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Adsorption potential of spherical ZnO particles for sufficient antibiotic removal: isotherm, kinetic and thermodynamics

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ABSTRACT

Due to the improvements of pharmaceutical industry, tetracycline (TC) is commonly detected in natural water environments, resulting in significant adverse impacts on living species. In this study, the TC adsorption over commercial spherical zinc oxide (ZnO) samples was systematically examined by considering adsorption isotherm models, kinetic model and thermodynamic behavior. The Langmuir kinetic model displayed the highest correlation coefficient (R^2 = 0.97) with a maximum adsorption capacity of 86.35 mg/g. According to the results of the kinetic studies, the adsorption could be driven by both the bulk transfer of adsorbate molecules towards the adsorbent surface within the solution and chemisorption on the surface and inside the pores. In addition, the TC adsorption on the ZnO particles promoted by increasing temperature. The commercial spherical zinc oxide can be considered as a sustainable strategy to eliminate the emerging toxic contaminant of tetracycline.

I. INTRODUCTION

Water pollution has been considered as the most threatening environmental issue, demanding immediate attention. The main sources of wastewater are industrial activities [1, 2]. The pollution in the industrial drain waters originates mainly from heavy metals, pesticides, and drugs. The discharge of drugs, particularly antibiotics, results in detrimental effects on the environment and living organisms [3]. Tetracycline (TC) is one of the most widely utilized broad-spectrum antibiotics against bactericidal infections for its low side effects, strong antimicrobial performance, and affordability [4, 5]. TC enters the ecosystem through unmetabolized waste from human and animal excretion and the disposal of expired medications [6]. Moreover, TC can be spread through bioaccumulation in the food chain, posing a severe threat to the entire ecosystem. It is therefore imperative to eliminate the antibiotic molecules from the aquatic ecosystem to decrease its potential health and environmental hazards [7].

To date, TC elimination from wastewater has been provided via various processes, namely enzymatic conversion, biodegradation, electrocoagulation, flocculation, membrane separation, coagulation-floatation, advanced oxidation, and adsorption. Among the wastewater treatment processes, adsorption has gained significant attention owing to its significant properties, namely environmental friendliness, ease of operation, low energy consumption and cost-effectiveness [6, 9, 10]. For this removal process, adsorbent selection is the crux step and until now, a wide range of materials such as carbon-based materials, biomass-based materials, metal-based materials, mineral-based materials, and polymer-based materials, have been explored as adsorbent for the adsorption of TC-

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contaminated water [11]. At this point, metal-based materials have been well reported in literature due to their excellent high capacity, ease of availability, simple regeneration step and sufficient thermal and chemical stability [12].

As a promising metal oxide-based adsorbent, zinc oxide (ZnO) particle has drawn considerable interest for their prospective application in adsorptive dye removal techniques since it shows high affinity towards colorful molecules, especially anionic dyes [13-15]. Lei et al. [13] stated that hierarchical porous ZnO microspheres showed excellent the adsorption capacity of Congo red (CR) in aqueous solution (334 mg/g) owing to their high surface area (57 m^2/g) and the related adsorption mechanism was assessed with pseudo-second-order kinetics and intraparticle diffusion models. Ranjbari et al. [14] also showed that the highest methylene blue adsorption removal was obtained at acidic pH conditions in the presence of ZnO particles since in the acidic environment the superior electrostatic attraction occurred between the negatively charged adsorbent surface and the dye molecules. Sharma depicted that heavy metal adsorption process over ZnO could be explained by Freundlich model, as well as the adsorption spontaneously occurred, and it had an endothermic nature. However, the traditional bulk ZnO material has limited specific surface area, limiting adsorption capacity and the sample struggles with difficulty in regeneration step, decreasing their utilization in potential in long term removal processes. The fixed structure might improve its resistance and durability [16]. Therefore, recent studies have been focused on utilizing metal oxide with hierarchical structures to obtain sufficient efficiency in the large-scale antibiotic removal systems.

In this study, we have aimed to examine the efficiency of micro spherical ZnO on tetracycline adsorption and based on literature search no such study has been reported. Kinetic experimental studies were carried out, and the as-observed data were fitted to isotherm and kinetic models. Thermodynamic study was also conducted to examine the temperature effect on the adsorption of the antibiotic molecules on the ZnO particles. Herein, ZnO particles with 2-5 mm of diameter were proposed to be long-lasting adsorption in continuous antibiotic removal processes.

II. EXPERIMENTAL METHOD / TEORETICAL METHOD

2.1 Materials

ZnO particles with 2-5 mm of diameter were purchased from Alfa Aesar. Tetracycline (TC, ≥98%), used as model pharmaceutical pollutant, was purchased from Sigma-Aldrich. All chemicals were used without further purification and all antibiotic solutions were prepared by using distilled water during experimental studies.

2.2. Adsorptive removal studies

Batch adsorption experiments were conducted in 50 mL Erlenmeyer flasks containing 20 mL of tetracycline solution (10 mg/L) and 0.03 g of the spherical ZnO samples. The adsorption isotherms of TC on the spherical adsorbent were investigated by applying different initial antibiotic concentration (10-60 mg/L) at constant atmosphere and temperature. After the flasks were shaken at 110 rpm for 24 h, the adsorption suspensions were filtered with a blue band filter paper and supernatants were analyzed with UV–vis spectrophotometer at the wavelength of 360 nm using the Lambert-Beer law. To establish the contact time effect on TC adsorption, 20 mL of 45 mg/L TC solution was added to 30 mg ZnO, and the samples were collected at certain time intervals to

predict equilibrium concentrations. The suspensions were also shaken in thermostatic water bath shaker at different temperatures (298, 313, 328 K) to determine thermodynamic behavior for the adsorption process.

III. RESULTS AND DISCUSSIONS

3.1 Adsorption Isotherm

Adsorption isotherms are primary models to characterize the interaction between the adsorption surface and adsorbate at various concentrations under constant temperature conditions. In order to determine the correlation between equilibrium concentration (C_e) and adsorption capacity (Q_e), adsorption isotherm models including Langmuir, Freundlich, and Temkin were established. The nonlinear isotherm curves of TC adsorption were presented in Figure 1. The isotherm model equations of the adsorption process were figured out using equations (1-3).

Non-linear Langmuir: $$q_e = \frac{(q_{max} K_L C_e)}{(1 + K_L C_e)} \quad (1)$$

Non-linear Freundlich: $$q_e = K_F C_e^{\left(\frac{1}{n}\right)} \quad (2)$$

Temkin: $$q_e = \frac{RT}{b_T} \ln A_T C_e \quad (3)$$

where, q_e is TC adsorption capacity, C_e is the TC concentration at equilibrium point, q_{max} is the maximum TC adsorption capacity of ZnO, K_L is the Langmuir isotherm constant, K_F and n are the Freundlich isotherm constants, K_T is the Temkin isotherm constant, b_T is Temkin equilibrium constant related to the adsorption heat, R is the gas constant (8.314 J/mol. K), T is the absolute temperature (K).

Adsorption parameters obtained from three distinct nonlinear adsorption isotherm models are presented in Table 1. Improved accuracy and precision are acquired by applying nonlinear variants of the isotherm models [7]. The best fitted isotherm model is evaluated using statistical error functions. To define the adsorption mechanism the isotherm model was selected based on the highest R^2 value. Table 1 represents that the Langmuir isotherm was the most appropriate model due to its superior determination coefficient of 0.97, whereas the Freundlich and Temkin models exhibited lower correlations with experimental data (0.95, 0.96). The Langmuir isotherm model characterized the uniform and monolayered dispersion of the adsorbate molecules over the ZnO surface. Thus, the adsorption model of TC on ZnO could be described as monolayered and accurately explained via the Langmuir equation [8]. The Langmuir isotherm model prediction yielded a theoretical maximum TC adsorption capacity of 86.35 mg/g. The separation factor (R_L), given in Eq (4), was calculated to indicate the favorability of the adsorption process.

$$R_L = \frac{1}{1+K_L x\, C_0} \quad (4)$$

Where C_0 is the initial TC concentration, K_L is the Langmuir isotherm constant. R_L values in the range of $0< R_L \leq 1$ indicates a convenient adsorption. When the value of $R_L = 0$, it states the irreversibility of adsorption process. The values of $R_L < 0$ or $R_L > 1$ displays the unfavorable adsorption. The R_L value of TC adsorption on ZnO was calculated as 0.41, providing the favorable adsorption process [9]. Moreover, the Freundlich isotherm model parameter (1/n), which signifies the surface heterogeneity of adsorbent, was calculated. The 1/n value of 0.59 showed that the TC adsorption on ZnO was an appropriate process [10]. In addition, the interaction between TC and ZnO molecules was investigated by Temkin isotherm model. The heat of TC adsorption on ZnO (b_T) was found as 11.36 kj/mol, stating that the adsorption process exhibits an endothermic reaction profile. It could be concluded that the TC molecules might uniformly adsorbed over ZnO particles in a monolayer, confirming that the adsorption could be explained via Langmuir model and the thermodynamic behavior of the adsorption was endothermic.

Table 1. Adsorption isotherm parameters of ZnO on TC adsorption

Isotherm Models	Parameters	Values
Langmuir	q_{max} (mg/g)	86.35
	K_L (L/mg)	0.014
	R^2	0.97
Freundlich	K_F (L/g)	1.51
	n	1.69
	R^2	0.95
Temkin	K_T (L/mol)	0.31
	B_T (kj/mol)	11.36
	R^2	0.96

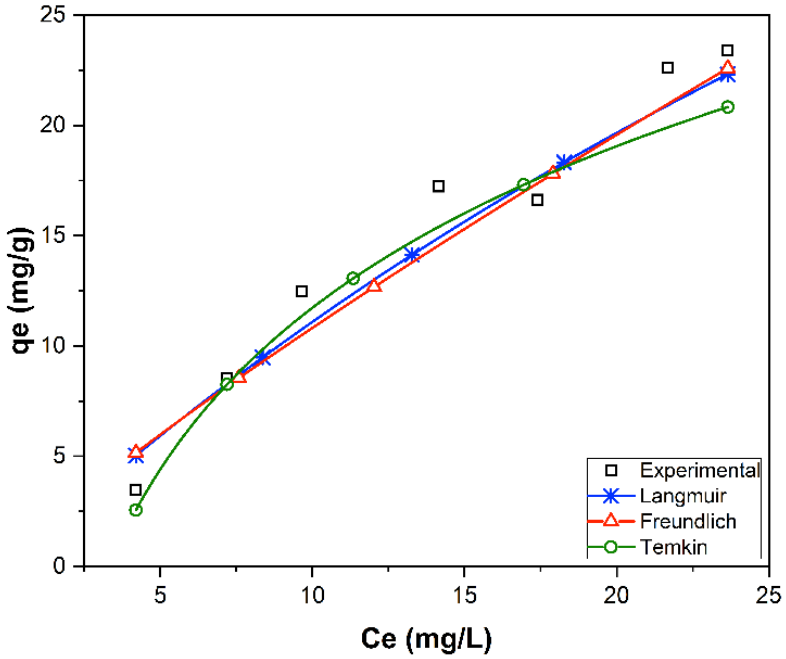

Figure 1. Isotherm models of ZnO on TC adsorption

3.2 Adsorption kinetics

The kinetic studies were performed to determine the required contact time until the TC adsorption process reached equilibrium and the accomplishment of adsorption process. Figure 2 shows the effect of the contact time on the maximum TC adsorption of ZnO and the equilibrium adsorption capacity. The TC adsorption capacity initially enhanced rapidly and achieved equilibrium point after 120 minutes. Three prevalent models were performed to clarify the adsorption mechanism and kinetic model and they were Pseudo first order (PSO), Pseudo second order, and intraparticle diffusion (IPD) kinetic models. Furthermore, nonlinear variants of the kinetic models were applied to obtain more accurate and reliable results. The nonlinear adsorption kinetic models derived from Eq. (5-7) were illustrated in Figure. 3.

Nonlinear pseudo-first order: $q_t = q_e(1 - e^{-k_1 t})$ (5)

Nonlinear pseudo-second order: $q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e^2 t}$ (6)

Intraparticle diffusion: $q_t = k_i t^{1/2} + c$ (7)

where k_1 is the pseudo-first order rate constant (min^{-1}), k_2 is the pseudo-second order rate constant (g/mg.min), k_i is the intra-particle diffusion rate constant ($mg.min^{0.5}/\cdot g$). c denotes the boundary layer thickness. q_e and q_t (mg/g) are the amount of TC adsorbed at equilibrium and time t (min), respectively.

In general approach, the pseudo first-order kinetic model explains the bulk transfer of adsorbate molecules towards the adsorbent surface within the solution whereas the pseudo second-order kinetic model was attributed to strong chemisorption. In terms of the intraparticle diffusion kinetic model, after the adsorbent surface becomes saturated, the adsorbate molecules move towards the pores of the adsorbent, occurring further adsorption [11]. Table 2 presents the kinetic model parameters of TC adsorption and the R^2 values of the three different nonlinear models were compared. Considering the maximum R^2 value, it was stated that the most compatible model for this adsorption was observed as the Pseudo second order kinetic model and thus, the step of chemisorption was recommended as a more effective mechanism for this adsorption mechanism. On the other hand, for the PSO kinetic model the adsorption capacity of TC was calculated as 23.42 mg/g that was quite close to the value of 25.13 mg/g, calculated for a contact time of 120 minutes. Notably, the PFO rate constant (k_1) was found higher than the PSO rate constant (k_2), approximately 15 times, which indicates that the bulk transfer of adsorbate molecules to the adsorbent surface was faster than the chemisorption step. To summarize, the antibiotic adsorption over ZnO could be driven by two mechanisms such as physical and chemical adsorption processes due to the occurrence of active sites on both the surface and inside the pores, indicating that the porosity of the metal oxide was appropriate for adsorbing TC molecules.

Table 2. Adsorption kinetic parameters of ZnO on TC adsorption

Isotherm Models	Parameters	Values
Pseudo-first order	q_e (mg/g)	22.20
	k_1 (L/min)	0.065
	R^2	0.87
Pseudo-second order	q_e (mg/g)	23.42
	k_1 (L/min)	0.0046
	R^2	0.96
Intraparticle diffusion	k_{int} (g/mg.min$^{1/2}$)	0.39
	C	10.85
	R^2	0.76

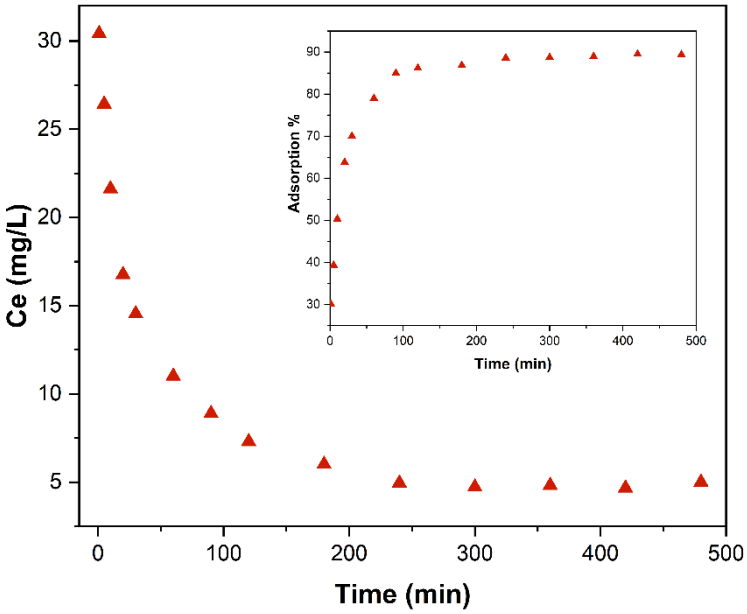

Figure 2. Time dependent TC adsorption capacity of ZnO

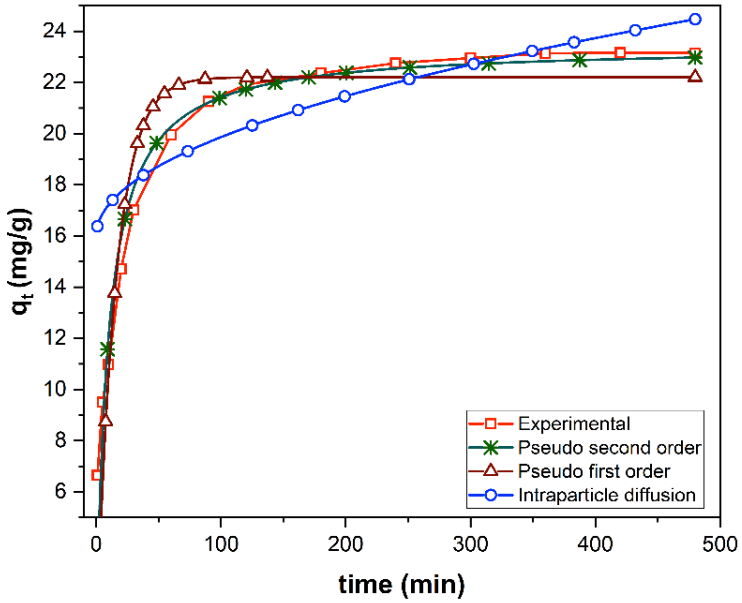

Figure 3. Kinetic models of ZnO on TC adsorption

3.3 Adsorption thermodynamics

Temperature is one of the most effective parameters to examine the thermodynamic behavior of the adsorption process and thus the adsorption process was performed under different temperatures. According to the results of the experimental studies, standard Gibbs free energy (ΔG^o), standard enthalpy change (ΔH^o) and standard entropy change (ΔS^o) parameters were predicted to estimate the thermodynamic nature of TC adsorption on ZnO surface. The thermodynamic parameters, calculated via Eq. (8-10), are utilized to estimate either the reaction endothermic or exothermic.

$$K_d = \frac{q_e}{C_e} \tag{8}$$

$$\Delta G^\circ = -RT\ln K_d \tag{9}$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{10}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where, ΔG°(kj/mol), ΔH° (kj/mol) and ΔS° (J/molK) represent the changes in Gibbs free energy, enthalpy and entropy, respectively. K_d is the distribution coefficient of kinetic energy change, R is the ideal gas constant (J/molK), T is adsorption process temperature (K), q_e is the adsorbed amount of TC (mg/g), C_e is the amount of TC in equilibrium solution (mg/L).

The as-estimated thermodynamic data are given in Table 3. The negative Gibbs free energy value indicated that the adsorption was a spontaneous and thermodynamically favorable process. Furthermore, the ΔG° value lower than 15 kJ/mol was assigned to physical adsorption [17]. The positive enthalpy changes remarked that the TC adsorption over ZnO was an endothermic reaction. In addition, the positive entropy change is supported by the increasing randomness of the system. In terms of TC adsorption on ZnO, the positive change of entropy defined an increase in system disorder. The thermodynamic results demonstrated that the adsorption of TC by ZnO was a temperature-promoted reaction system [18].

Table 3. Thermodynamic parameters of ZnO on TC adsorption

T (K)	ΔH° (kJ/mol)	ΔG° (kJ/mol)	ΔS° (J/mol K)
298		-1533.60	
318	2.49	-1636.69	5.15
338		-1739.79	

3.4 Effect of initial solution pH on adsorption

In order to the effect of pH, the adsorptive removal of TC was evaluated at five pH conditions (2.55, 4.01, 6.05, 8.53 and 12.00). As depicted in Figure 4, the adsorption efficiencies were greatly affected by pH and the removal performances were calculated as 30.8%, 61.5%, 89.7%, 41.5% and 58.0% for 2.55, 4.01, 6.05, 8.53 and 12.00 of pH values, respectively. That is, the highest removal was calculated as 89.2 % at pH 6.05 after 24 h, while the minimum value was found to be 30.8 % at pH 2.55. The difference in the activity could be related with the charge properties of the ZnO surface and pKa values of TC molecule. Based on its different pKa values (3.3, 7.7, 9.7 and 12), TC molecules could be found in different forms under various pH value: (a) H_4TC^+ at pH lower than 3.3, (b) H_3TC in the pH from 3.3–7.7, (c) H_2TC^- in the pH from 7.7–9.7 and (d) HTC^{2-} at pH higher than 12. On the other hand, in acidic conditions, spherical ZnO surface could be positively charged, while it could be negatively charged in a basic atmosphere. It was therefore stated that the adsorption could be limited by the increased electrostatic repulsion between H_4TC^+ and positively charged ZnO surface at pH 2.55. The similar phenome was observed at basic pH (pH 8.53 and pH 12.00), which the repulsion forces were between H H_2TC^- / H_2TC^{2-} and negatively charged catalyst surface. When the solution pH was 6.05, the electrostatic attraction forces were observed between neutral molecule antibiotic molecule (H_3TC) and negative surface functional groups, improving adsorption efficiency. Considering this, sufficient TC removal was obtained in the natural environment.

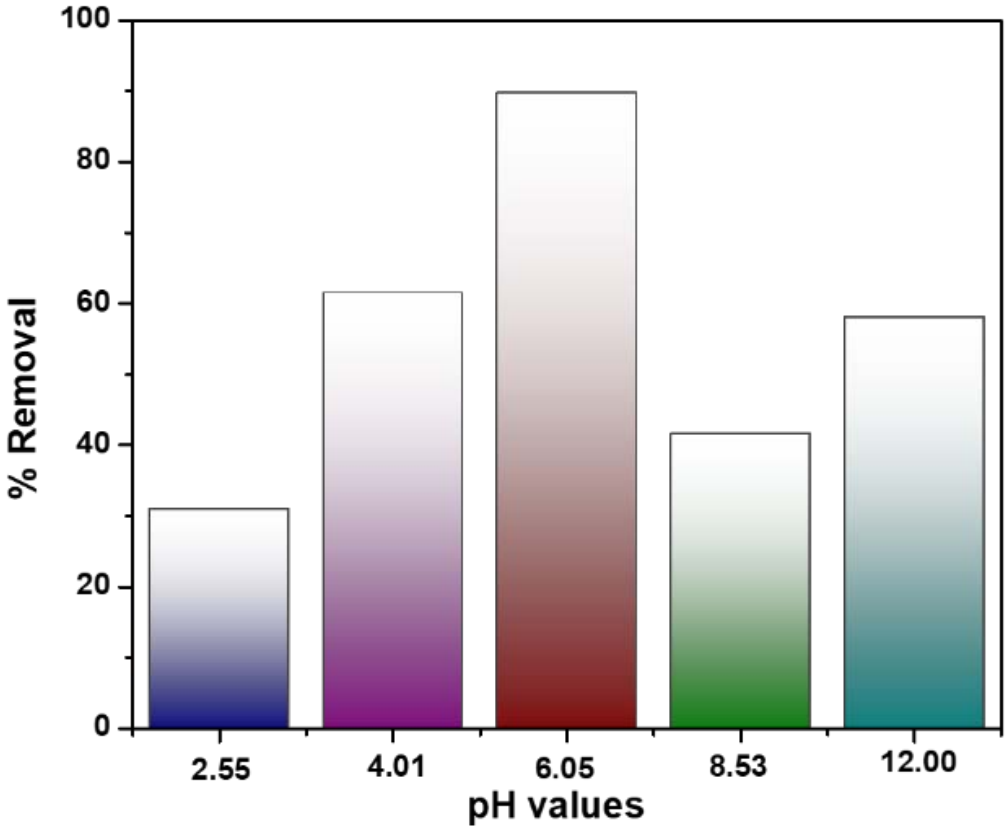

Figure 4. Effect of pH value on TC adsorption over ZnO

IV. CONCLUSIONS

Overall, the adsorptive removal of tetracycline from the aqueous media was investigated by using spherical zinc oxide with the diameter of 2-5 mm. The pseudo-first-order and pseudo-second-order kinetic models fitted best to the experimental data while thermodynamic data verified that the tetracycline adsorption process was exothermic and spontaneous in nature. The best fitting of the non-linear form of Langmuir model indicated that the antibiotic adsorption on ZnO samples consisted of both physical and chemical forces. To conclude, this study introduces commercial ZnO samples with hierarchical structure samples as a promising adsorbent for antibiotic removal and it can be utilized in future studies.

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