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Binary Adsorption Kinetics of Tetracycline and Doxycycline on HKUST-1: Modification Pseudo First and Second Order Models

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Abstract. The investigation of kinetics is crucial for optimizing the adsorption process, particularly in multicomponent systems where several adsorbates compete for active sites on the adsorbent particle. This study presents a novel approach to improve the pseudo-first-order and pseudo-second-order kinetic models by integrating a competition parameter. This parameter quantifies the influence of the adsorbate interaction on the adsorption process. Empirical data of binary adsorption involving doxycycline (DXC) and tetracycline (TTC) were used to validate the improved models. The results indicate that the adjusted pseudo-first-order and pseudo-second-order kinetic models effectively depict the adsorption kinetics when the R^2 values approach unity. The competition factor, denoted by the parameter α, quantifies the degree to which one adsorbate affects the adsorption capacity of the other. This study indicates that the revised models offer a more thorough understanding of adsorption kinetics in multicomponent systems, thereby facilitating more effective selection of adsorbents and optimization of the process.

Introduction

A critical consideration in designing an efficient sorption system is accurately assessing the rate at which pollutants are effectively eliminated within a specific solid/solution system. Considerable efforts have been undertaken to develop comprehensive mathematical equations that may effectively elucidate the kinetics of sorption in these systems. The advances in this domain seem constrained by the complexity involved in accurately articulating sorption kinetics, surpassing the theoretical depiction of sorption equilibria. The emergence of this phenomenon can be attributed to the recognition that the governing equations for thermodynamic quantities at equilibrium are fundamentally functional representations of the equations that account for the temporal changes in these values under non-equilibrium circumstances [1].

Some models for interfacial kinetics, like the Langmuir model, can be used as a starting point for making a good model, which can then be changed to fit a specific sorption system. This methodology has resulted in formulating numerous expressions on the phenomenon of a chemical reaction on a surface and its structural arrangement [1]. The predominant interfacial kinetic adsorption models employed to simulate adsorption kinetics in liquid systems are pseudo-first-order and pseudo-second-order [2-8].

The pseudo-first-order equation, commonly called the Lagergren equation, is widely recognized as an elementary model equation that provides insight into the sorption rate in liquid-phase systems.

Furthermore, this equation has been extensively employed in the field of kinetic adsorption until the present time [1]. The phenomenon known as pseudo-second-order kinetics is commonly observed in cases where the pace of the direct adsorption/desorption process, which can be viewed as a chemical reaction, governs the overall sorption kinetics. Blanchard et al. [9] originally introduced the mathematical equation associated with this model to elucidate the kinetics of heavy metal elimination by utilizing natural zeolites.

The applicability of all adsorption kinetic models derived from interfacial kinetics extends to single-component adsorption systems. Typically, the adsorption process does not include a single component in real conditions. Instead, practically all adsorption processes in real conditions involve the adsorption of many adsorbate components. Up to this point, developing adsorption kinetic models to represent multicomponent systems has remained extremely rare, particularly for pseudo-first-order and pseudo-second-order kinetic models. Thus, this work presents a straightforward adjustment to the pseudo-first-order and pseudo-second-order adsorption kinetic equations to accurately describe the adsorption kinetic data of binary component systems. The adsorbent employed was the metal-organic framework HKUST-1 to accomplish this objective, whereas the binary system adsorbate consisted of the antibiotics tetracycline and doxycycline.

The rationale for choosing tetracycline and doxycycline as adsorbates is their extensive application in treating infections caused by diverse bacterial strains. Nonetheless, both antibiotics are challenging for the body to absorb during metabolism, resulting in substantial excretion into the environment. Moreover, both antibiotics are not readily degradable in the environment. During the preliminary assessment, HKUST utilized in this work showed a significant capacity to adsorb both antibiotics, with HKUST-1 serving as the adsorbent and tetracycline and doxycycline as the adsorbates.

Materials and Methods

Materials. The raw materials used for the synthesis of HKUST-1 were $Cu(NO_3)_2 \cdot 3H_2O$ (Merck, puriss. p.a., 99-104%), trimesic acid/benzene-1,3,5-tricarboxylic acid/H_3BTC (Merck, 95%), reverse-osmosis water, ethanol (≥99.5%, ACS reagent) and NaOH (Merck, reagent grade, ≥98%, pellets (anhydrous)). Meanwhile, the antibiotics used as adsorbates are tetracycline hydrochloride (Merck, ≥95% (European Pharmacopoeia HPLC assay)) and doxycycline (Merck).

Methods

Synthesis of MOF HKUST-1. The metal-organic framework HKUST-1 was synthesized at 30 ºC with the following procedure [10]: The first step involved weighing 0.96 grams of $Cu(NO_3)_2 \cdot 3H_2O$ particles and dispersing them in 100 milliliters of deionized water. The solution was alkalized to a pH of around 13 by adding 1 M NaOH. Once NaOH was added, the solution was agitated at ambient temperature for 8 hours, forming blackish-green $Cu(OH)_2$ precipitates. Next, the nanoparticles were isolated from the reaction mixture by centrifugation, rinsed with deionized water until the pH reached neutral (6–7), and dried in the oven. The dispersion of the dry nanoparticles (0.46 g) in 230 mL of deionized water was achieved by ultrasonication. An additional 230 mL of a 20 mM ethanol solution of H_3BTC was introduced into the suspension and agitated at ambient temperature for 2 hours. The precipitated products were obtained by centrifugation and rinsed repeatedly with deionized water and ethanol. The resultant product was ultimately desiccated using vacuum pressure.

Characterization of MOF HKUST-1. XRD, nitrogen sorption, and scanning electron microscopy (SEM) techniques were employed to analyze the crystalline structure, pore structure, and surface topography of HKUST-1. The X-ray diffraction (XRD) pattern of the Metal-Organic Framework (MOF) was obtained using a PANalytical X'Pert Pro X-ray diffractometer fitted with a Cu Kα radiation source with a wavelength of 0.15406 nm. The material's pore structure was determined using the Micromeritics ASAP 2020 sorption analyzer. The scanning electron microscopy (SEM) image of MOF HKUST-1 was obtained using the JSM-6390 field emission SEM from JEOL, Ltd., Japan.

Determination of antibiotics concentration. Post-experiment, the initial and residual antibiotic concentrations of the solution being studied were quantified using a UV–Vis spectrophotometer

(SHIMADZU UV/VIS-1700 PharmaSpec) at peak wavelengths of 276.5 nm for tetracycline and 373.5 nm for doxycycline [10].

Adsorption kinetics. The kinetics of adsorption for tetracycline and doxycycline in a binary system using HKUST-1 adsorbent were investigated by the following method: Eight Erlenmeyer flasks were filled with a solution containing tetracycline and doxycycline, each at a concentration of 200 ppm. Each flask was filled with 50 mL of antibiotic solution. Then, 50 mg of HKUST-1 was added to each flask, which was immersed in a shaking water bath and agitated at 200 revolutions per minute. One Erlenmeyer flask was collected at specific intervals to examine the residual tetracycline and doxycycline levels following the adsorption procedure. The amount of tetracycline ($q_{t,t}$) and doxycycline ($q_{t,d}$) adsorbed by HKUST-1 at time t are given by Eq. 1 and Eq. 2, respectively.

$$q_{t,t} = \frac{(C_{o,t} - C_{t,t})}{m} V \quad (1)$$

$$q_{t,d} = \frac{(C_{o,d} - C_{t,d})}{m} V \quad (2)$$

Where m is the mass of HKUST-1, and V is the volume of the antibiotics mixture. The symbols $C_{o,t,}$ and $C_{o,d}$ represent the initial concentration of tetracycline and doxycycline, respectively. The concentration of tetracycline and doxycycline during the adsorption process at time t is given by the symbols $C_{t,t,}$ and $C_{t,d}$, respectively.

Results and Discussions

Characterization of HKUST-1. Fig. 1 displays the surface topography and form of HKUST-1, which was synthesized from $Cu(NO_3)_2$ and H_3BTC at ambient thermal conditions. An octahedral shape with well-visible edges characterizes the HKUST-1 structure. The particles produced from HKUST-1 exhibit a morphology that closely resembles that of HKUST-1 synthesized using $CuCl_2$ as a metal source [10].

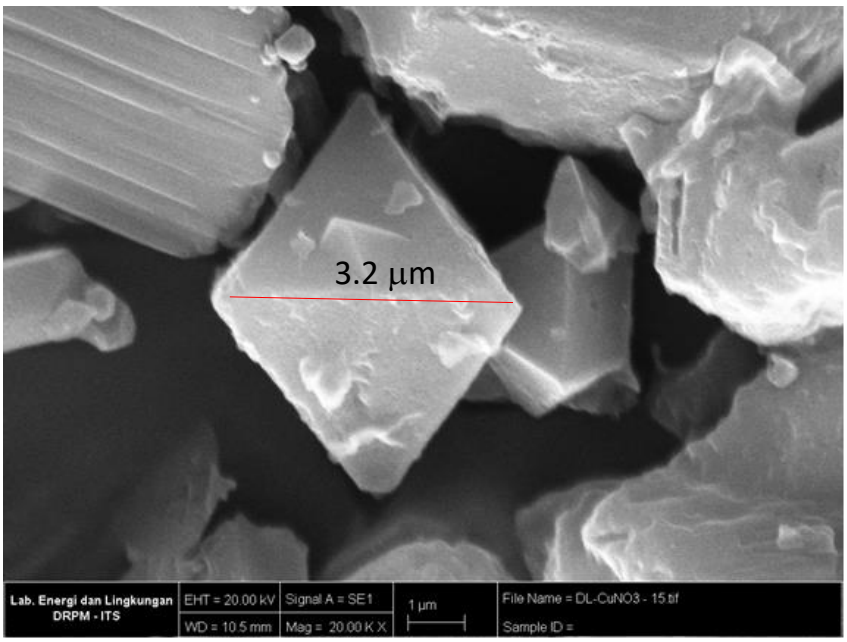

Fig. 1. SEM image of HKUST-1 synthesized from $Cu(NO_3)_2$ and H_3BTC under alkaline condition

HKUST-1's crystallinity was determined using X-ray diffraction (XRD) analysis. The diffraction profile of HKUST-1 is depicted in Figure 2. Sharp peaks in X-ray diffraction (XRD) patterns indicate a significant level of crystallinity in HKUST-1 obtained from $Cu(NO_3)_2$ and H_3BTC. From Fig. 2, it can be seen that diffraction peaks of HKUST-1 are observed at 2θ of 6.61°, 9.36°, 11.50°, 13.27°,

14.48°, 16.35°, 17.33°, 18.90°, 20.10°, 25.80°, 28.60°, 29.18°, 35.06°, and 36.26°. The diffraction peaks correspond to the diffraction indices: 200, 220, 222, 400, 331, 422, 511, 440, 600, 731, 822, 751, 773, and 882. The X-ray diffraction (XRD) results obtained in this work are consistent with the XRD results of HKUST-1 obtained by Laysandra et al. [10]. The synthesis of HKUST-1 was achieved by employing $CuCl_2$ as a metal cluster and H3BTC as an organic ligand. The analysis suggests that the Cu salt employed has minimal impact on the crystal structure or crystallinity of the HKUST-1 produced. The particle size of HKUST-1 obtained is in the range of 0.6–3.2 μm.

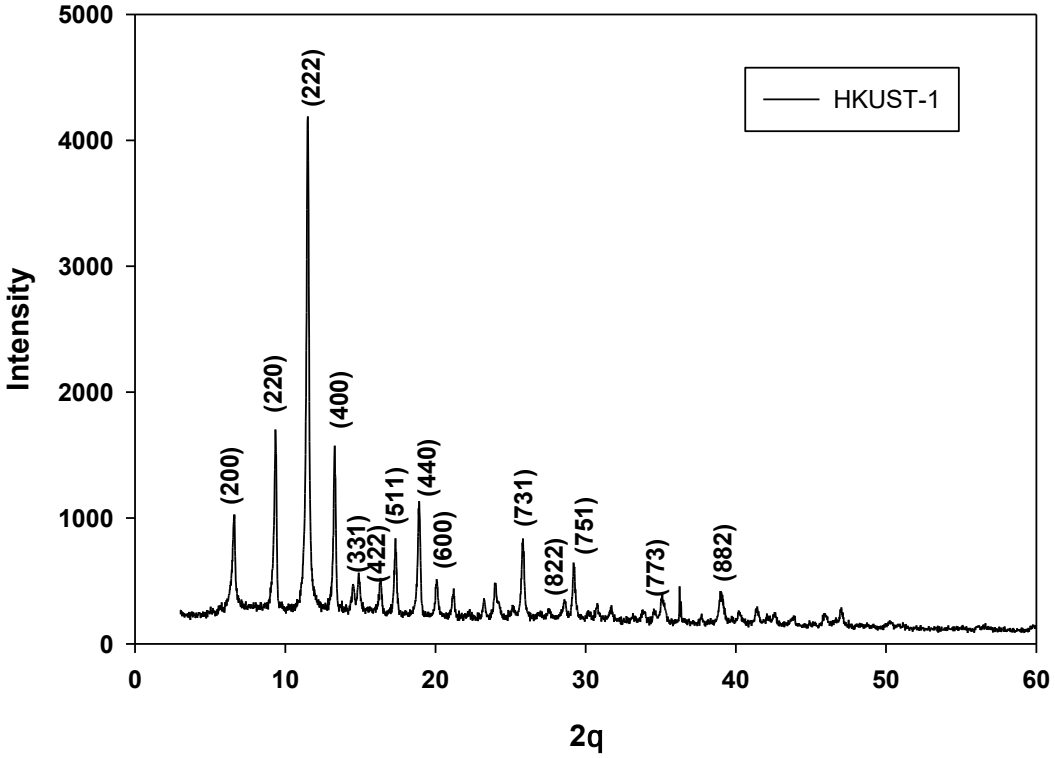

Fig. 2. XRD diffractogram of HKUST-1 synthesized from $Cu(NO_3)_2$ and H_3BTC

The measurement of nitrogen gas adsorption and desorption curves in HKUST-1 was conducted at a nitrogen boiling temperature of -196 °C. Figure 3 presents the obtained results. The presented Figure provides clear evidence that HKUST-1, as obtained in this study, displays both micropores (indicated by significantly high nitrogen adsorption at low relative pressure (< 0.05)) and mesopores (characterized by consistent nitrogen adsorption at moderate pressure, followed by a rapid rise in adsorption at relatively high pressure). The BET surface area of HKUST-01 was determined by applying the BET equation throughout the relative pressure range of 0.05-0.25. The resulting value was 1041 m2/g. HKUST-01, with its large BET surface area, is particularly well-suited as an adsorbent for removing dangerous chemicals from aqueous environments.

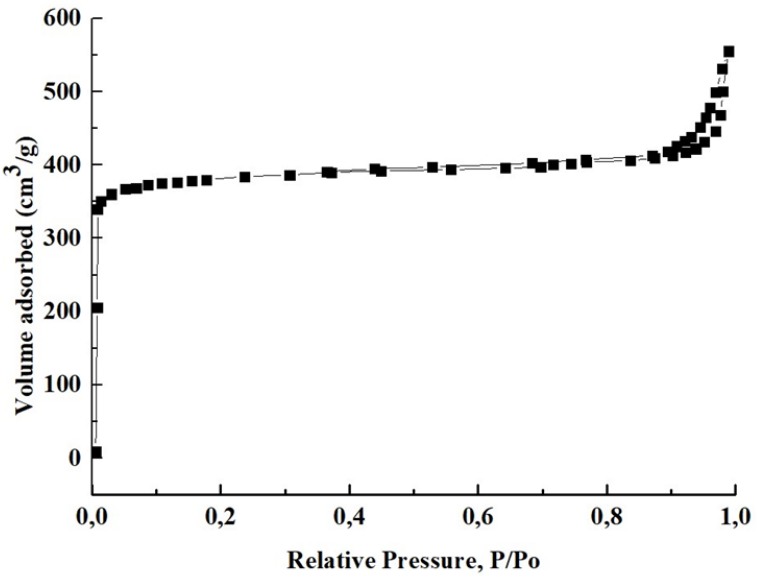

Fig. 3. Nitrogen sorption isotherm of HKUST-1 synthesized from $Cu(NO_3)_2$ and H_3BTC

The pore size distribution of HKUST-1 was obtained by applying the NL-DFT equation to nitrogen adsorption data, and the results are given in Fig. 4. HKUST-1 possesses both micropores and mesopores as indicated by the NL-DFT pore size distribution (Fig. 4). The sizes of micropores are 0.4 to 2 nm, while the mesopores mostly between the range 2 to 5.2 nm. Larger sizes of micropores are also observed, but only in a small fraction.

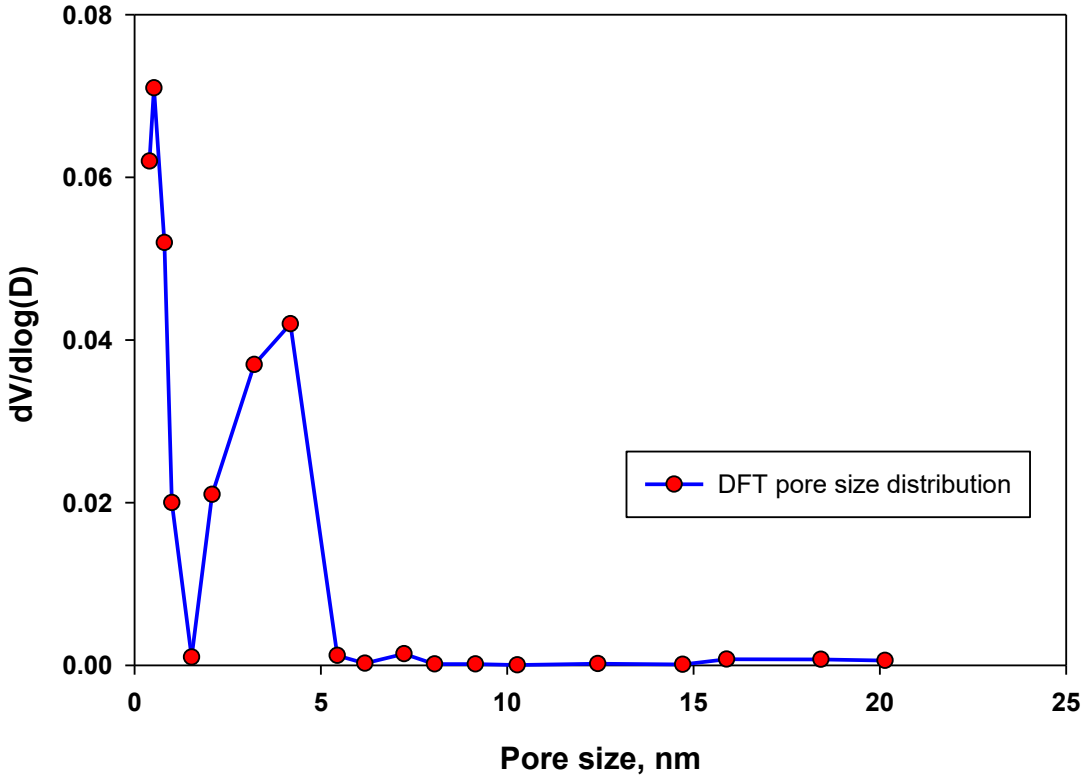

Fig. 4. DFT pore size distribution of HKUST-1 synthesized from $Cu(NO_3)_2$ and H_3BTC

Adsorption kinetics. In the late 19th century, Lagergren introduced the empirical rate equation by which oxalic and malonic acids are adsorbed onto charcoal [1]. The pseudo-first-order equation, often known as the Lagergren equation, is among the oldest known equations describing the sorption rate in liquid-phase media. Furthermore, it remains one of the most extensively employed kinetic equations. The Pseudo-first equation has the mathematical expression as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

Integration Eq. 3 gives the following result:

$$q_t = q_e\big(1 - exp(-k_1 t)\big) \tag{4}$$

We define q_e as the quantity of adsorbate adsorbed by the adsorbent under equilibrium circumstances and q_t as the quantity adsorbed by the adsorbent at time t. Parameter k_1 is defined as a time constant [1]. To find the values of q_e and k_1 parameters, the well-established linear regression approach, based on the linear version of Equation 4, is used. The k_1 parameter is a time-scaling factor determining the rate at which a system can achieve equilibrium. A higher k_1 value indicates a shorter time required for a system to achieve equilibrium. In several adsorption systems, the pseudo-first-order performance is less favorable than that of the pseudo-second-order [11-18].

Typically, pseudo-second-order kinetics refers to the scenario where the direct adsorption/desorption rate, considered a chemical reaction, governs the total sorption kinetics. The mathematical formulation associated with this model was introduced explicitly by Blanchard et al. [9] to elucidate the kinetics of heavy metal elimination by natural zeolites. The assumption was made that the ion exchange reaction rate on the surface determines the removal kinetics. It was also assumed that the kinetic order of this reaction is 2 with the number of adsorption sites available for the exchange [1]. The differential form of pseudo-second-order kinetic is as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

Parameter k_2 is a pseudo-second-order constant, usually obtained through linear or non-linear regression of the experimental data. Several investigations and the widespread application of the pseudo-second-order model have demonstrated that specific operating conditions significantly influence the value of k_2. The value of the k_2 constant varies significantly with the initial solute concentration applied. Reducing k_2 with rising initial concentration is a well-established fact in interpreting k_2 as a time-scaling factor. Specifically, a longer time is needed to attain equilibrium when the starting concentration value is higher. Integration of Eq. 5 gives the result as follows:

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

In the adsorption methodology for treating industrial wastewater, the constituents present in the wastewater consist of a diverse combination of different components. Hence, the adsorption equations, encompassing both kinetics and equilibrium, designed for individual components generally lack applicability in representing the kinetics or equilibrium of adsorption for binary or more components. Therefore, it is necessary to modify or develop the existing adsorption kinetic or equilibrium equations so that they can represent multicomponent adsorption data.

Extensive adjustments have been made to adsorption isotherm equations to accurately characterize multicomponent adsorption systems [10, 19-23]. However, development or modification to adsorption kinetics for multicomponent systems remains uncommon. The process phenomena in the binary system adsorption process are more complicated than those in a single-component process. Competition for the active surface occurs between adsorbate A and adsorbate B and between adsorbate A and the solvent and adsorbate B and the solvent. Furthermore, there is contact between adsorbates A and B among the competition on the surface of the adsorbent. The existence of competitive elements on the active surface and the interaction between adsorbates results in a reduced quantity of adsorbate trapped on the adsorbent compared to the adsorption process involving a single component.

To consider the phenomenon of competitive adsorption between tetracycline and doxycycline included in the solution, competition factors α_T and α_D (T is tetracycline and D is doxycycline) were introduced, modifying the equilibrium adsorption capacities as follows:

$$q_{e,T} = q_{e,T}(1 - \alpha_D) \tag{7}$$

$$q_{e,D} = q_{e,D}(1 - \alpha_T) \tag{8}$$

Substitution Eqs. 7 and 8 into Eq. 4 give the following pseudo-first-order kinetic for the binary adsorption process:

$$q_{t,T} = q_{e,T}(1 - \alpha_D)\big(1 - exp(-k_1 t)\big) \tag{9}$$

$$q_{t,D} = q_{e,D}(1 - \alpha_T)\big(1 - exp(-k_1 t)\big) \tag{10}$$

For the pseudo-second-order model, the inclusion of competition factors α_T and α_D are conducted in Eq. 5 as follows:

$$\frac{dq_{t,T}}{dt} = k_{2,T}\big(q_{e,T} - q_{t,T} - \alpha_T q_{t,D}\big)^2 \tag{11}$$

$$\frac{dq_{t,D}}{dt} = k_{2,D}\big(q_{e,D} - q_{t,D} - \alpha_D q_{t,T}\big)^2 \tag{12}$$

Integration Eqs. 11 and 12 resulting the following equations

$$q_{t,T} = \frac{q_{e,T}^2 k_{2,T} t - 2q_{e,T}\alpha_T q_{t,D} k_{2,T} t + \big(\alpha_T q_{t,D}\big)^2 k_{2,T} t}{1 + q_{e,T} k_{2,T} t - \alpha_T q_{t,D} k_{2,T} t} \tag{13}$$

$$q_{t,D} = \frac{q_{e,D}^2 k_{2,D} t - 2q_{e,D}\alpha_D q_{t,T} k_{2,D} t + \big(\alpha_D q_{t,T}\big)^2 k_{2,D} t}{1 + q_{e,D} k_{2,D} t - \alpha_D q_{t,T} k_{2,D} t} \tag{14}$$

The modified models were validated by fitting experimental data of binary adsorption of doxycycline (D) and tetracycline (T). The parameters of Eqs. 9, 10, 13, and 14 were obtained by fitting experimental adsorption kinetics. The fitting process was carried out simultaneously using Eqs. (9) and (10) or (13) and (14) on the binary adsorption data of tetracycline and doxycycline.

Table 1 presents the fitting results for the modified pseudo-first-order and pseudo-second-order equations. Both models demonstrate high conformity to the experimental data, with R^2 values approaching 1. Figure 5 presents the theoretical plots and experimental kinetic data for the binary adsorption of tetracycline and doxycycline on HKUST-1 gel.

Table 1. Parameters of modified pseudo-first-order and pseudo-second-order for adsorption of tetracyclin and doxycyclin on HKUST-1.

Modified Pseudo First Order	**q_e (mg g^{-1})**	**k_1 (g mg^{-1} min^{-1})**	***α***	**R^2**
Doxycyclin	-5.0536	0.1447	1.3511	0.9960
Tetracyclin	-0.4280	0.1843	0.1318	0.9979
Modified Pseudo Second Order	**q_e (mg g^{-1})**	**k_2 (g mg^{-1} min^{-1})**	***α***	**R^2**
Doxycyclin	132.7106	0.0025	0.0070	0.9976
Tetracyclin	130.5425	0.0026	0.0714	0.9865

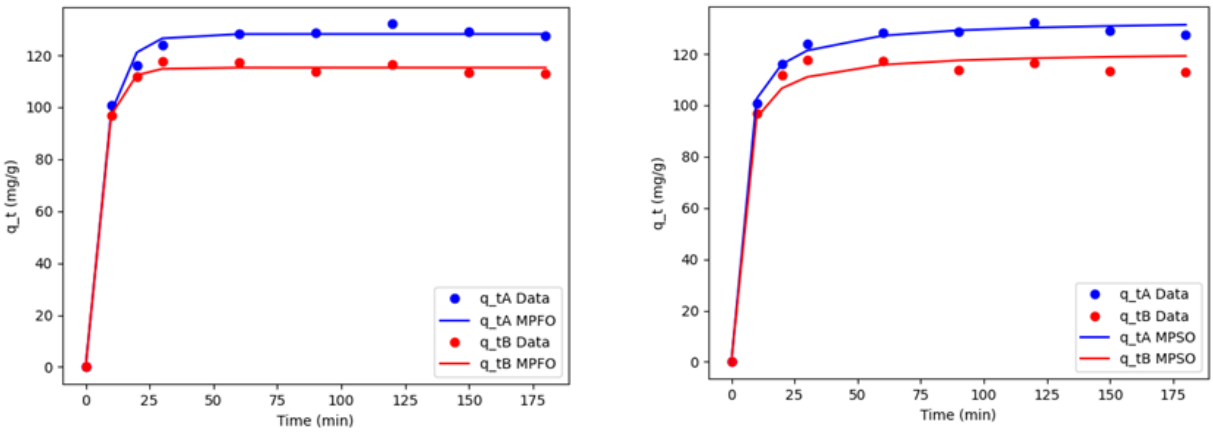

Fig. 5. Binary adsorption experimental data of tetracyclin and doxycycline on HKUST-1 and theoretical values calculated using modified pseudo-first-order and pseudo-second-order

Upon a cursory examination of Fig. 5 and the R^2 values indicated in Table 1, it is evident that the equations derived from the pseudo-first-order and pseudo-second-order modifications effectively depict the adsorption data of the binary compounds tetracycline and doxycycline on HKUST-1. To assess the suitability of an adsorption equation in representing the adsorption experimental data, it is essential to evaluate the experimental data fitting results' parameters thoroughly. This evaluation should not rely simply on the R^2 value or the visual manifestation of the theoretical results. The values of the parameters obtained must have physical meaning and be reasonable. Upon further examination of Table 1, it is evident that the q_e parameter for the pseudo-first-order modification is negative for both combinations of antibiotics. The qe parameter provides the equilibrium state of an adsorption system and is required to be positive. A negative value obtained from the fitting results of the experimental data suggests that the pseudo-first-order modification is inadequate in representing the experimental data of the adsorption of the tetracycline and doxycycline binary system on HKUST-1.

The competition factors, α_T and α_D, were analyzed to determine the impact of one adsorbate on the adsorption of the other. Values of α_T or α_D greater than 1 suggest a significant competitive effect, while values less than 1 indicate a relatively small impact. If the competition factor approaches zero, it implies that the adsorption of one adsorbate is nearly unaffected by the presence of the other, indicating weak interaction or adsorption at different sites. The competition parameters for tetracycline and doxycycline listed in Table 1 are relatively low, with values of 0.007 for doxycycline and 0.0714 for tetracycline. The low competition parameter values observed for both antibiotics suggest a lack of competition between them for the active group of HKUST-1.

Doxycycline is a tetracycline antibiotic that shares identical physiological characteristics with other tetracycline antibiotics. Both antibiotics possess three pKas, for which their values are nearly identical. Tetracycline has pKa_1 = 3.5 (acidic, tricarbonyl methane moiety), pKa_2 = 7.7 (slightly alkaline, phenoldiketone moiety), and pKa_3 = 9.5 (strong alkaline, ammonium ion moiety). Doxycycline has pKa1 = 3.3 (acidic, tricarbonyl methane moiety), pKa2 = 7.3 (slightly alkaline, phenoldiketone moiety), and pKa3 = 9.4 (strong alkaline, ammonium ion moiety). Closely matched pKa values diminish competition for active adsorption groups for both antibiotics.

Conclusions

The proposed modifications to the pseudo-first-order and pseudo-second-order kinetic models effectively integrate the phenomenon of adsorbate competition within a multicomponent system. The revised models offer a more comprehensive understanding of adsorption and exhibit high precision in forecasting adsorption kinetics, as indicated by R^2 values closely approaching unity. Their implications for designing and optimizing adsorption systems in industrial applications, where multicomponent adsorption is prevalent, are substantial. It is recommended that future studies should

prioritize the investigation of the suitability of these modified models for other systems and enhance the competition parameters to accommodate more intricate situations.

Acknowledgment

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