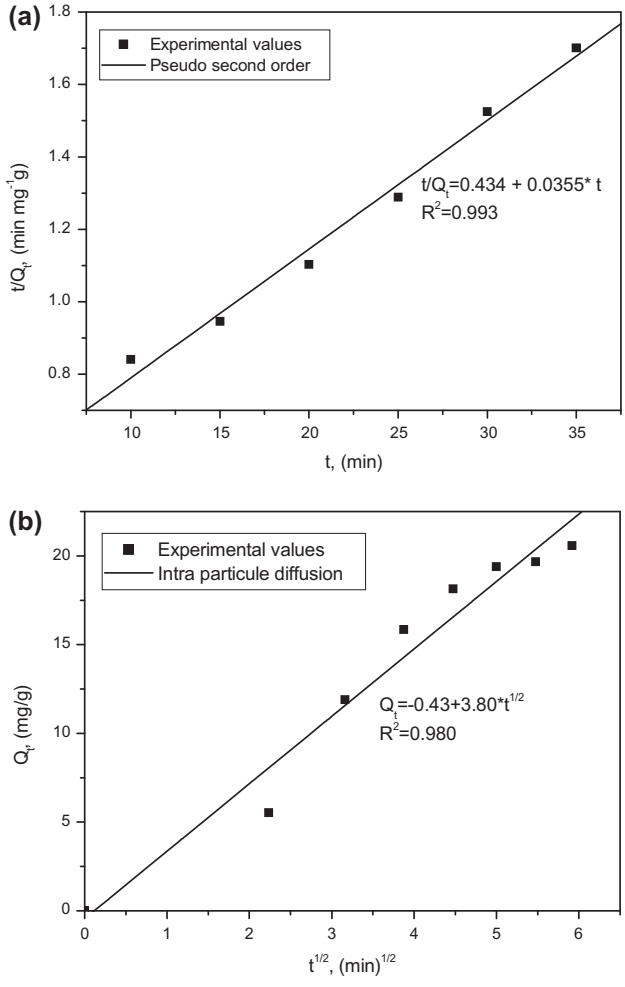

Fig. 9. Adsorption kinetics amoxicillin onto modified wheat grains: (a) pseudo-first-order kinetic, (b) pseudo-second-order kinetic, and (c) intraparticle diffusion kinetic isotherm. Experiment condition: T = 25°C, pH 7, ω = 300 rpm, m = 4 g, C_0 = 0.24 g/L, particle size of 150 μm.

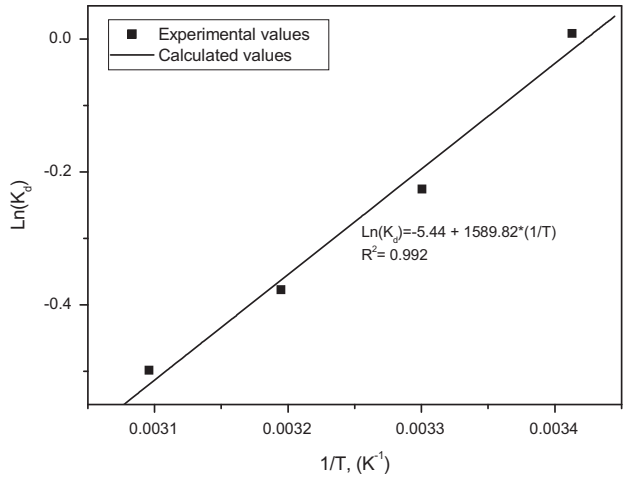

Fig. 10. Estimation of thermodynamic parameters for amoxicillin adsorption onto modified wheat grains (T = 25°C, pH 7, ω = 300 rpm, m = 4 g, C_0 = 0.24 g/L, particle size of 150 μm).

As can be seen, the correlation coefficient for the pseudo-first-order was 0.986. The value of first-order rate constant k_1 was obtained from the slope and was equal to 0.024 min^{-1} (Fig. 9(a)). This means that in case of strict surface adsorption, a variation in rate should be proportional to the concentration of amoxicillin.

The values of Q_e and k_2 for the pseudo-second-order were determined to be 28.16 mg/g and 0.0029 (g/mg min), respectively, and the correlation coefficient was R^2 = 0.993 (Fig. 9(b)). It is clear from the nature of the fit and the correlation coefficients that the adsorption of amoxicillin onto modified wheat grains followed a pseudo-second-order.

The plot of Q_t vs. $t^{1/2}$ for intra-particle diffusion in the adsorption of amoxicillin onto modified wheat grains (Fig. 9(c)) was used to obtain the diffusion rate parameters. The intra-particle diffusion plot gave a straight line with slope K_{id} and intercept C indicating that there is a difference between the rates of mass transfer in the initial and final steps of sorption, and that some other mechanisms, along with intra-particle diffusion are involved.

The value of K_{id} for intra particle diffusion was calculated to be 3.80 (mg/g $min^{1/2}$) with a correlation coefficient of R^2 = 0.980.

From this linear fitting, the initial sorption rate $h = K_2 Q_e^2$ was calculated and was 64.27 (mg/g min).

6. Thermodynamic study

In any adsorption process, both energy and entropy considerations must be taken into account in order to determine which process should occur spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process [59,60]. The amount of amoxicillin adsorbed at equilibrium at different temperatures 20, 30, 40, and 50°C were examined to obtain the thermodynamic parameters for the adsorption system.

Thermodynamic parameters, such as standard free energy change (ΔG), standard enthalpy change (ΔH), and standard entropy change (ΔS) can be calculated using the following equation:

$$\Delta G = -RT \ln K_d \tag{23}$$

where R is the universal gas constant (2 cal/mol K), T is the temperature (K), and K_d is the equilibrium constant resulting from the ratio of the equilibrium concentrations of amoxicillin on that of the adsorbent in the solution.

The enthalpy (ΔH) and entropy (ΔS) parameters were estimated from the following equation:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{24}$$

ΔG, ΔH, and ΔS can be calculated from a plot of ln K_d vs. $1/T$ (Fig. 10). Table 3 summarizes the thermodynamic parameters at various temperatures for the adsorption of amoxicillin onto modified wheat grains.

The values of enthalpy ΔH = −3.18 kcal/mol indicated that the adsorption of amoxicillin using modified wheat grains was exothermic and physisorptive in character since ΔH value lower than 10 kcal/mol was obtained.

Table 3
Thermodynamic parameters for amoxicillin adsorption onto modified wheat grains

			ΔG (kcal/mol)			
	ΔH (kcal/mol)	ΔS (cal/mol K)	20°C	30°C	40°C	50°C
Modified wheat grains	–3.18	–10.88	−0.59	−0.48	−0.43	−0.39

The negative values of ΔG characterized a decrease of the Gibb's free energy, showing the feasibility of the process and its spontaneous nature in the considered experimental conditions. In the meantime, the negative entropy change (ΔS°) value (−10.88 cal/mol K) corresponded to a decrease in the degree of freedom of the adsorbed species.

7. Conclusions

The aim of this study was to investigate the ability of wheat grains modified with 20% of tartaric acid to remove amoxicillin antibiotics from wastewater. Under batch conditions, equilibrium was attained within 5 min. The study allowed to establish the following optimal conditions: particle size 150 μm, adsorbent dose of 4 g, agitation of 300 rpm, and temperature of 25°C.

The effects of several parameters on the transfer of amoxicillin antibiotic between the aqueous phase and the organic phase were studied; and it was shown that the kinetic transfer process was successfully modeled using the general two-film theory of mass transfer to flat interface.

The kinetic of amoxicillin adsorption onto modified wheat grains was examined using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models, showing that amoxicillin adsorption onto modified wheat grains followed a pseudo-second-order kinetic model.

Among the four tested models (Langmuir, Freundlich, Temkin, and D–R models), the Temkin model was the most appropriate to describe amoxicillin adsorption isotherm.

The values of the thermodynamic parameters, ΔG, ΔH, and ΔS, indicated that the adsorption process of amoxicillin onto modified wheat grains was spontaneous and exothermic.

To conclude, wheat grains were found to be a good adsorbent for the removal of amoxicillin antibiotics from wastewater.

Abbreviations

A	—	total interfacial area between the two phases (m^2)
C_1^*	—	concentration of phase 1 at interface (g/L)
C_2^*	—	concentration of phase 2 at interface (g/L)
C_1	—	concentration of phase 1 (g/L)
C_2	—	concentration of phase 2 (g/L)
J	—	mass transfer rate (m/s)
K	—	overall mass transfer coefficient (m^2/s)
K_{aq} A	—	individual aqueous phase mass transfer coefficient (m^3/s)
K_{org} A	—	individual organic phase mass transfer coefficient (m^3/s)
KA	—	combined mass transfer coefficient (m^3/s)
m	—	equilibrium partition coefficient (–)
Q	—	amount of amoxicillin adsorbed per g of sorbent (mg/g)
V_1	—	volume of phase 1 (mL)
V_2	—	volume of phase 2 (mL)
V_r	—	phase volume ratio (–)
α	—	first model parameter (s^{-1})
β	—	second model parameter (–)

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