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# Kinetic and equilibrium of cefradine adsorption onto peanut husk

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## ABSTACT

Adsorption of cefradine onto peanut husk from aqueous solution was investigated in the paper. All the experiments were conducted at the same adsorbent dose (1.0 g/ml) and the same temperature of 293 K to investigate the effects of initial concentration of cefradine, contact time, ionic strength and solution pH. The results showed that it was effective to remove cefradine in the acidic medium and the equilibrium adsorption was practically achieved in 60 min. The presence of NaCl or $MgCl_2$ inhibited the adsorption of cefradine onto peanut husk, while the presence of $CaCl_2$ enhanced the adsorption capacity. The pseudo-second order kinetic equations could describe the adsorption kinetics rationally and the rate-limiting step was the intraparticle diffusion process. The Langmuir model provided the best correlation of the experimental data and could interpret the adsorption process and the Langmuir adsorption capacity was found to be 35.73 mg/g. Chemical modification of peanut husk could help to improve adsorption capacity of cefradine in aqueous solution. It was implied that peanut husk may be suitable as adsorbent material for adsorption of cefradine from aqueous solution.

*Keywords:* Peanut husk; Adsorbent; Adsorption; Cefradine; Adsorption kinetics; Adsorption isotherms

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## 1. Introduction

Since Penicillin was discovered by Alexander Fleming in 1928, antibiotics have attracted much attention from scientists worldwide. Antibiotics are one of the most successful families of drugs which aim for improving human health as well as reducing potential costs to cure certain diseases [1]. Due to the poor absorption of antibiotics, most kinds of them are excreted unchanged through faeces and urine and finally enter the environment after being used. Although from the economic and environment-friendly perspectives, it is an advisable choice to apply animal wastes as non-artificial fertilizers, there lies a potential risk that these drugs might lead to long-lasting antibiotic resistance to the other organisms. Frequent utilization of antibiotics has already raised concerns about increased antibiotic resistance of microorganisms [2–3].

As stated above, the removal of antibiotics from the environment should be highlighted and a removal method of low-cost and high-efficiency is urgently in need. A number of techniques have been developed for treating waste waters which contained organic contaminants, including antibiotics. It includes chemical precipitation, reverse osmosis, membrane filtration, and adsorption [4], etc. The former three methods are effective, but have a relatively higher costs and more complex operations than adsorption. In fact, adsorption is a promising technique which can remove trace amount of adsorbate from aqueous solution effectively and efficiently. Besides the conventional adsorbents, such as active carbons, more and more by-products of agriculture activities have been successfully adopted in water treatment. For example, several studies

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on the removal of basic dyes using various kinds of these non-conventional materials have been reported, such as: yellow passion fruit wastes [5], rice straw [6], cotton fiber [7], marine alga [8], sunflower seed shells [9], Parthenium [10], orange peel [11], etc.

Peanut husk, an agricultural waste available in large quantity in China, is often burned or discarded directly into the farm lands, which would produce waste gas and dust or unpleasant smell. Fortunately, we find a possible solution that is to utilize peanut husk as an adsorbent material to remove contaminants from waste water. It will solve both of the problems we concern about above and bring economic and environmental benefits to the industrial wastewater treatment. Therefore, researchers have studied about the removal of heavy metal onto peanut husk from aqueous solutions or how to modify peanut hulls [12].

In our research, the focus is fixed on the removal of cefradine, which is one of the most widely used antibiotics in China, from aqueous solution onto peanut husk to simulate the conditions of natural water. The effects of several factors including contact time, ions, pH, were discussed. The isotherms and kinetics of cefradine adsorption were studied to understand the adsorption mechanism of cefradine onto peanut husk.

## 2. Materials and methods

### 2.1. Preparation of cefradine solutions

Cefradine (FW = 349.41), one of the typical and the most widely used compound of antibiotics drugs, was purchased from Beijing Sino Tau Intl. Co. Ltd., China and used as received without further purification. The typical functional groups of cefradine contain amino group and carboxyl group and pKa are 7.3 and 2.5, respectively. The stock solutions of cefradine (400 mg/l) were prepared in distilled water. All working solutions were prepared by diluting the stock solution with distilled water to the required concentration.

### 2.2. Adsorbent preparation

Crude peanut husk (PH) were collected from a local market as solid wastes. They were washed with distilled water for several times, and dried in an oven at 328 K for 72 h untill a constant weight was reached. The dried PH were ground into particles with diameters between 0.15 and 0.20 mm by a metal ball-mill. The PH granules were stored before use. The chemical modification of PH consisted of three steps [13]: (1) PH formation of polyporus structures by 20% iso-propyl alcohol, the resulting adsorbent was used as the second adsorbent, abbreviated as APH; (2) APH alkali saponification by 0.1 mol/l NaOH, the resulting third adsorbent was abbreviated as SPH; (3) APH acidification by 0.1 mol/l phosphonic acid, the resulting forth adsorbent was abbreviated as PPH.

### 2.3. Batch adsorption experiments

Bioadsorption experiments were carried out in an isothermal rotary shaking at 250 rpm and 293 K 20°C using a series of 500 ml conical flasks containing 400 ml of different initial concentrations of cefradine solution. The initial pH values of the solutions were previously adjusted with 0.1 mol/l HCl or NaOH. Before determining optimum pH, the experiments were carried out at the original pH of the cefradine solution (pH 5.74). Meanwhile, the effects of different anions on the adsorption of cefradine were also studied. The adsorbent was added to each flask, and then the flasks were sealed up. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and the cefradine solutions were separated from the adsorbent by filtration with micro filter (0.45 μm). The cefradine concentrations were measured by a UV/V is spectrophotometer (Model UV 752, China) at 264 nm. The adsorption capacity ($q_t$) and the removal percentage of cefradine ($R$) were calculated using the following equations:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

$$R(\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \tag{2}$$

where $q_t$ (mg/g) is the capacity of cefradine adsorbed, $C_0$ (mg/l) is the initial cefradine concentration and $C_t$ (mg/l) is the cefradine concentration at time $t$, $V$ ($L$) is the initial volume of cefradine solution, and $W$ (g) is the amount of adsorbent used.

The effect of each parameter was studied by fixing the values of other parameters. In order to reduce adsorption error during the experiments, each experiment was conducted in triplicate under identical conditions, and then the mean values were obtained.

## 3. Results and discussion

### 3.1. Effects of contact time and initial cefradine concentrations on adsorption

The effect of initial concentrations of cefradine on the capacity of adsorption onto PH was studied. It was evident from Fig. 1 that the capacity adsorbed on the PH at a

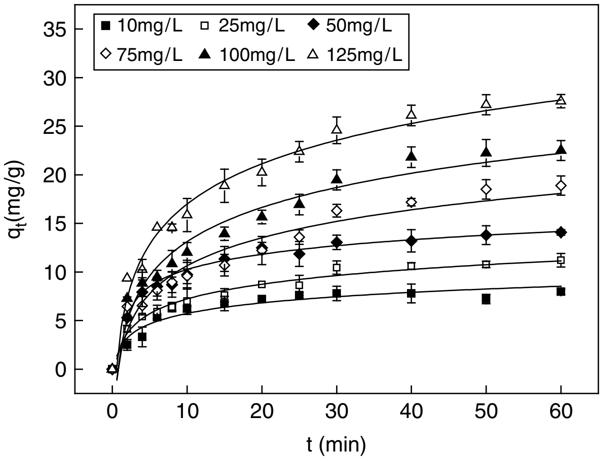

Fig. 1. Effect of initial concentration on removal of cefradine by PH (adsorbent dose: 1.0 g/l; temperature: 293 K; pH: 5.74; shaking speed: 250 r/min; contact time: 60 min).

lower initial concentration of cefradine was smaller than the corresponding capacity when higher initial concentrations were used. However, the percentage removal of cefradine was greater at lower initial concentrations and smaller at higher initial concentrations. Along with the increase of initial cefradine concentrations from 10 to 125 mg/l, the adsorption capacity increased from 7.96 to 28.53 mg/g , however, the removal percentage decreased from 79.62 to 22.82% and it remained constant after reaching equilibrium time. Also, Fig. 1 indicated that the removal of cefradine was rapid in the initial stages of contact time and gradually decreases with lapse of time until saturation. The rapid adsorption at the initial contact time is due to the availability of the positively charged surface of the PH for adsorption of cefradine at pH 5.74. The later slow percentage of cefradine adsorption is probably occurred due to the electrostatic hindrance or repulsion between the adsorbed negatively charged sorbate species onto the surface of PH and the available anionic adsorbate species in solution as well as the slow pore diffusion of the solute ions into the bulk of the adsorbent [14]. The equilibrium was found to be nearly 60 min when the maximum cefradine adsorption onto PH was reached.

### 3.2. Effect of ionic strength

The adsorption of cefradine on PH was studied by the addition of $CaCl_2$, $MgCl_2$, and NaCl to the test solution with concentration of 75 mg/l respectively (Fig. 2). It can be learned from the Fig. 2, the presence of $CaCl_2$ slightly enhanced the adsorption of cefradine, and the removal capacity increased from 18.12 mg/g to 21.00 mg/g within 60 min, while the existence of $MgCl_2$ and NaCl performed the absolutely opposite results, the removal capacity of which reduced to 16.60, 16.87 mg/g, respectively. The explanation of increasing in the adsorption capacity by $CaCl_2$ was that: (1) $Ca^{2+}$-cefradine complex formed in the adsorption process which would adhere to PH, which leading to a positive effect on adsorption; (2): the electrolyte metal ions in the text solution could compete with cefradine for solvent molecules, which leading to the reduction of heterozygosity and water solubility of cefradine, so the molecularized cefradine is easier to be adsorbed onto PH [15]. The interpretation of the opposite phenomenon was that: the pKa value of the amino hydrogen is 7.4 so the amino is protonated in aqueous solution and become the ion of ammonium that carrying a positive charge. So $Mg^{2+}$ and $Na^{-}$ as the inhibitors compete with carboxyl group for the limited active sites on the surface of PH reduce the adsorption percentages and capacity, whose mechanism has been reported by ion exchange [16].

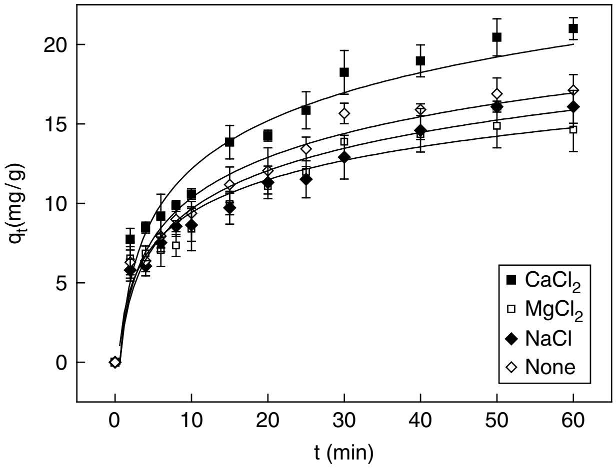

Fig. 2. Effect of ionic strength of $CaCl_2$, $MgCl_2$ and NaCl on removal of cefradine by PH (adsorbent dose: 1.0 g/l; concentration of cefradine: 75 mg/l; concentration of ion: 75 mg/l; temperature: 293 K; pH: 5.74; shaking speed: 250 r/min; contact time: 60 min).

### 3.3. Effect of initial pH

The effects of pH of cefradine solution were investigated in the research by adjusting initial pH over a range from 3.07 to 10.11 (Fig. 3). Within 60 min, the removal capacity decreased from 22.94 mg/g to 18.08 mg/g with increasing initial pH values of cefradine solution. A reduction in removal percentages from 30.59% to 24.12% was also observed, which indicates that an acidic medium will enhance the absorption. The effect of pH can be explained considering the surface charge on the adsorbate. pKa of carboxyl group and amino group in cefradine are 2.5 and 7.3 respectively. At any pH higher

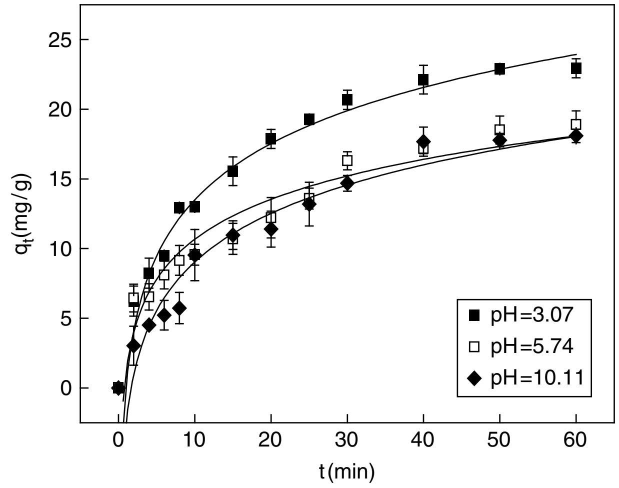

Fig. 3. Effect of pH of cefradine solution on removal of cefradine by PH (adsorbent dose: 1.0 g/l; concentration of cefradine: 75 mg/l; temperature: 293 K; shaking speed: 250 r/min; contact time: 60 min).

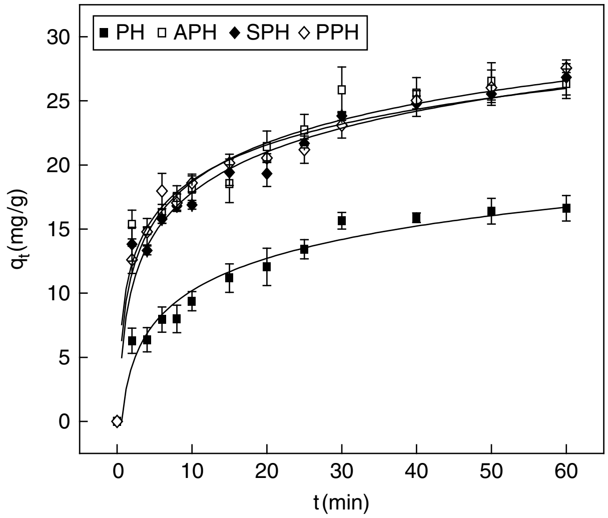

Fig. 4. Effect of different adsorbents on removal of cefradine (adsorbent dose: 1.0 g/l; concentration of cefradine: 75 mg/l; pH: 5.74; temperature: 293 K; shaking speed: 250 r/min; contact time: 60 min).

than 2.5, the carboxyl group will ionize and release a proton. A similar situation is that at any pH lower than 7.3, the amino groups will grab a proton. When pH is 3.07, an overall possible situation is the cefradine molecule has become a positively charged ion, thus it tended to be compete with protons for positively charged sites of PH [17]. However, when pH increased, high density of negative charges attacked the active sites. Unfortunately, cefradine had a weaker competitiveness than hydroxyl group which resulted in the reduction in the removal percentage and capacity.

### 3.4. *Effect of different adsorbents*

The effects of different adsorbents (PH, APH, SPH and PPH) on the capacity of adsorption were studied and shown in Fig. 4. According to experimental data, the capacity adsorption of cefradine at equilibrium time for APH, SPH and PPH have increased respectively by 53.86%, 56.72% and 60.98% compared to that of PH, which elucidated that chemical modification of PH can help to improve its adsorption capacity of cefradine in aqueous solution. The chemical modification mechanism could be explained as follows [18]: (1) Role of using 20% isopropyl alcohol was to discolor the PH and remove some polarity compound and organic small molecule, which led to form much polyporus structures on the PH surface; (2) Reactive phosphonic acid anhydride combined with cellulosic hydroxyl groups of PH to form an ester linkage and introduce sulfonic groups to the fiber, and the addition of carboxyl functions increased binding with positively charged amino groups in the structure of cefradine; (3) Role of using alkali saponification was to undergo the crosslinking reaction, increase some active binding sites and remove further hemicellulose, pigment, and so on, which can also help to improve adsorption capacity of cefradine by PH. A similar observation had been reported in previous literature [13,18].

### 3.5. *Adsorption kinetics*

Adsorption kinetics give information about adsorption capacity and rate of the biosorption process occurs. It is important to determine appropriate kinetic model that provides best-fitting with the experimental data. In this study, common used models, pseudo-first-order, second-order models and intraparticle diffusion model were applied to analyze experimental data and the kinetic adsorption process was elucidated.

#### 3.5.1. *Pseudo-first-order model*

The pseudo-first-order equation of Lagergren was generally expressed as follows [19]:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{3}$$

A linear form of pseudo-first-order model was described as below:

$$\ln\left(q_e - q_t\right) = -\frac{k_1 t}{2.303} + \ln q_e \tag{4}$$

where $q_e$ and $q_t$ (mg/g) are the amounts of cefradine adsorbed per unit weight of biosorbent at equilibrium and at time $t$, respectively, and $k_1$ ($\text{min}^{-1}$) is the rate constant of pseudo-first-order adsorption. The value of $k_1$ for cefradine adsorption by PH was determined from the plot of $\ln(q_e - q_t)$ against $t$.

### 3.5.2. Pseudo-second-order model

Also, the pseudo-second-order equation based on adsorption equilibrium capacity can be expressed as follows [20]:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{5}$$

A linear form of pseudo-second-order model was described as below:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{\left(k_2 q_e^2\right)} \tag{6}$$

where $k_2$ (g/mg · min) is the equilibrium rate constant of pseudo-second-order. The value of $k_2$ can be calculated from the slope and intercept of the plots $t/q_t$ versus $t$.

The values of $k_1$, $k_2$, $R_1^2$ (correlation coefficient for pseudo-first-order model) and $R_2^2$ (correlation coefficient for pseudo-second-order model) were calculated and shown in Table 1. According to Table 1, the correlation coefficients ($R_2^2$) values were found to be in the range 0.96–0.99, which indicated that the data conformed well to the pseudo-second-order kinetic model. The high agreement that exist between the calculated and experimental $q_e$ values of the pseudo-second-order kinetic model over the other model renders it best in adsorption of cefradine on PH. This confirms that the adsorption data are well represented by the pseudo-second-order kinetics for the entire adsorption period. The increase in values of the adsorption capacity, $q_e$ with an increase in the initial cefradine concentration could be attributed to the increase in the driving force for mass transfer, allowing more cefradine molecules to reach the surface of the adsorbents in the whole process [21].

### 3.5.3. Intraparticle diffusion model

The adsorbate species are most probably transported from the bulk of the solution into the solid phase through an intraparticle diffusion process, which is often the rate-limiting step in many adsorption processes. The possibility of intraparticle diffusion was explored by using the intraparticle diffusion model [22]:

$$q_t = K_{\text{id}} t^{0.5} + C \tag{7}$$

where $C$ is the intercept and $K_{\text{id}}$ is the intraparticle diffusion rate constant ($\text{mg/g} \cdot \text{min}^{0.5}$). The values of $q_t$ were found to give two lines part with values of $t^{0.5}$ (Fig. 5) and the values of

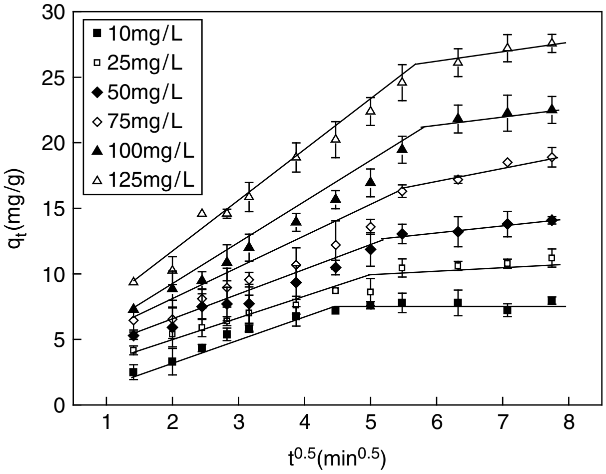

Fig. 5. Intraparticle diffusion constants for different initial cefradine concentrations.

Table 1
Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constant and calculated and experimental $q_e$ value obtained at different initial cefradine concentrations

| $C_0$(mg/l) | Pseudo-first-order kinetic model | | | | Pseudo-second-order kinetic model | | |
|---|---|---|---|---|---|---|---|
| | $q_{e,\text{exp}}$ mg/g | $q_{e,\text{cal}}$ mg/g | $k_1$ $\text{min}^{-1}$ | $R_1^2$ | $q_{e,\text{cal}}$ mg/g | $K_2$ g/(mg · min) | $R_2^2$ |
| 10 | 7.96 | 1.79 | 0.0656 | 0.6351 | 8.17 | 0.0344 | 0.9918 |
| 25 | 10.79 | 2.53 | 0.0639 | 0.9453 | 12.10 | 0.0123 | 0.9896 |
| 50 | 14.42 | 2.63 | 0.0682 | 0.9482 | 14.79 | 0.0144 | 0.9971 |
| 75 | 18.12 | 3.55 | 0.0662 | 0.9338 | 20.19 | 0.0047 | 0.9691 |
| 100 | 22.20 | 3.99 | 0.0823 | 0.9372 | 24.93 | 0.0041 | 0.9803 |
| 125 | 27.86 | 3.91 | 0.0568 | 0.9871 | 30.21 | 0.0041 | 0.9918 |

rate constant $K_{id}$ and intercept $C$ directly evaluated from the slope of plot of $q_t$ versus $t^{0.5}$ which is related to the thickness of the boundary layer was reported in Table 2. The shape of Fig. 5 confirmed that adsorption of the cefradine onto the PH was independent of one another, as plot usually showed two intersecting lines depending on the exact mechanism; the first one of these lines representing surface adsorption at the beginning of the reaction and the second one is the intraparticle diffusion at the end of the reaction. As still there is no sufficient indication about which of the two steps is the rate-limiting step. Ho [23] pointed out that it is essential for the $q_t$ versus $t^{0.5}$ plots to go though the origin if the intraparticle diffusion is the sole rate-limiting step. In the present study, any plot did not passed through the origin. This indicated that although intraparticle diffusion was involved in the adsorption process, it was not the sole rate-controlling step. This also confirms that adsorption of cefradine on the adsorbent was a multi-step process, involving adsorption on the external surface and diffusion into the interior [24]. The similar phenomenon was also observed for Direct N Blue-106 adsorption onto activated carbon from orange peel [25].

From Table 2, the constant $C$ was found to increase with increase of cefradine concentration from which indicating the increase of the thickness of the boundary layer and decrease of the chance of the external mass transfer and hence increase of the chance of internal mass transfer. The $R^2$ values given in Table 2 were close to unity indicating the application of this model, which may confirm that the rate-limiting step was the intraparticle diffusion process. The intraparticle diffusion rate constant, $K_{id}$, were in the range of 0.72–3.07 $\text{mg/g}^{-1} \cdot \text{min}^{-0.5}$ and it increased with increase of initial cefradine concentration.

### 3.6. Adsorption isotherms

To optimize the design of an adsorption system for the removal of adsorbate, it is important to establish the most appropriate correlation for the equilibrium data.

Table 2
The parameters obtained from intraparticle diffusion model using different initial cefradine concentrations

| $C_0$(mg/l) | Intraparticle diffusion model | | |
|---|---|---|---|
| | $K_{id}$ (mg/(g · min$^{0.5}$)) | $C$ | $R^2$ |
| 10 | 0.7245 | 3.2127 | 0.9014 |
| 25 | 1.1254 | 3.2180 | 0.9524 |
| 50 | 1.1526 | 3.4649 | 0.9537 |
| 75 | 2.2079 | 3.5028 | 0.9779 |
| 100 | 2.6620 | 3.5894 | 0.9768 |
| 125 | 3.0722 | 6.0325 | 0.9594 |

Various isotherm equations have been used to describe the isotherm curve. The relative parameters of each equation are obtained using the residual sum of squares (RSS) between the calculated data and the experimental data by nonlinear regressive analysis. The calculated expression of RSS is given as Eq. (8):

$$\text{RSS} = \sum (q_c - q)^2 \tag{8}$$

where, $q_c$ is the predicted (calculated) capacity of cefradine adsorbed onto PH according to the adsorption models, and $q$ is the experimental data.

The experimental data was tested with the Langmuir, Freundlich, Tempkin, Dubinin–Radushkevich isotherm equations. Linear regression was frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations was compared by judging the correlation coefficients.

### 3.6.1. The Langmuir adsorption isotherm

The Langmuir adsorption isotherm suggests that when the adsorbate occupies a site further adsorption can not take place at that site. All sites are energetically equivalent and there is no interaction between molecules adsorbed on neighboring sites [26]. The Langmuir equation was described as follows:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{9}$$

Above equation can be linearized in following reciprocal form:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{(K_L Q_m)} \tag{10}$$

where $C_e$ (mg/l) is the concentration of the cefradine at equilibrium, $q_e$ (mg/g) is the amount of cefradine adsorbed at equilibrium, $Q_m$ is the maximum adsorption capacity, $K_L$ is the Langmuir constant related to the affinity of the binding sites and energy of adsorption.

### 3.6.2. The Freundlich adsorption isotherm

Similarly, the Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface and suggests a multilayer adsorption. Adsorption energy exponentially decreases on completion of the adsorption centers of an adsorbent [27]. The Freundlich isotherm was commonly presented as follows:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{11}$$

Freundlich equation can be linearized as follows:

$$\ln q_e = \left(\frac{1}{n}\right)\ln C_e + \ln K_F \tag{12}$$

where $K_F$ and $n$ are the Freundlich constants related to the adsorption capacity and the adsorption intensity of the adsorbent, respectively. $1/n$ is the heterogeneity factor and $n$ is a measure of the deviation from linearity of adsorption.

### *3.6.3. The tempkin isotherm*

Tempkin isotherm model contains a factor that explicitly takes into account adsorbing species–adsorbate interactions [28]. The Tempkin isotherm has commonly been applied in the following form (Eq. (13)):

$$q_e = \frac{RT}{b_T}\ln(A_T C_e) \tag{13}$$

The linear form of Tempkin isotherm (Eq. (13)) can be expressed as:

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{14}$$

where $B_T = (RT)/b_T$, $T$ is the absolute temperature in Kelvin and $R$ is the universal gas constant, 8.314 J/mol · K. The constant $b_T$ is related to the heat of adsorption [29].

### *3.6.4. The Dubinin–Radushkevich (D–R) isotherm*

Another equation used in the analysis of isotherms was proposed by Dubinin–Radushkevich. D–R model was applied to estimate the porosity apparent free energy and the characteristic of adsorption [30–31]. The D–R isotherm is dose not assume a homogeneous surface or constant sorption potential and it has commonly been applied in the following form (Eq. (15)) and its linear form can be shown in Eq. (16):

$$q_e = Q_m \exp(-K\varepsilon^2) \tag{15}$$

$$\ln q_e = \ln Q_m - K\varepsilon^2 \tag{16}$$

where $K$ is a constant related to the adsorption energy, $Q_m$ the theoretical saturation capacity, ε is the Polanyi potential can be calculated from Eq. (17):

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{17}$$

The slope of the plot of ln versus $q_e$ gives $K$ (mol$^2$/kJ$^2$) and the intercept yields the adsorption capacity, $Q_m$ (mg/g). The mean free energy of adsorption ($E$), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the sorbent, was calculated from the $K$ value using the following relation (Eq. (18)) [32]:

$$E = \frac{1}{\sqrt{2K}} \tag{18}$$

All relative parameters of the isotherm equations, the determined coefficients ($R^2$), and the values of other parameters are listed in Table 3, respectively. Fig. 6 depicted the experimental equilibrium data and the fitted equilibrium curve by four various isotherms, respectively.

Table 3
Correlation isotherm parameters and correlation coefficients for adsorption of cefradine onto PH adsorbent

| Isotherm models | Correlation parameter | | Correlation coefficient |
|---|---|---|---|
| | Name | Value | $R^2$ |
| Langmuir isotherm | $Q_m$ (mg/g) | 35.73 | 0.9672 |
| | $K_L$ (l/mg) | 0.03 | |
| | RSS | 19.33 | |
| Freundlich isotherm | $K_F$ (l/mg) | 5.23 | 0.9437 |
| | $1/n$ | 0.34 | |
| | RSS | 33.16 | |
| Tempkin isotherm | $A_T$ (l/g) | 0.59 | 0.9456 |
| | $B_T$ (mg/L) | 6.43 | |
| | $b_T$ | 378.84 | |
| | RSS | 32.05 | |
| Dubinin–Radushkevich isotherm | $Q_m$ (mg/g) | 31.13 | 0.7633 |
| | $K$ (mol$^2$/kJ$^2$) | 3.89 | |
| | $E$ (kJ/mol) | 0.36 | |
| | RSS | 121.98 | |

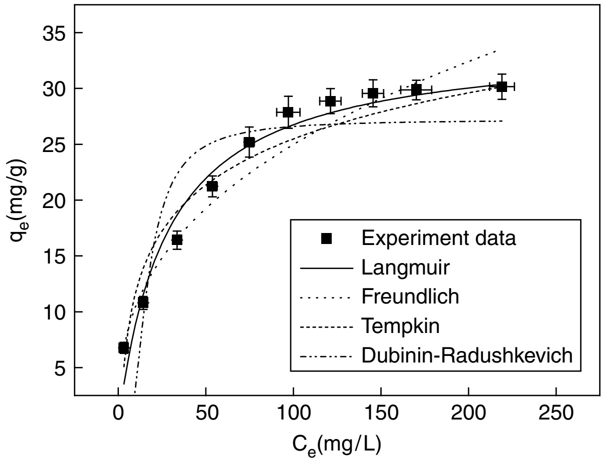

Fig. 6. Comparison of different isotherm models for cefradine adsorption onto PH (adsorbent dose: 1.0 g/l; temperature: 293 K; shaking speed: 250 r/min; contact time: 60 min).

From Table 3, it was observed that the equilibrium data were fitted to four isotherm equations (the Langmuir, Tempkin, Freundlich and Dubinin–Radushkevich expressions), with $R^2$ values of 0.9672, 0.9456, 0.9437 and 0.7633 respectively. The values of RSS became larger in the order of the Langmuir, Tempkin, Freundlich and Dubinin–Radushkevich expressions with 19.33, 32.05, 33.16 and 121.98 respectively. The lower determined coefficient with larger value of RSS for the Dubinin–Radushkevich isotherm confirmed the non-applicability of this model for cefradine/PH systems. By comparing between the experimental data and fitted curves, it was found the Langmuir isotherms can predict equilibrium adsorption behavior. The higher determined coefficient of 0.9672 and the lower determined RSS of 19.33 for the Langmuir isotherm predicted the monolayer coverage of cefradine onto peanut particles. A similar observation had been reported in previous literature when peanut husk was utilized as low-cost adsorbent to remove Neutral Red from aqueous solution [20].

In this study, the *E* value calculated from Eq. (18) was calculated as 0.36 kJ/mol for cefradine on the PH medium. This indicated that physisorption played a significant role in the adsorption process.

From Table 3, it can be seen that the values of $Q_m$ from Langmuir and D-R models were similar. The reported values of $Q_m$, the Langmuir constant related to saturated monolayer adsorption capacity for powdered and granular activated carbon [33], natural zeolite [34], are 257.90, 325.30 and 19.80 567 antibiotics mg/g, respectively. Furthermore, peanut husk has been utilized as low-cost adsorbent to remove dyes from aqueous solution in previous paper and the values of $Q_m$ obtained from Langmuir was 37.5 mg/g at 295K [20]. In the present study, the cefradine adsorption capacity of PH at 293 K estimated from Langmuir isotherm is 35.73 mg/g, which indicated that PH is competitive to other adsorbents for the uptake of cefradine from their aqueous solutions. Further more, as an agricultural by-product, peanut husk is vast and cheap, and therefore, it can be used to remove cefradine from solution.

## 4. Conclusions

This study confirmed that peanut husk, a low cost agricultural by-product, could effectively remove cefradine from aqueous solution. The results showed that it was effective to remove cefradine in the acidic medium and the equilibrium adsorption was practically achieved in 60 min. The presence of NaCl or $MgCl_2$ inhibited the adsorption of cefradine onto peanut husk, while the presence of $CaCl_2$ enhanced the adsorption capacity. The equilibrium adsorption data were analyzed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models. The results indicated that the Langmuir model provided the best correlation of the experimental data and the adsorption capacity was found to be 35.73 mg/g. The kinetic study of cefradine on PH was performed based on pseudo-first-order, pseudo-second-order and intraparticle diffusion equations. The adsorption kinetics followed pseudo-second-order kinetic model very well and the rate-limiting step was the intraparticle diffusion process. Chemical modification of PH can help to improve its adsorption capacity of cefradine. Based on this research, an application of PH on wastewater treatment could efficiently remove antibiotics in the solution and solve the problems of solid waste as well.

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