Mechanisms and Models of Adsorption: TiO₂-Supported Biochar for Removal of 3,4-Dimethylaniline

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ABSTRACT: Here, 3,4-dimethylaniline (3,4-DMA) was selected as a representative organic substance of aniline compounds. A biochar-titanium dioxide (BC-TiO₂) composite was prepared by the sol–gel method to investigate its adsorption ability toward the 3,4-DMA compound. Simultaneously, the prepared composite’s adsorption ability and physical and physicochemical properties were also investigated. The isotherm studies confirmed that the adsorption of 3,4-DMA on both BC and BC-TiO₂ composite agrees with the Langmuir and Toth adsorption models, which means the formation of a monolayer of 3,4-DMA on the surface. The maximum adsorption capacity of 3,4-DMA was 322.58 mg g⁻¹ and 285.71 mg g⁻¹ for BC and BC-TiO₂, respectively. Furthermore, the adsorption process of 3,4-DMA on BC and the BC-TiO₂ composite is controlled by the pseudo-second-order kinetic model with an R² of 0.99.

1. INTRODUCTION

Exponential population and social civilization have expanded over the past several decades, wealthy lifestyles and resource use have changed, and continued industrial and technological advances have been accompanied by sharp modernization and metropolitan growth.¹ The increase in industrial activities results in multiple deteriorations for both human health and the environment. The imposition of rigid rules and regulations concerning the emission of pollutants from industrial waste streams by various regulatory agencies has been promulgated.² At the same time, the advancement of research into several treatment technologies (precipitation, coagulation-flocculation, sedimentation, flotation, filtration membrane processes, electrochemical methods, biological processes, chemical reactions, ion exchange, and adsorption) with varying degrees of success has stimulated the developments in the scientific community significantly.³⁻¹⁰ The technique for wastewater treatment is critical and has to be made considering the contaminants present in wastewater.¹¹,¹² Several organic and inorganic materials have been found in industrial wastewater, and the most common materials are phenolic compounds, aromatic compounds, dyes, and heavy metals.¹³ Aniline wastewater belonging to refractory wastewater received intensive attention these days. To achieve a fast, economical, and practical treatment process, several studies have been conducted with various methods, including biological treatment, adsorption, advanced oxidation, and filtration. For instance, Chen et al.¹⁴ verified the possibility of using biofilm systems such as aerobic/anerobic systems to recycle aniline wastewater and methane-derived aniline wastewater simultaneously. Jiang et al.¹⁵ developed an anaerobic/aerobic/anoxic system to achieve COD, NH₄⁺ for simultaneous removal of aniline wastewater, —N, TN, and TP. Guo et al.¹⁶ showed that the activation energy of 2-nitro-4-methoxyaniline treated by the Fenton method was 30.23 kJ mol⁻¹, indicating that Fenton treatment is highly efficient. Further study was done by Sawai et al.¹⁷ using a silicone rubber membrane via a permeation and chemical desorption (PCD) method to investigate the separation of the aniline and 4-substituted phenol derivatives from aqueous solutions.

Economically speaking, the adsorption method is considered feasible, where the adsorption capacity of the adsorbents and operating conditions display critical roles in this process. Moawed et al.¹⁸ could remove the aniline blue and crystal violet in laundry wastewater by an adsorption method. This study found that the adsorption capacity of the two pollutants on an iodine polyurethane adsorbent was 188.9 and 183.6 mg g⁻¹, respectively. The reverse osmosis membrane and liquid membrane were also utilized to treat the aniline wastewater.¹⁹ 3,4-DMA is a member of the aniline family of hydrocarbons in which the hydrogen atom at the 3,4 position is substituted by a methyl group. Since it contains one amino group and contains two methyl groups, its physicochemical properties are...
comparatively, indicating that the loading of TiO₂ did not destroy the original functional groups on the surface of the biochar, and the original adsorption characteristics of the biochar could be retained. The BC-TiO₂ sample has O–O bond vibration absorption peaks at 800 cm⁻¹, indicating that there are peroxy bonds on the surface of the biochar after loading TiO₂. After loading TiO₂, the absorption peaks around 1450 cm⁻¹ weakened, and two tiny stretching vibration absorption peaks appeared at 1434 and 1336 cm⁻¹ frequency for BC-TiO₂ reflecting the stretching vibration of Ti–O–Ti bonds in crystalline TiO₂ which further signified the BC-TiO₂ prepared. With the BC-TiO₂ composite adsorbing 3,4-DMA, it can be observed that the peaks at 1168 and 1092 cm⁻¹ of the composite were diminished, indicating formation. In the FTIR spectra for the BC-TiO₂ composite after adsorption, an obvious decrease in the peak at 1638 cm⁻¹ was observed. This decrease may be credited to the fact that a part of −NH₂ groups in the composite was protonated.²²

2.3. XRD. The XRD patterns in Figure 1b showed that the as-prepared TiO₂ nanoparticles display an amorphous structure with a group of broad diffraction peaks centered at 25.33, 37.8, 48.1, 53.9, 55, 62.18, and 68.8° assignable for the (101), (004), (200), (105), (211), (213), and (116) planes, respectively. All peaks matched well with the standard card (JCPDS no. 84-1286), which suggests the successful preparation of TiO₂ nanoparticles.³³ The patterns of BC show two graphite peaks and the long-range disordered structure at 2θ of 26.60 and 42.50°, assignible for the (002) and (100) planes, respectively, with the standard card (JCPDS no. 64-6212). Compared to BC and TiO₂, the as-prepared BC-TiO₂ composite shows four broad peaks for the TiO₂ anatase phase at 25.31, 37.8, 53.92, and 68.81° assignible for

2. RESULTS AND DISCUSSION

2.1. BET Surface Area of the As-Prepared Materials. The calculated BET surface areas and the related pore volumes are presented in the Supporting Information (S-4). The BET surface area of BC is 979.5 m²/g, which is within the expected range for biochar.²⁰ The decreasing BET surface area of BC-TiO₂ is 767 m²/g, which is mainly attributed to the precipitation of TiO₂, which would cover most of the mesopores and micropores and was consistent with previous studies. However, compared with BC, BC-TiO₂ showed an obvious beneficial synergistic advantage and thus better adsorption capacity. The main reason was that the supportive structures provided by nano-TiO₂ made the distribution of surface-active adsorption sites of the BC-TiO₂ composite more uniform. Therefore, the average pore diameter was higher than that of BC, which would increase the content of oxygen-containing functional groups in the composite, thus making it fairly conducive to the diffusion of organic pollutants to the surface of the BC-TiO₂ composite for adsorption.

2.2. FTIR Analysis. From the FTIR spectrum in Figure 1a, all analyzed materials (biochar, BC-TiO₂ composite, and composite-loaded 3,4-DMA) displayed a distinct broad absorption peak of surface −OH group stretching vibration in the range of 3350–3500 cm⁻¹.²¹ While the broad absorption peak of stretching vibration of the OH group on the surface of BC-TiO₂ becomes weak and shifted from 3426 to 3430 cm⁻¹, there is an aromatic ring C=C and C=O characteristic. Stretching vibration absorption peaks are present at 1529 and 1642 cm⁻¹ before and after TiO₂ loading, and these peaks decrease slightly after loading, indicating that the aliphatic ketone and conjugated carbonyl functional groups are on the surface of biochar after TiO₂ loading. Here, the deformation vibration of −CH₂ and the stretching vibration of C–O display that after loading TiO₂, there are more types of functional groups on the surface of biochar with phenolic or hydroxyl functional groups on the surface. The characteristic stretching vibration of C–O–C shows two obvious peaks around 1093 cm⁻¹ before and after loading. The absorption peaks of Si–O at 469 cm⁻¹ and the two points before and after loading did not change

![Figure 1](https://pubs.acs.org/acsomega/journal/acsodf)
the (101), (004), (105), and (116) planes with the standard card (JCPDS no. 83-2243). Moreover, the rutile phase at a 2θ of 42.50° assignable for the (210) plane also appeared. This revealed good dispersion of the TiO2 nanoparticles in the BC paste. The broad peaks of the TiO2 and BC-TiO2 indicate that these materials are in the amorphous phase.

2.4. Morphological Analysis. The microstructure and morphology of the as-prepared materials were investigated by SEM images (Figure 2). The images show an irregular plate-like structure, which is favorable for the adsorption process. Furthermore, obvious pores resulting from the slits among the plate-like particles can also be observed (observations also corroborated by BET characterization). The SEM images and EDX (Figure S1, S-4; Supporting Information) spectra with the insets of elemental analysis of BC, BC-TiO2, and BC-TiO2 after adsorption are presented. The EDX spectra of the material show the presence of elements in each material.24 SEM images of biochar and BC-TiO2 present the structures of biochar and BC-TiO2, respectively. The images revealed that miniature TiO2 granules were well dispersed on the biochar with little agglomeration.25 SEM micrographs of the BC and BC-TiO2 are shown in Figure 2 with various magnifications. Figure 2a,b shows the smooth and bulky morphology of the bare BC. However, Figure 2c,e for BC-TiO2 indicates the presence of fine spherical nanostructures. With a simple comparison of the XRD results, EDX spectra, and SEM images of BC with those of the BC-TiO2, it is obviously seen that TiO2 nanoparticles were synthesized and immobilized on the BC surface.

2.5. Effect of Contact Time. The effect of contact time on the amount of 3,4-DMA adsorbed on biochar (BC) and biochar-modified TiO2 (BC-TiO2) has been experimentally investigated in a 3,4-DMA solution at 200 mg L−1 initial 3,4-DMA concentration. Figure 3a indicates that the adsorption of 3,4-DMA is fast at the preliminary stage and then slows down near the equilibrium. It would be because a great number of unoccupied surface sites are present for adsorption during the preliminary stage of the treatment time, and some time had elapsed; the remaining vacant surface sites are difficult to be occupied because of repulsive forces between 3,4-DMA adsorbed on the surface of BC and BC-TiO2 and the solution phase. It has been witnessed that the 3,4-DMA adsorption increased with an increase in contact time.

2.6. Effect of pH. The initial pH of the 3,4-DMA solution is a critical operational parameter, which can considerably affect the adsorption mechanisms of the solvent molecules and the adsorbent. For 3,4-DMA, the pKₐ value at pH 5.18–5.28 (basic) in aqueous solution was very low. This low removal was primarily due to the electrostatic repulsion between the positively charged protonated form (BC and BC-TiO2) and the positively charged anilinium cation.22 The electrostatic repulsion did not facilitate the adsorption of 3,4-DMA onto BC and BC-TiO2. From Figure 3b, increasing the pH from 3.0 to 9.0, which was higher than the pKₐ of aniline, aniline was mainly in the molecular form, enhanced the removal of 3,4-DMA.

Figure 2. SEM images of (a,b) pure BC, (c,d) BC-TiO2, and (e,f) BC-TiO2 after adsorption.

Figure 3. (a) Effect of contact time in 3,4-DMA adsorption capacity (C₀ is 200 mg L⁻¹, adsorbent dosage is 50 mg, and V is 100 mL). (b) Effect of initial pH in removal % with C₀ = 200 mg L⁻¹ and 50 mg adsorbent dosage.
DMA due to dispersive interactions between aniline and BC and BC-TiO₂.  

3,4-DMA is a slightly basic compound. Since its adsorption by BC-TiO₂ increases as pH increases, this can be elucidated by the fact that as the solution becomes more basic, hydroxide ions can react with some protons or partially positive elements found in the BC-TiO₂ and for hydroxyl groups. These hydroxyl groups will form hydrogen bonds with 3,4-DMA. This will increase as OH⁻ concentration increases. Therefore, the removal percentage by BC and BC-TiO₂ increases from 47 and 50% at pH 3 to 89.18% and 82.43 mg g⁻¹ at pH 9, respectively. Besides the van der Waals force, H-bonding interactions from solutes as hydrogen-bonding donors followed by π-electron polarizability may play vital roles on the adsorption of 3,4-DMA by biochar and BC-TiO₂ in the aqueous environment.

2.7. Adsorption Isotherm. 2.7.1. Langmuir Isotherm. The basic thing of the Langmuir model is that the development of a monolayer occurs on the surface of the adsorbent, indicating that adsorption is possible for only one pollutant molecule on one adsorption site, and the intermolecular forces decrease with the distance. It is also determined that the surfaces of an adsorbent are homogeneous in character and consist of indistinguishable and energetically equivalent adsorption sites. The linear version of the Langmuir model based on this assumption can be explained by the following eq 1

\[
\frac{C_e}{q_e} = \frac{1}{a_L k_L} + \frac{a_L}{k_L} C_e
\]

where \(q_e\) is the amount of 3,4-DMA adsorbed per unit of adsorbent (mg), and \(a_L\) and \(k_L\) are the Langmuir constant for the energy of adsorption (L g⁻¹). The values of \(a_L\) and \(k_L\) can be obtained from Figure 4a from the slopes and intercept of the linear plot of \(C_e/q_e\) versus \(C_e\) and are given in Table 1 with the values of \(R^2\).

The isotherm is linear over the entire concentration range and shows a reasonable fit to the adsorption data. The data indicate that the maximum capacity of adsorbed 3,4-DMA onto all two adsorbents examined did not exceed 400 mg g⁻¹.

The favorability and viability of the adsorption process can be calculated by the separation factor \(R_L\) in the analysis of data by the Langmuir isotherm. It is given by the following eq 2.

\[
R_L = \frac{1}{1 + k_L C_0}
\]

The shape of the isotherm depends on the value of \(R_L\) as follows: The isotherm is unfavorable (\(R_L > 1\)), linear (\(R_L = 1\)), favorable (0 < \(R_L < 1\)), or reversible (\(R_L = 0\)). In the present study, the value of \(R_L\) in all the cases lies between 0 and 1, indicating that 3,4-DMA adsorption by biochar and modified biochar-TiO₂ is favorable; Figure 4b demonstrates the change in the separation factor with initial concentration for various adsorbents.

2.7.2. Freundlich Isotherm. The Freundlich isotherm is the earliest documented relationship explaining the non-ideal and reversible adsorption, unrestricted to the formation of a monolayer. The application of this empirical model is it relates to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. In this perspective, the amount adsorbed is the summary of adsorption on all sites (each having bond energy), with the stronger binding sites, which are occupied first until adsorption energy is drastically decreased upon the completion of the adsorption process. The experimental equilibrium data for the adsorption of 3,4-DMA onto BC and BC-TiO₂ have also been analyzed using the Freundlich linear isotherm, as given by eq 3.
log \( q_e = \log k_i + \frac{1}{n} \log C_e \)  

(3)

where \( k_i \) and \( n \) are the Freundlich constants and represent the adsorption capacity and measure of heterogeneity, respectively. The values of \( k_i \) and \( n \) can be obtained from the slope and intercept of the linear plot of \( \log q_e \) versus \( \log C_e \) presented in Figure 5, and the values are in Table 1.

The linearized Toth equation was applied to liquid—solid adsorption experimental data. The Toth isotherm may be rearranged to give a linear form as follows

\[
\frac{C_e}{q_e} = \left( \frac{1}{q_{m} b_T} \right)^T + \frac{1}{q_{m}^T} \right) C_e^T
\]

For the adsorption heterogeneity parameter \( T \), when adsorption occurs on a uniform surface, \( T \) is equal to 1, and the Toth equation becomes the Langmuir model, and the smaller the \( T \) value, the higher the degree of heterogeneous adsorption. Figure 5b shows that the adsorption unevenness of BC to 3,4-DMa is about 0.5, and most of the adsorption occurs on heterogeneous surfaces. On the BC-TiO2, the adsorption heterogeneity coefficient is close to 1.0; adsorption will tend to occur on homogeneous surfaces.

2.8. Adsorption Kinetics. The effect of contact time on the adsorption of 3,4-DMa on BC and BC-TiO2 was studied. The 3,4-DMa adsorption increased with increase in contact time. The maximum amount of 3,4-DMa was adsorbed at 24 h for both the two adsorbents. Pseudo-first-order kinetics, pseudo-second-order kinetics, intraparticle diffusion, and Elovitch models to comprehend the dynamics of the adsorption process were used to examine the experimental data.

2.8.1. Pseudo-First Order. The pseudo-first-order kinetic model, also called the Lagergren kinetic equation, is widely utilized to understand the kinetic behavior of the system. The pseudo-first-order model is usually used to explain the initial state of adsorption. It is described by eq 7

\[
\frac{dq}{dt} = k_1 (q_e - q_t)
\]

(7)

The effect of Lagergren pseudo-first-order on the rate of adsorption can be assessed by the plot of \( \ln (q_e - q_t) \) versus time \( t \), which should give a linear relationship from which the pseudo-first-order rate constant \( k_1 \) (min\(^{-1}\)) and \( q_t \) can be calculated from the slope and intercept, respectively (Figure 6a). Integrating eq 6 with respect to boundary conditions \( q_t = 0 \) at \( t = 0 \) and \( q = q \) at \( t \). As shown in eq 8, gives

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

(8)

The calculated values of \( k_1 \) as shown in Table 2, are much lower than the experimental values. The values of correlation coefficients of the pseudo-second-order model are higher than the pseudo-first-order model (shown in Figure 7b), indicating that the 3,4-DMa adsorption does not obey pseudo-first-order kinetics.
2.8.2. Pseudo-Second Order. The pseudo-second-order kinetic model was used to further treat the kinetic data. The pseudo-second-order model can be used to dictate behavior over the entire range of the adsorption process. The pseudo-second-order differential equation is the following

$$\frac{dq}{dt} = k_2(q_e - q_t)^2$$

where \(k_2\) is the equilibrium rate constant of pseudo-second-order adsorption \((g \, mg^{-1} \, min^{-1})\). Integrating eq 9 for the boundary condition \(t = 0\) to \(t\) and \(q_t = 0\) to \(q_e\) gives

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + \frac{k_2 t}{q_e}$$

This is the integrated rate law for a pseudo-second-order reaction. Equation 10 can be reorganized to obtain a linear form

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

The value of \(k_2\) and \(q_e\) can be obtained from the slope and intercept of the plot of \(t/q_t\) versus \(t\) (Figure 6b). The values of the rate constants, maximum amount adsorbed, and the correlation coefficients are listed in Table 2.

| kinetic model | constant | BC | BC-TiO$_2$
|---------------|----------|----|----------------|
| pseudo-first order | \(k_1\) | 0.19 | 0.12 |
| \(q_e, exp\) | 318.91 | 286.49 |
| \(q_e, cal\) | 38.27 | 99.01 |
| \(R^2\) | 0.787 | 0.928 |
| \(\chi^2\) | 101997 | 38270 |
| pseudo-second order | \(k_1\) | 0.0019 | 0.0082 |
| \(q_e, exp\) | 318.91 | 286.49 |
| \(q_e, cal\) | 322.58 | 285.71 |
| \(R^2\) | 1 | 0.999 |
| \(\chi^2\) | 1975 | 99.04 |
| intraparticle diffusion | phase 1 | 2 | 2 |
| \(k_d\) | 160.297 | 1.773 |
| | BC-TiO$_2$ phase 1 | 126.93 | 6.021 |
| \(C\) | 87.335 | 306.75 |
| \(R^2\) | 0.88 | 0.53 |
| \(\chi^2\) | 38270 | 99.04 |
| Elovich | \(\alpha\) | 34.757 | 34.383 |
| \(\beta\) | 0.0328 | 0.0340 |
| \(R^2\) | 0.813 | 0.918 |

Figure 6. Adsorption kinetics of 3,4-DMA with \(C_0\) of 200 mg L$^{-1}$, pH 7, adsorbent dosage of 50 mg, and \(V\) of 100 mL. (a) Pseudo-first order, (b) pseudo-second order, (c) intraparticle diffusion model, and (d) Elovich model.

Figure 7. Effect of temperature on 3,4-DMA adsorption with \(C_0\) of 200 mg L$^{-1}$, pH 7, adsorbent dosage of 50 mg, \(V\) of 100 mL, and \(T\) of 20, 30, 40, and 50 °C.
The pseudo-second-order model depends on the supposition that the rate-limiting step could be chemisorption, with valence forces involved by electron exchange or sharing between the adsorbate and the adsorbent.37 The maximum adsorption capacities \( q_e \) determined by the pseudo-second-order model are in accordance with the values gained from the experiment, which show that the adsorption obeys a pseudo-second-order model. The plot of \( t/q_t \) versus \( t \) is linear, showing that the main rate-controlling step of the adsorption process is chemisorption.

### 2.8.3. Intraparticle Diffusion Model

Weber and Morris developed the model that can be used to evaluate the area where intraparticle diffusion is rate-limited and to determine the intraparticle diffusion rate. The intraparticle diffusion can be determined by Amin et al. in eq 1238

\[
q_t = k_d t^{0.5} + C
\]

where \( k_d \) is the intraparticle rate constant (g mol\(^{-1}\) min\(^{-0.5}\)), and \( C \) is the intercept. The intraparticle diffusion model is applied by drawing \( q_t \) against \( t^{0.5} \), and all parameters are given in Table 2. The line obtained must be a straight one with an intercept \( C \) that provides an indication about the thickness of the boundary layer if the adsorption process follows this model. The larger the value of \( C \), the thicker is the boundary layer. If the straight line passes through the origin, the intraparticle diffusion is the sole rate-determining step. Otherwise, other mechanisms may be involved. Fitting of the data to the intraparticle diffusion model is depicted in Figure 6c. Since the lines obtained from fitting the data to the intraparticle diffusion do not pass through the origin, it may be assumed that intraparticle diffusion is not the sole mechanism that controls the adsorption. It could be assumed that only at the initial adsorption stages, the transfer of the external mass is significant, and the intraparticle diffusion controls the final stages.39 As indicated in Figure 6c, the uptake of 3,4-DMA on the adsorbent goes through different stages. The uptake rate should be very fast at the beginning of the adsorption process. With the passage of time, this uptake rate decreases until reaching the equilibrium state. At the beginning stages of the adsorption process, boundary layer resistance may be involved. Piecewise analysis is conducted, in which every stage can be analyzed separately in a process for making a conclusion about the relation between the time and uptake of 3,4-DMA. At the initial stage of adsorption, while applying the piecewise linear regression, especially, it will indicate the different stages of mass transport.

Some researchers41,42 documented that the intraparticle diffusion plots might be classified into more than one region (phase). At the initial stage, the first sharp region is attributed to the instantaneous adsorption, most probably because of the interaction between the functional groups at the adsorbent’s external surface and the adsorbate molecules (external surface adsorption). The gradual adsorption characterizes the second region where the intraparticle diffusion is the rate-limiting step. The intraparticle diffusion model is shown in Figure 6c. The plot of \( q_t \) vs. \( t^{0.5} \) describes multilinearity over the entire range of reaction time, implying that intraparticle diffusion was not the only rate-determining step. The high initial uptake rate from 0 to (1.5 h)\(^{0.5} \) due to the higher concentration gradient between the adsorbate and the adsorbent on the external surface was controlled by surface adsorption. Once the saturation was reached, 3,4-DMA began to enter the pores of the adsorbent and was absorbed by the interior surface, where intraparticle diffusion is the rate-limiting step. As the intraparticle diffusion begins to slow down, the adsorption equilibrium was acquired.43 Therefore, both the intraparticle diffusion and surface adsorption contributed to the rate-determining step during the adsorption of 3,4-DMA by BC and BC-TiO\(_2\).

#### 2.8.4. Elovich Model

The fitting of the experimental data to both Elovich (shown in Figure 6d) and pseudo-second-order models provided important information about the adsorbate uptake, the rate of adsorption, and the nature of the adsorption process (chemisorption).44 The Elovich model can be explained by eq 1338

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta t) + \frac{1}{\beta} \ln t
\]

where \( \alpha \) (mg g\(^{-1}\) min\(^{-1}\)) is the initial adsorption rate of the Elovich equation, and \( \beta \) (g mg\(^{-1}\)) is the desorption constant correlated to the extent of surface coverage and energy activation for chemisorption.

However, Elovich and pseudo-second-order models do not give more detailed information about the adsorption mechanism. Four consecutive stages are followed by the adsorption of the adsorbate. First, the adsorbate molecules move from the bulk of the solution to the thin layer of adsorbate surrounding the surface of the adsorbent. During the second stage, the adsorbate molecules diffuse through the thin aqueous layer surrounding the adsorbent. In the third stage, the penetration of the adsorbate molecules passes through the pores on the surface of the adsorbent. In the final stage, the adsorbate molecules are adsorbed on the surface of adsorbent.34

### 2.9. Effect of Temperature and Adsorption Thermodynamics

The effect of temperature on the 3,4-DMA adsorption on BC and BC-TiO\(_2\) was investigated using initial pollutant concentrations of 200 mg L\(^{-1}\) at 20, 30, 40, and 50 °C. Thermodynamic parameters show the feasibility and spontaneity of the adsorption process. The parameters, namely, change in Gibb’s free energy (\( \Delta G^0 \)), enthalpy (\( \Delta H^0 \)), and entropy (\( \Delta S^0 \)), were determined from the given equations45

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0
\]

\[
\Delta G^0 = -RT \ln K_e
\]

\[
K_e = \frac{q_e}{C_e}
\]

\[
\ln K_e = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
\]

where \( K_e \), \( R \), and \( T \) are the equilibrium constants, general gas constant (8.31 J mol\(^{-1}\) K\(^{-1}\)), and absolute temperature (K), respectively. Similarly, \( \Delta G^0 \), \( \Delta H^0 \), and \( \Delta S^0 \) are the change in Gibb’s free energy (kJ mol\(^{-1}\)), enthalpy (kJ mol\(^{-1}\)), and entropy (J mol\(^{-1}\) K\(^{-1}\)), respectively. The plots of \( \ln K_e \) versus \( 1/T \) for adsorption of 3,4-DMA on BC and BC-TiO\(_2\) are shown in Figure 7. The adsorption enthalpy (\( \Delta H^0 \)) and entopy (\( \Delta S^0 \)) were determined from the slope and the intercept of Figure 7. The thermodynamic parameters for 3,4-DMA adsorption on BC and BC-TiO\(_2\) are recorded in Table 3.
organic compounds is the formation of conjugated complexes rate controlling step. The main adsorption mechanism of for adsorption. At this time, chemical adsorption becomes the dominant role, which has nothing to do with the surface adsorption site. The negative values of enthalpy indicate that the process is exothermic. The change in enthalpy lies between $\Delta H^0$ and $\Delta H^\circ$. Enthalpy of BC-TiO$_2$ is higher than pure BC, indicating that the adsorption of 3,4-DMA on BC and BC-TiO$_2$ is an exothermic process. The negative values of $\Delta G^0$ indicate that the sorption processes are spontaneous under the conditions applied. The negative value of enthalpy $\Delta H^0$ indicates that the adsorption of 3,4-DMA on BC and BC-TiO$_2$ is an exothermic process. Similarly, the negative values of entropy $\Delta S^0$ represent a decrease in randomness at the adsorbent interface during the adsorption of 3,4-DMA on BC and BC-TiO$_2$. The enthalpy of BC-TiO$_2$ is higher than pure BC, indicating that the 3,4-DMA molecules are held more strongly by BC-TiO$_2$. The negative values of enthalpy indicate that the process is exothermic. The change in enthalpy lies between $\Delta H^0$ and $\Delta H^\circ$. With the increase of cracking temperature, the adsorption capacity of 3,4-DMA was 322.58 mg g$^{-1}$ for BC and 285.71 mg g$^{-1}$ for BC-TiO$_2$, respectively. The results of the current study denote that BC and BC-TiO$_2$ can be successfully employed for the elimination of 3,4-DMA over a wide concentration range. Moreover, BC and BC-TiO$_2$ have the potential to replace high-cost adsorbents such as activated carbon, as biochar is a low-cost adsorbent and is plentiful. BC-TiO$_2$ gel was dried, calcined, and solidified at a certain temperature to prepare a composite material having a molecular or nanostructure.

### Table 3. Thermodynamic Parameters for 3,4-DMA Adsorption on Biochar and Biochar-TiO$_2$ at Different Temperatures

| Adsorbent   | $T$ (°C) | $K$ | $\Delta G^0$ (kJ mol$^{-1}$) | $\Delta H^0$ (kJ mol$^{-1}$) | $\Delta S^0$ (J mol$^{-1}$ K$^{-1}$) |
|-------------|----------|-----|-----------------------------|-----------------------------|----------------------------------|
| BC          | 20       | 17.5| $-6.5$                      | $-2.13$                     | $-2.83$                          |
|             | 30       | 16.1| $-6.3$                      |                             |                                  |
|             | 40       | 14.9| $-6.1$                      |                             |                                  |
|             | 50       | 12.9| $-5.8$                      |                             |                                  |
| BC-TiO$_2$  | 20       | 4.7 | $-3.5$                      | $-1.789$                    | $-9.43$                          |
|             | 30       | 4.3 | $-3.3$                      |                             |                                  |
|             | 40       | 4.1 | $-3.2$                      |                             |                                  |
|             | 50       | 3.6 | $-2.9$                      |                             |                                  |

The 3,4-DMA adsorption on BC and BC-TiO$_2$ has been examined. The experimental results indicated that pure BC has the highest adsorption capability for 3,4-DMA in comparison to the BC-TiO$_2$ adsorption over a concentration range of 30–200 mg L$^{-1}$. Moreover, the percentage of 3,4-DMA removal displayed an increase with increasing shaking time. Also, the removal percent of 3,4-DMA was strongly affected by increasing the pH value. Meanwhile, the adsorption capacity of the prepared BC-TiO$_2$ slightly decreased with increasing the temperature. The negative value of enthalpy $\Delta H^0$ ($-2.13$ and $-1.79$) indicates that the adsorption of 3,4-DMA on BC and BC-TiO$_2$ is an exothermic process. The negative values of $\Delta G^0$ indicate that the sorption processes are spontaneous under the conditions applied. The adsorption of 3,4-DMA on BC and the BC-TiO$_2$ composite was matched with the Toth model. For the adsorbent BC, the linear optimal regression coefficient $R^2 = 0.998$, the $T$ value is about 0.50, which means that adsorption mainly occurs on a uniform surface. For the adsorbent BC-TiO$_2$, the linear optimal regression coefficient $R^2 = 0.9659$; the $T$ value is 0.998, and the fitting curve is close to the Langmuir model. The Langmuir isotherm signifies that 3,4-DMA forms a monolayer on the adsorbent. The kinetics of 3,4-DMA adsorption on BC and BC-TiO$_2$ was evaluated by pseudo-first-order kinetics, pseudo-second-order kinetics, an intraparticle diffusion model, and an Elovich model. The maximum adsorption capacity of 3,4-DMA was 322.58 and 285.71 mg g$^{-1}$ for BC and BC-TiO$_2$, respectively. The results of the current study denote that BC and BC-TiO$_2$ can be successfully employed for the elimination of 3,4-DMA over a wide concentration range. Moreover, BC and BC-TiO$_2$ have the potential to replace high-cost adsorbents such as activated carbon, as biochar is a low-cost adsorbent and is plentiful. BC-TiO$_2$ could be used as an adsorbent microelectrode in photocatalytic and electrocatalytic degradation systems.

### 4. MATERIALS AND METHODS

#### 4.1. Materials

Tetraethyl titanate (C$_4$H$_9$O$_4$Ti), absolute ethanol, nitric acid, hydrochloric acid, sodium hydroxide, sodium sulfate, and 3,4-DMA were purchased from Sinopharm Chemical Reagent Co., Ltd. The detailed information for 3,4-DMA is presented in S-2 of the Supporting Information. Concentrated sulfuric acid (H$_2$SO$_4$) was purchased from Xinyang Chemical Reagent Factory, China, and was of analytical grade. Peach shell biochar (BC) was obtained from the local market.

#### 4.2. Synthesis of Biochar-TiO$_2$

First, BC was washed thoroughly with deionized (DI) water to remove any impurities and dried at 120 °C for 24 h followed by grinding and sieving for the particle size to pass through a 35–45 mesh sieve. The principle of biochar-supported TiO$_2$ is to use tetraethyl titanate as a precursor and uniformly disperse TiO$_2$ with biochar under liquid phase conditions, simultaneously achieving hydrolysis and condensation chemical reaction to gain a stable, transparent sol system in the mixedphase. The TiO$_2$ sol containing biochar undergoes slow polymerization after aging and loses fluidity and gradually forms a TiO$_2$ gel having a three-dimensional network structure. The obtained BC-TiO$_2$ gel was dried, calcined, and solidified at a certain temperature to prepare a composite material having a molecular or nanostructure.
The principle of the impregnation method is embodied in two aspects. First, when the void of the solid substance is immersed and in contact with the liquid, capillary pressure is generated under the action of the surface tension. The liquid penetrates the inside of the solid capillary so that the doping substance can reach the inside of the carrier.

The specific steps in the current work are described as follows:

(a) Carrier pretreatment: In this step, a certain amount of granular biochar was rinsed with DI water then soaked in 0.1 mol L⁻¹ HCl for 12 h followed by its removal and thoroughly washed with DI water. Then, it was soaked in 0.1 mol L⁻¹ sodium hydroxide for 12 h. After that, it was washed again with DI water and boiled in water for 30 min. The obtained product was dried at 100 °C for 24 h to be ready for use.

(b) Preparation of hydrolyzate and TiO₂ precursor solution: The hydrolyzate was prepared by mixing 125 mL of absolute ethanol with 250 mL of DI water. Then, 50 mL of tetrabutyl titanate was added to 125 mL of pure ethanol, and 5 mL of concentrated nitric acid was added and uniformly mixed into a precursor solution with the aid of a magnetic stirrer under constant temperature.

(c) Carrier-supported TiO₂: Two grams of the pretreated carrier was immersed in the TiO₂ precursor solution, with stirring for 30 min, and the hydrolyzate was slowly added dropwise to the precursor solution, and the dropping process was kept on a constant temperature stirrer until the end of the dropwise addition, and stirring was maintained. The stirring stops after 2.5 h. After the stirring was completed, the mixture was dried using an oven at 120 °C, and the sample was sealed after leaving it at maintained room temperature. The last two steps were repeated twice to obtain the TiO₂-modified biochar for use. Pure TiO₂ was prepared by the same method without adding BC.

4.3. Characterization. The effect of modification on the surface properties of BC and BC-TiO₂ was analyzed using various characterization tools, including the Brunauer-Emmett-Teller (BET) method using a TriStar II Plus 3030 and ASAP 2460 Version 3.00 surface area analyzer (Micromeritics) using nitrogen adsorption isotherms at −196 °C, and Fourier transform infrared (FT-IR) spectra of powder samples was recorded using dry KBr pellets at room temperature. The spectra were recorded in the range from 4000–400 cm⁻¹ using a Nicolet 6700 FT-IR with a Smart orbit attenuated total reflectance (ATR) accessory. X-ray diffraction (XRD) was performed on a Bruker D8 advance X-ray diffractometer using a Cu Kα radiation source. The SEM images were taken using a JEOL instrument JSM-IT300 at an accelerating voltage of 15 kV, beam size of 3.0, working distance of 10, and magnification of 8000.

4.4. Batch Adsorption Experiment. Batch adsorption experiments were conducted in the present study to achieve optimum operating conditions. BC and BC-TiO₂ weighed 50 mg. All experiments of batch adsorption were executed with a shaking of 160 rpm on a water bath shaker. The system was shaken constantly until the attainment of adsorption equilibrium at the temperature of 25 °C. As previous literature studies were conducted on biochar using other organic compounds, the adsorption equilibrium for the present studies was conducted over 24 h. The 3,4-DMA concentration in the supernatant was measured using a UV-1100 spectrophotometer (Shanghai Mei-puda Instrument Co., Ltd.) at λ = 456 nm, and the absorbance was measured with deionized water as a reference. The adsorption capacity of BC and BC-TiO₂ (qₑ) per gram was calculated using

\[ qₑ = \frac{C₀ - Cₑ}{M} \times V \]  \hspace{1cm} (18)

Here, C₀ and Cₑ are the initial and equilibrium analytic solution concentrations (mg L⁻¹), respectively, V is the solution volume (L), and M is the total mass of adsorbent added (g).

4.4.1. Effect of Contact Time. A study on the effect of contact time on the adsorption of 3,4-DMA on BC and BC-TiO₂ was carried out. Fifty milligrams of adsorbent was added to 100 mL of 3,4-DMA solution with the initial concentration of 200 mg L⁻¹ and pH 7. The contents in the flask were agitated in the water bath shaker. This process of agitation was conducted for all samples for different times ranging from 5 min to 72 h. The flasks were taken out of the shaker at predetermined time intervals. The samples were passed through a 0.22 μm filter, and the concentration of 3,4-DMA in the filtrate was determined by spectrophotometry.

4.4.2. Effect of pH. An analysis of the effect of pH on the adsorption of 3,4-DMA adsorption on BC and BC-TiO₂ was conducted. The pH of the 3,4-DMA solution with the initial concentration of 200 mg L⁻¹ was adjusted with 0.1 M HCl and 0.1 M NaOH. A specific amount of adsorbent was added to the 3,4-DMA solution of the desired pH value. The pH of the initial 3,4-DMA solution was maintained at pH values of 3, 4, 5, 6, 7, 8, and 9, and the samples were then passed through a 0.22 μm filter. Afterward, spectrophotometry was used to determine the concentration of 3,4-DMA in the filtrate.

4.4.3. Effect of Temperature. To determine the effect that temperature has on the adsorption of 3,4-DMA on BC and BC-TiO₂, the sample was tested at temperatures of 20, 30, 40, and 50 °C. A known amount of adsorbent was added to 50 mL of 3,4-DMA solution with a preliminary concentration of 200 mg L⁻¹. The contents in the flasks were mixed for 24 h, after which they were filtered through a 0.22 μm filter, and the concentration of 3,4-DMA in the supernatant was determined.

4.5. Adsorption Isotherm and Kinetics. 4.5.1. Adsorption Isotherm. The adsorption isotherm can be defined as the equilibrium relationship between the concentration in the adsorbent phase of the adsorbent particles and the concentration in the liquid phase at a given temperature. To explain the adsorption of 3,4-DMA on BC and BC-TiO₂, the experimental data obtained was analyzed utilizing adsorption isotherms. In this study, the Freundlich, Langmuir and Toth models were applied to analyze the recorded data in solid–liquid adsorption systems.

4.5.2. Adsorption Kinetics. In the design of the adsorption system, a critical stage is represented by the kinetics analysis of any adsorption process. Establishing the time needed for the adsorption process to reach equilibrium is imperative. This equilibrium time is a result of the kinetics analysis of the adsorption system. The kinetics analysis regulates the mechanism of adsorption and, therefore, the rate-determining step. Analysis of the experimental data was conducted using the pseudo-first-order model, pseudo-second-order model, intraparticle diffusion model, and Elovich model.
### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00619.

Target adsorbate product, BET surface area of the as-prepared materials, and EDX analysis (PDF)

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**Notes**

The authors declare no competing financial interest.

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### REFERENCES

(1) Foo, K. Y.; Hameed, B. H. Utilization of biodiesel waste as a renewable resource for activated carbon: application to environmental problems. Renewable Sustainable Energy Rev. 2009, 13, 2495–2504.

(2) Foo, K. Y.; Hameed, B. H. Value-added utilization of oil palm ash: A superior recycling of the industrial agricultural waste. J. Hazard. Mater. 2009, 172, 523–531.

(3) Marti, N.; Bouzas, A.; Seco, A.; Ferrer, J. Struvite precipitation assessment in anaerobic digestion processes. Chem. Eng. J. 2008, 141, 67–74.

(4) Basaleh, A. A.; Al-Malack, M. H.; Saleh, T. A. Methylene Blue removal using polyamide-vermiculite nanocomposites: Kinetics, equilibrium and thermodynamic study. J. Environ. Chem. Eng. 2019, 7, 103107.

(5) Saleh, T. A.; Ali, I. Synthesis of polyamide grafted carbon microspheres for removal of rhodamine B dye and heavy metals. J. Environ. Chem. Eng. 2018, 6, 5361–5368.

(6) Liang, Z.; Wang, Y.; Zhou, Y.; Liu, H. Coagulation removal of melanoids from biologically treated molasses wastewater using ferric chloride. Chem. Eng. J. 2009, 152, 88–94.

(7) Macfarlane, A. L.; Prestidge, R.; Farid, M. M.; Chen, J. J. J. Dissolved air flotation: A novel approach to recovery of organosolv lignin. Chem. Eng. J. 2009, 148, 15–19.

(8) Foo, K. Y.; Hameed, B. H. A short review of activated carbon assisted electroosorption process: An overview, current stage and future prospects. J. Hazard. Mater. 2009, 170, 552–559.

(9) Nardelli, P.; Gatti, G.; Eusebi, A. L.; Battistoni, P.; Cecchi, F. Full-Scale Application of the Alternating Oxic/Anoxic Process: An Overview. Ind. Eng. Chem. Res. 2009, 48, 3526–3532.

(10) Sanjrani, M. A.; Zhou, B.; Zhao, H.; Zheng, Y. P.; Wang, Y.; Xia, S. B. The Influence of Wetland Media in Improving the Performance of Pollutant Removal during Water Treatment: A Review. Appl. Ecol. Environ. Res. 2019, 17, 3803–3818.

(11) Fadillah, G.; Saputra, O. A.; Saleh, T. A. Trends in Polymers Functionalized Nanostructures for Analysis of Environmental Pollutants. Trends Environ. Anal. Chem. 2020, 26, e00084.

(12) Alswat, A. A.; Ahmad, M. B.; Saleh, T. A. Zeolite modified with copper oxide and iron oxide for lead and arsenic adsorption from aqueous solutions. J. Water Supply: Res. Technol.-AQUA 2016, 65, 465–479.

(13) Al-Asheh, S.; Banat, F.; Abu-Aitah, L. Adsorption of phenol using different types of activated bentonites. Sep. Purif. Technol. 2003, 33, 1–10.

(14) Chen, S.; Sun, D.; Chung, J.-S. Simultaneous methanogenesis and denitrification of aniline wastewater by using anaerobic–aerobic biofilm system with recirculation. J. Hazard. Mater. 2009, 169, 575–580.

(15) Jiang, Y.; Wang, H.; Shang, Y.; Yang, K. Simultaneous removal of aniline, nitrogen and phosphorus in aniline-containing wastewater treatment by using sequencing batch reactor. Bioresour. Technol. 2016, 207, 422–429.

(16) Guo, Y.; Chen, H.; Zhang, H.; Pang, H.; Wang, H.; Wang, N.; Chang, S. Characteristics and kinetic characteristics of oxidative degradation of 2-nitro-4-methoxyaniline by Fenton. Environ. Sci. Res. 2017, 30, 1613–1621. [Translated from chinese]

(17) Sawai, J.; Ito, N.; Minami, T.; Kikuchi, M. Separation of low volatile organic compounds, phenol and aniline derivatives, from aqueous solution using silicone rubber membrane. J. Membr. Sci. 2005, 252, 1–7.

(18) Moawed, E.; Abulkibash, A.; El-Shahat, M. Synthesis and characterization of iodo polyurethane foam and its application in removing of aniline blue and crystal violet from laundry wastewater. J. Taibah Univ. Sci. 2015, 9, 80–88.

(19) Gómez, J. L.; León, G.; Hidalgo, A. M.; Gómez, M.; Murcia, M. D.; Grínán, G. Application of reverse osmosis to remove aniline from wastewater. Desalination 2009, 245, 687–693.

(20) Chen, B.; Chen, Z.; Lv, S. A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. Bioresour. Technol. 2011, 102, 716–723.

(21) Saleh, T. A. Simultaneous adsorptive desulfiturization of diesel fuel over bimetalllic nanoparticles loaded on activated carbon. J. Cleaner Prod. 2018, 172, 2123–2132.

(22) Huang, R.; Yang, B.; Liu, Q.; Liu, Y. Simultaneous adsorption of aniline and Cr (VI) ion by activated carbon/chitosan composite. J. Appl. Polym. Sci. 2014, 131, 1.

(23) Thamaphat, K.; Limsuwan, P.; Ngotawornchai, B. Phase characterization of TiO2 powder by XRD and TEM. Kasetsart J.(Nat. Sci.) 2008, 42, 357–361.

(24) Saleh, T. A.; Naemullah; Tuzen, M.; Sari, A. Polyethyleneimine modified activated carbon as novel magnetic adsorbent for the removal of uranium from aqueous solution. Chem. Eng. Res. Des. 2017, 117, 218–227.

(25) Kim, J. R.; Kan, E. Heterogeneous photocatalytic degradation of sulfamethoxazole in water using a biochar-supported TiO2 photocatalyst. J. Environ. Manage. 2016, 180, 94–101.

(26) Roshan, B.; Kadirvelu, K.; Kumar, N. S. Investigation of aniline adsorption onto spherical carbon: optimization using response surface methodology. Int. J. Eng. Res. Appl. 2013, 3, 943–952.
(27) Yang, K.; Wu, W.; Jing, Q.; Zhu, L. Aqueous Adsorption of Aniline, Phenol, and their Substitutes by Multi-Walled Carbon Nanotubes. *Environ. Sci. Technol.* 2008, 42, 7931−7936.

(28) Yan, L.; Kong, L.; Qu, Z.; Li, L.; Shen, G. Magnetic biochar decorated with ZnS nanocrystals for Pb (II) removal. *ACS Sustainable Chem. Eng.* 2014, 3, 125−132.

(29) Aly, Z.; Luca, V. Uranium extraction from aqueous solution using dried and pyrolyzed tea and coffee wastes. *J. Radioanal. Nucl. Chem.* 2013, 295, 889−900.

(30) Freundlich, H. Über die adsorption in lösungen. *Zeitschrift für physikalische Chemie* 1907, 57U, 385−470.

(31) Foo, K. Y.; Hameed, B. H. Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.* 2010, 156, 2−10.

(32) Wu, K.-T.; Wu, P.-H.; Wu, F.-C.; Jreng, R.-L.; Juang, R.-S. A novel approach to characterizing liquid-phase adsorption on highly porous activated carbons using the Toth equation. *Chem. Eng. J.* 2013, 221, 373−381.

(33) Ho, Y. S. Selection of optimum sorption isotherm. *Carbon* 2004, 42, 2115−2116.

(34) Magdy, Y. H.; Allaher, H. Kinetic analysis of the adsorption of dyes from high strength wastewater on cement kiln dust. *J. Environ. Chem. Eng.* 2018, 6, 834−841.

(35) Ahmed, M. H. Removal of Insecticide (METHOMYL) From Of The Aqueous SOLUTIONS Using Low-Cost Adsorbents; Minia University: 2007.

(36) Bashir, A.; Manzoor, T.; Malik, L. A.; Qureashi, A.; Pandith, A. H. Enhanced and Selective Adsorption of Zn(II), Pb(II), Cd(II), and Hg(II) Ions by a Dumbbell- and Flower-Shaped Potato Starch Phosphate Polymer: A Combined Experimental and DFT Calculation Study. *ACS Omega* 2020, 5, 4853−4867.

(37) Wang, L.; Wang, A. Adsorption properties of Congo Red from aqueous solution onto surfactant-modified montmorrillonite. *J. Hazard. Mater.* 2008, 160, 173−180.

(38) Amin, M. T.; Alazba, A. A.; Shalg, M. Application of biochar derived from date palm biomass for removal of lead and copper ions in a batch reactor: Kinetics and isotherm scrutiny. *Chem. Phys. Lett.* 2019, 722, 64−73.

(39) Fierro, V.; Torné-Fernández, V.; Montané, D.; Celzard, A. Adsorption of phenol onto activated carbons having different textural and surface properties. *Microporous Mesoporous Mater.* 2008, 111, 276−284.

(40) Tsibranska, I.; Hristova, E. Comparison of different kinetic models for adsorption of heavy metals onto activated carbon from apricot stones. *Bulg. Chem. Commun.* 2011, 43, 370−377.

(41) Hameed, B. H.; Tan, I. A. W.; Ahmad, A. L. Adsorption isotherm, kinetic modeling and mechanism of 2,4,6-trichlorophenol on coconut husk-based activated carbon. *Chem. Eng. J.* 2008, 144, 235−244.

(42) Wu, F.-C.; Tseng, R.-L.; Juang, R.-S. Comparisons of porous and adsorption properties of carbons activated by steam and KOH. *J. Colloid Interface Sci.* 2005, 283, 49−56.

(43) Ahmad, Z. U.; Yao, L.; Wang, J.; Gang, D. D.; Islam, F.; Lian, Q.; Zappi, M. E. Neodymium embedded ordered mesoporous carbon (OMC) for enhanced adsorption of sunset yellow: Characterizations, adsorption study and adsorption mechanism. *Chem. Eng. J.* 2019, 359, 814−826.

(44) Wu, F.-C.; Tseng, R.-L.; Juang, R.-S. Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems. *Chem. Eng. J.* 2009, 150, 366−373.

(45) Batool, S.; Idrees, M.; Hussain, Q.; Kong, J. Adsorption of copper (II) by using derived-farmyard and poultry manure biochars: Efficacy and mechanism. *Chem. Phys. Lett.* 2017, 689, 190−198.

(46) El Haddad, M.; Slimani, R.; Mamouni, R.; ElAntri, S.; Lazar, S. Removal of two textile dyes from aqueous solutions onto calcined bones. *J. Assoc. Arab Univ. Basic Appl. Sci.* 2013, 14, 51−59.

(47) Vimonses, V.; Lei, S.; Jin, B.; Chow, C. W. K.; Saint, C. Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials. *Chem. Eng. J.* 2009, 148, 354−364.