N-doped Porous Carbon Derived from Bamboo Fiber as a High-performance Adsorbent for Methylene Blue

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N-doped porous carbon materials derived from bamboo fibers (NBFCs) were synthesized through a simple simultaneous activation and carbonization method. The effects of the adsorbent dosage, absorption temperature, pH of the solution, initial concentration, and contact time on the absorption of methylene blue were investigated. The equilibrium, kinetics, isotherms, and thermodynamics of the adsorption process were also analyzed. The results showed that NBFC-800 had a good adsorption capacity of 816.0 mg/g and a high removal efficiency of 93.3% during the optimum absorption process with an adsorbent dosage of 0.8 g/L. adsorption temperature of 25 °C, initial concentration of 700 mg/L, and a solution pH of 9.0. The adsorption process included instantaneous adsorption or external surface adsorption, intraparticle diffusion, and an equilibrium process. Methylene blue adsorption of NBFC-800 agreed with the pseudo second-order model and belonged to the Langmuir isotherm model. The results will be useful for the development of high-performance NBFCs to efficiently remove methylene blue from wastewater.

Keywords: Porous carbon; N-doped; Bamboo fiber; Methylene blue; Adsorption mechanism.

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INTRODUCTION

Methylene blue (MB) is a contributing pollution source from dyeing wastewater, which is extensively applied in various industries: paper, textiles, leather, plastics, food, cosmetic, printing, etc. (Luo et al. 2010). Methylene blue is harmful to the environment and to human health and can cause vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans (Gong et al. 2013). Therefore, wastewater that includes MB must be purified before it is discharged into the ecosystem. The main purification methods include flocculation, coagulation, precipitation, photocatalytic degradation, oxidation, micellar-enhanced ultrafiltration, membrane separation, electrochemical treatment, and adsorption. Adsorption is the most promising method due to its availability, easy operation, low cost, profitability, effectiveness, and lack of by-products (Cao et al. 2016). Porous carbon materials can be used to remove MB from wastewater, due to their super high adsorption rate and exceptionally large surface area (Apul and Karanfil 2015). These qualities are especially present in N-doped porous carbon materials, as the incorporation of a nitrogen atom into the carbon framework improves the wettability of the carbon in an aqueous solution (Lorenc-Grabowska et al. 2013). The dispersion forces between the carbon surface and the MB are improved by the nitrogen-containing functional groups. It is confirmed that N-doped porous carbon materials have a strong adsorption capacity for the removal of MB (Li *et al.* 2016). However, most of the previously N-doped porous carbons are complex, have a high cost, and have a time-consuming adsorption process, which limits commercial applications. Therefore, it is necessary to further enhance the adsorption performance and explore new raw materials for the preparation of cost-effective N-doped porous carbon.

Biomass is the most promising precursor for N-doped porous carbon materials. It is primarily comprised of cellulose, hemicellulose, and lignins, with unique surface properties and the presence of various polar functional groups, such as alcohols, aldehydes, carboxylics, ketones, phenolics, etc. These polar functional groups greatly enhance the affinity for MB (Angelova et al. 2016). Bamboo is an abundant type of biomass material, which has been used to remove MB from wastewater in China. Hameed et al. (2007) investigated the MB adsorption characteristics of bamboo-based activated carbon and found that the equilibrium data for MB adsorption fit well with the Langmuir equation with a maximum monolayer adsorption capacity of 454.2 mg/g. Zhang et al. (2014a) applied a bamboo shoot shell to remove MB from a solution and found that the maximum adsorption capacity was 226 mg/g and could achieve a removal efficiency of 99.0%. Shaibu et al. (2014) investigated the MB adsorption properties of synthesized nanoscale zero-valent iron-bamboo and manganese-bamboo composites. Shaibu et al. (2014) found that the synthesized nanoscale zero-valent iron-bamboo composite was more effective than the manganese-bamboo composite in terms of a higher MB dye adsorption capacity of 322.5 mg/g, compared to an adsorption capacity of 264 mg/g for the manganese-bamboo composite. Guo et al. (2014) removed MB from aqueous solutions via chemically modified bamboo and found that the MB adsorption with the chemically modified bamboo fit the Langmuir mode well, and achieved a maximum adsorption capacity of 606 mg/g at 298 K. Ghosh and Bandyopadhyay (2017) used citric acid treated carbonized bamboo to remove MB and found that the highest MB removal percentage was 99.97% and the highest adsorption capacity was 725 mg/g. Bamboo fiber is one of the main components of bamboo and has a multi-layer wall structure, which is helpful in the preparation of porous carbon materials (Ni et al. 2018). Zhao et al. (2015) prepared bamboo activated carbon fiber (BACFs) through a new type of facile gas carrying water activation technology. Zhao et al. (2015) found that the as-prepared BACFs had a specific surface area of up to 2169 m^2/g and had superior performance in terms of xenon storage, with a maximum intake of 158.5 cm^{3}/g . Jiao *et al.* (2016) reported a lightweight and superhydrophobic carbon fiber aerogel derived from bamboo fiber, which showed efficient and fast adsorption of organic liquids from wastewater. Fujishige et al. (2017) prepared activated carbon using bamboo-cellulose fiber. The largest specific surface area of the activated carbon was 2366 m²/g, with a micropore volume of 0.71 cm³/g and a mesopore volume of 0.06 cm³/g. Based on these proofs, bamboo fiber has great potential as a raw material for porous carbon materials. However, to the best of the author's knowledge, there is a lack of sufficient information on N-doped porous carbon material derived from bamboo fibers used as an adsorbent to remove MB from wastewater. Therefore, N-doped porous bamboo fiber carbon materials (NBFCs) were synthesized through a simple simultaneous activation and carbonization method. In this research, bamboo fiber was used as a carbon precursor, glycineas was used as a nitrogen source, and KHCO3 was used as an activator. Methylene blue was selected as a model compound to evaluate the adsorption characteristics of NBFCs. The adsorption efficiency was also controlled *via* the pH value of the wastewater, the nitrogen doping level, and the nitrogen species (Ghaedi et al. 2013; Feng et al. 2015). The effects of the adsorbent dosage, the absorption temperature, the pH of the solution, the solution concentration, and

the contact time on the adsorption characteristics of NBFCs were investigated. Furthermore, the equilibrium, kinetics, isotherms, and thermodynamics of the adsorption process were also analyzed. The purpose of this research was to develop a new type of high-performance NBFCs to efficiently remove MB from wastewater.

EXPERIMENTAL

Materials

Bamboo fiber was acquired from Paper Manufacturing Co., Ltd. (Guizhou Chitianhua Paper Mill, China). Glycine (Gly), potassium bicarbonate (KHCO₃), and MB ($C_{16}H_{18}CIN_3S \cdot 3H_2O$) were purchased from the Beijing chemical glass station (Beijing, China), the Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China), and the Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China), respectively.

Preparation of the NBFCs

First, 2.0 g of bamboo fibers were put into a saturated solution with 5.0 g of glycine and 20 mL of deionized water and was ultrasonically mixed for 15 min; 8.0 g of KHCO₃ was added to the mixture, which was soaked for 12 h. The mixture was frozen for 30 min in a liquid nitrogen environment and was freeze-dried for 3 d using a lyophilizer (Labconco, FreeZone, Kansas City, MO, USA) with a temperature of -85 °C and vacuum of 0.06 MPa. The mixture was carbonized through a tube furnace (Zhengzhou Kejing Electric Furnace Co., Ltd., GSL1600X, Henan, China). The carbonization temperature was increased from room temperature (20 ± 5 °C) to the target temperature (600 °C, 700 °C, 800 °C, and 900 °C, respectively) for 1.0 h with a heating rate of 5 °C/min under a N₂ atmosphere. The obtained NBFCs were washed in 1 M HCl and distilled water until the pH of the washing solution was 7.0. Finally, the NBFCs were oven-dried at 103 ± 2 °C until the mass stabilized. They were labeled as NBFC-X (where X was the carbonization temperature). The sample without the addition of KHCO₃ and carbonized at a temperature of 800 °C was labeled as BFC-800.

Characterizations

The morphology of the NBFCs was observed on a field-emission scanning electron microscope (FE-SEM) (FEI XL30 FEG, Hillsboro, OR, USA). The C, H, and N content of the NBFCs was determined *via* an elemental analyzer (Elementar, Vario EL cube, Langenselbold, Hesse, Germany). The N₂ adsorption-desorption analyses were determined with a N₂ adsorption desorption tester (Micromeritics, 3Flex, Atlanta, GA, USA) at -196 °C. The specific surface area of the NBFSs was calculated using the Brunauer-Emmett-Teller (BET) equation. The Fourier-transform infrared (FTIR) spectra of the NBFCs were collected using an 80V FTIR spectrometer (Thermo Electron Co., Thermo-Nicolet Nexus 670, Waltham, MA, USA).

Determination of the Adsorption Properties

Batch adsorption experiments were carried out in a 100 mL stopper Erlenmeyer flask, which was shaken at 120 rpm in a thermostatted orbital shaker (Taicang Haocheng Experimental Instrument Manufacturing Co., Ltd., HCY-12B, Taicang, China). The adsorption process was optimized by adjusting the adsorbent dosage between 0.2 g/L and 2 g/L, the pH value of the solution between 3 to 11, the ambient temperature to 25 °C, 35

°C, and 45 °C, the initial dye concentration between 400 mg/L and 700 mg/L, and the contact time between 0 min and 500 min. The pH value of the solution was adjusted by the addition of 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. The absorption property was determined with a UV-vis spectrometer (PerkinElmer, Lambda 35, Waltham, MA, USA) at a maximum wavelength (λ_{max}) of 664 nm. The adsorption capacity of MB at the equilibrium (q_e , mg/g) and the removal efficiency (R) were calculated by Eqs. 1 and 2, respectively,

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

$$R(\%) = \frac{C_0 - C_e}{C_0}$$
(2)

where C_0 and C_e (mg/L) are the initial and equilibrium liquid-phase concentrations of the solution, respectively. V(L) is the volume of the solution and W(g) is the mass of adsorbent.

Determination of the Adsorption Kinetics

To characterize the adsorption process of the adsorbent under the different initial dye concentrations, the pseudo-first-order, pseudo-second-order, and Elovich kinetic models were applied to fit the experimental data. The concentration of the solutions was determined at different time intervals, and the amount of adsorption at time *t*, defined as q_t (mg/g), was calculated by Eq. 3,

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{3}$$

where C_0 (mg/L) is the initial concentration of the solution and C_t (mg/L) is the concentration of the solution at time *t*. *V*(L) is the volume of the solution, and *W*(g) is the mass of adsorbent.

The pseudo-first-order kinetic model was defined by Lagergren (1898), as shown as Eq. 4,

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

where k_1 (1/min) is the adsorption rate constant of the pseudo-first-order, and q_t (mg/g) and q_e (mg/g) are the amounts of adsorption at time *t* and at equilibrium, respectively.

The pseudo-second-order kinetic model (Ho *et al.* 1999) is defined as shown in Eq. 5,

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

where k_2 (1/min) is the adsorption rate constant of the pseudo-second-order, and q_t (mg/g) and q_e (mg/g) are the amounts of adsorption at time *t* and at equilibrium, respectively.

The Elovich kinetic equation (Elovich and Zhabrova 1939) is defined as shown in Eq. 6,

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t) \tag{6}$$

where $a \pmod{g/g} \times \min$ is the initial adsorption rate and $b \pmod{g/mg}$ is the adsorption rate constant. The value of (1/b) is indicative of the available number of sites for adsorption while $(1/b) \ln{(ab)}$ is the adsorption quantity when $\ln t$ is 0.

It is well known that the adsorption type of most adsorbents is carried out through

intraparticle diffusion, which was analyzed *via* the diffusion model (Weber and Morris), shown in Eq. 7,

$$q_t = k_p t^{1/2} + C (7)$$

where $k_p \pmod{g \times \min^{0.5}}$ and *C* are the diffusion rate constant and the thickness of the boundary layer, respectively.

To distinguish between the pore and the film diffusion step during the adsorption process, the adsorption kinetic data was further analyzed using the Boyd model (Boyd *et al.* 1947), shown in Eq. 8,

$$B_t = -0.4997 - \ln\left(1 - \frac{q_t}{q_e}\right)$$
(8)

where $q_e (mg/g)$ and $q_t (mg/g)$ are the adsorption capacity of MB at equilibrium and at time *t*, respectively.

Determination of the Adsorption Isotherm Parameters

To determine the interaction between the MB and the NBFCs, and to evaluate the performance of the NBFCs, the adsorption isotherms parameters were analyzed *via* the Langmuir, Freundlich, and Tempkin isotherm models. The Langmuir isotherm was defined by Langmuir (1918), as shown as Eq. 9,

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

where $C_e \text{ (mg/L)}$ is the dye concentration at equilibrium in the solution, $K_L \text{ (L/mg)}$ is the Langmuir constant, and $q_e \text{ (mg/g)}$ and $Q_m \text{ (mg/g)}$ are the dye concentrations onto the adsorbent at equilibrium and the monolayer forms on the adsorbent, respectively.

The values of Q_m and K_L were calculated according to the slopes and intercepts. The isotherm can be used to describe the adsorption affinity between the MB and the NBFCs, which also reflected the adsorption process in terms of the dimensionless separation factor R_L , as shown in Eq. 10,

$$R_L = \frac{1}{1 + K_L C_0} \tag{10}$$

where R_L is the dimensionless separation factor, C_0 (mg/L) is the initial concentration of the adsorbate, and K_L (L/mg) is the Langmuir constant.

The Freundlich model (1906) is defined as Eq. 11,

$$Logq_e = LogK_F + \frac{1}{n}LogC_e \tag{11}$$

where $K_F[(mg/g) \ge (mg/L)^{1/n}]$ and *n* are the Freundlich constants related to the capacity and favorability of adsorption, respectively.

The Tempkin isotherm model (Tempkin and Pyzhev 1960) was shown as Eq. 12,

$$q_e = \frac{RT}{b_T} ln K_T + \frac{RT}{b_T} ln C_e \tag{12}$$

where R (8.314 J/mol x K) is the gas universal constant, b_T (J/mol) is the Tempkin constant, and K_T (L/g) is the equilibrium banding constant.

Determination of the Adsorption Thermodynamic Parameters

In order to determine the effect of the temperature on the adsorption properties, absorption experiments were carried out with an initial MB concentration of 600 mg/L at

temperatures of 25 °C, 35 °C, and 45 °C. The thermodynamic parameters were calculated by Eqs. 13 through 15,

$$K_D = \frac{q_e}{C_e} \tag{13}$$

$$\Delta G^0 = -RT ln(K_D) \tag{14}$$

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{15}$$

where K_D is the equilibrium partition constant, ΔG^0 (kJ/mol) is the change in Gibbs free energy, ΔH^0 (kJ/mol) is the change in enthalpy, ΔS^0 (kJ/mol·K) is the change in entropy, R(8.314 J/mol x K) is the universal gas constant, and T (K) is the temperature.

RESULTS AND DISCUSSION

Selection of the High-performance NBFC

The optimum NBFC configuration was obtained in this research based on its high adsorption capacity and removal efficiency. Figure 1 shows that the carbonization temperature had a major effect on the MB absorption ability of the NBFCs. With an increase in carbonization temperature from 600 °C to 800 °C, the adsorption capacity and the removal efficiency of the NBFCs gradually increased. Sample NBFC-800 had a maximum adsorption capacity of 1114 mg/g and the highest removal efficiency at 74.3%. It is well known that a high adsorption capacity of an absorbent is closely related to the pore characteristics. The morphology and the microstructure of the NBFCs are shown in Fig. 2. It was found that the inactivated bamboo fiber (as shown in Fig. 2a) still maintained their original rod structure with smooth surfaces. After the bamboo fiber was activated *via* KHCO₃, the NBFCs exhibited a porous structure, as shown in Fig. 2b, 2c, 2d, and 2e.

Table 1 shows the specific surface area and the pore size of the NBFCs. Similar to the results shown in Fig. 2, the pore structures of the NBFCs were obviously improved when they were activated. The specific surface area of the NBFCs increased from 653.7 m^2/g to 2037.5 m^2/g , its pore volume increased from 0.291 cm³/g to 1.086 cm³/g, and its mesopore proportion increased from 0.160 to 0.776 with an increase in the carbonization temperature from 600 °C to 800 °C. However, the specific surface area and pore volume decreased to $1700.6 \text{ m}^2/\text{g}$ and $0.951 \text{ cm}^3/\text{g}$ respectively when the temperature was increased to 900°C. This was attributed to the excessive temperature causing the pore structure to collapse, thereby reducing the specific surface area and adsorption properties of the activated carbon. The specific surface areas and the pore volume of the NBFCs played a key role in the adsorption capacity of the MB solution. A higher specific surface area and larger pore volume provided more active sites on the surface of the NBFCs, which was helpful for the adsorption and diffusion of the MB solution. It was obvious that the adsorption capacity and the removal efficiency of NBFCs was higher than BFC-800. This indicated the effects of elemental N and the functional groups on the MB absorption of the NBFCs. Table 2 shows the element compositions of samples, and the H, N, and O content of the NBFCs was higher than BFC-800, except for NBFC-900. The N and O content in the NBFCs decreased with an increase in the carbonization temperature. This was due to the thermal decomposition of elemental N and O during the carbonization process. Sample NBFC-800 had the maximum adsorption capacity and the highest removal efficiency, indicating that the pore characteristics had a greater effect on the MB absorption than that of the N element. However, NBFC-800 remained at a higher N (2.49%) and O (34.42%) content, which could improve the wettability of the surface and the interface of the NBFCs in an aqueous solution (Chen *et al.* 2016). Furthermore, the elemental N in the NBFCs redistributed the surface charge on the carbon matrix due to the high electronegativity of N, which improve the surface affinity for the MB solution and the NBFCs (Tong *et al.* 2013).

When N-containing functional groups were introduced on the surface of the NBFCs, they could drastically increase hydrophilicity. Figure 3 shows that the NBFCs had some O-containing functional groups such as -OH, C=O, C-O, *etc.* These O-containing functional groups could also effectively improve the hydrophilicity of the samples and act as active adsorption sites (Zhang *et al.* 2014b). The changes in peak position (3450 cm⁻¹ and 1642 cm⁻¹ shifted to 3438 cm⁻¹ and 1637 cm⁻¹) also suggested that there were other adsorption interactions, such as π - π interactions and hydrogen bonding during the MB adsorption process (Wu *et al.* 2014; Fu *et al.* 2015). Furthermore, it was shown in preliminary experiments that there was no significant change in the functional groups after adsorption. Thus, the adsorbed infrared spectrum is not shown here. Based on the above characterization and analysis, the MB adsorption ability of the NBFCs was an interaction process of multiple factors. Sample NBFC-800 was selected as an absorbent to remove MB in this research.



Fig. 1. Adsorption capacity and removal efficiency of the samples

Samples	$S_{\text{BET}}(m^2/g)$			Pore volume (cm ³ /g)					Dp
	Total	Micro	Meso	Ratio ^a	Total	Micro	Meso	Ratio ^b	(nm)
BFC-800	9.389	-	-	-	-	-	-	-	-
NBFC-600	653.7	549.2	104.5	0.160	0.291	0.212	0.079	0.271	1.78
NBFC-700	1500.9	961.2	539.7	0.360	0.701	0.389	0.312	0.445	1.87
NBFC-800	2037.5	456.3	1581.2	0.776	1.086	0.175	0.911	0.839	2.13
NBFC-900	1700.6	224.5	1476.1	0.868	0.951	0.116	0.835	0.878	2.24

Table 1.	Pore	Characteristics	of	the	Sam	oles
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a: Ratio of mesopore area to total area; b: Ratio of mesopore vol. to total vol.; *D*_p: Avg. pore diam.

 Table 2. Elemental Composition of the Samples

Samples	C (%)	H (%)	N (%)	O (%)
BFC-800	86.45	1.92	0.92	10.71
NBFC-600	62.82	3.20	6.82	27.16
NBFC-700	55.78	4.01	4.73	35.48
NBFC-800	59.76	3.33	2.49	34.42
NBFC-900	33.54	0.71	0.59	65.16



Fig. 2. FE-SEM images of the NBFCs; a) BFC-800, b) NBFC-600, c) NBFC-700, d) NBFC-800, e) NBFC-900



Fig. 3. FTIR spectra of the samples

Adsorption Characteristics of NBFC-800

Adsorbent dosage

The effects of the adsorbent dosage range (from 0.2 g/L to 2 g/L) on the MB adsorption ability of NBFC-800 were investigated using a 600 mg/L solution that contained 50 ml of MB at 25 °C. As shown in Fig. 4a, when the adsorbent dosage increased from 0.2 g/L to 0.8 g/L, the MB removal efficiency increased from 43.8% to 99.9%. This indicated that absorbent dosage obviously improved the MB removal efficiency, due to the increase in surface area and adsorption sites (Roosta *et al.* 2014). When the absorbent dosage was further increased from 0.8 g/L to 2.0 g/L, the removal efficiency of NBFC-800 slightly increased. This was due to the fact that the adsorption medium was balanced at a low MB concentration before reaching saturation (Zhang *et al.* 2013; Liu *et al.* 2014). In contrast, the MB unit adsorption capacity of NBFC-800 gradually decreased with an increase in adsorbent dosage; since the concentration of NBFC-800 led to less of the specific surface area of the adsorbent coming in contact with the MB, which further reduced the unsaturated adsorption sites of the adsorbent. Therefore, the optimal adsorbent dosage was 0.8 g/L.





Fig. 4. Effects of the adsorbent dosage (a), absorption temperature (b), initial concentration and contact time (c), and solution pH (d) on the MB adsorption ability of NBFC-800.

Absorption temperature

Temperature is a key factor related to the driving force during the adsorption process. Figure 4b shows the adsorption capacity and the removal efficiency of NBFC-800 at 25 °C, 35 °C, and 45 °C. The adsorption capacity showed a progressive increase. With an increase in absorption temperature, the adsorption capacity also increased. The adsorption capacity reached equilibrium after approximately 6.0 h with the values of 1121, 1145, and 1158 mg/g at 25 °C, 35 °C, and 45 °C, respectively. This indicated that the MB adsorption process by NBFC-800 was an endothermic process. Considering the slight difference in adsorption capacity at the three different temperatures, and in an effort to keep low costs and conserve energy, the optimal adsorption temperature of NBFC-800 for MB was 25 °C.

Initial concentration and contact time

Figure 4c shows the effects of the contact time on the MB adsorption capacity at seven different initial concentrations (ranging from 400 mg/L to 700 mg/L). The adsorption capacity increased at contact time of 0 min to 20 min, which was due to the presence of multiple vacant surface adsorption sites. The adsorption capacity slightly increased with an increase in contact time from 20 min to 180 min, indicating that the MB absorption capacity of NBFC-800 gradually reached saturation. The maximum adsorption corresponded to a contact time of approximately 360 min, when all the activation sites were coated by dye molecules and no binding adsorption sites were provided (Bayramoğlu et al. 2006). In addition, the MB equilibrium adsorption capacities of NBFC-800 at different concentrations followed a gradually increasing trend. The maximum equilibrium adsorption capacity was increased to 1229 mg/g when the initial concentration was 700 mg/L. This was due to the fact that a higher initial concentration could provide a stronger driving force for overcoming the mass transfer resistance between the adsorbent and the MB dye (Borah et al. 2015). This indicated that the adsorption process depended on the initial concentration of the MB solution. The higher the initial concentration of the solution, the greater the amount of adsorption. The initial concentration of 700 mg/L was taken as the optimal initial concentration in this experiment based on the factors considered.

Solution pH value

The effects of the pH value of the solution on MB adsorption were investigated at 25 °C, as shown in Fig. 4d. With an increase in pH from 3.0 to 11.0, the adsorption capacity and the removal efficiency of MB increased from 854 to 1495 mg/g and 56.9 to 99.7%, respectively. This was due to the changes in the surface charge of NBFC-800, which depended on the pH of the solution (Ghaedi *et al.* 2014). The lower adsorption capacity and removal efficiency in acidic pH conditions may be due to the strong repulsive force between the MB solution and the cationic adsorbent surface or by competition of the blank charged MB cationic dye adsorption sites with excess H⁺ ions (Abbad and Lounis 2014). The increase in adsorption capacity and removal efficiency was attributed to the number of negatively charged sites, which decreased the electrostatic repulsion between the MB and the adsorbent surface with an increase in the pH value (Pandimurugan *et al.* 2016). Furthermore, the adsorption capacity and removal efficiency showed a sharp increase when the pH value was 9, compared to pH values of 3.0 to 8.0. When the pH was higher than 9.0, the increase in the adsorption capacity and the removal efficiency of NBFC-800 was minimal. Therefore, the optimum pH value was 9.0.

The adsorbent dosage, the pH of the solution, the absorption temperature, and the contact time had a major effect on the adsorption of MB for NBFC-800. In this research, the optimal adsorbent dosage was 0.8 g/L, the optimal adsorption temperature was 25 °C, the optimal initial concentration of the MB solution was 700 mg/L, and the optimal pH of the solution was 9.0. To further confirm the absorption capacity and the removal efficiency of NBFC-800, the absorption determination process was carried out five times at the optimal conditions. Figure 5 shows that NBFC-800 has prominent adsorption stability. The average MB absorption capacity of NBFC-800 was 816.0 mg/g and its removal efficiency was up to 93.3%, higher than that of other absorbents, as shown in Table 3.

Entry	Adsorbent	Adsorption Capacity	References
1	Platanus orientalis leaf	114.9 mg/g	Peydayesh <i>et al</i> . (2015)
2	Rice husks	178.0 mg/g	Postai <i>et al</i> . (2016)
3	Cotton stalk	294.1 mg/g	Deng <i>et al</i> . (2010)
4	Waste potato residue	330.0 mg/g	Zhang <i>et al</i> . (2014c)
5	Oxalic acid modified Swede rape straw	432.0 mg/g	Feng <i>et al</i> . (2013)
6	Albizia lebbeck seed pods	501.1 mg/g	Foo and Hameed (2011)
7	Waste tea activated carbon	554.3 mg/g	Auta and Hameed (2011)
8	Bamboo leaves powder	725.0 mg/g	Ghosh <i>et a</i> l. (2017)
9	Bamboo fiber	816.0 mg/g	This work



Fig. 5. MB adsorption capacity and the removal efficiency of NBFC-800 under optimal absorption conditions

Adsorption kinetics

Adsorption kinetics are one of the most important parameters for the explanation of the adsorption mechanisms and for the determination of the adsorption efficiency. Therefore, it is necessary to evaluate the kinetic parameters of adsorption *via* different mathematical models. In this research, three models were selected to investigate the kinetics of the adsorption process. The kinetic parameters of the pseudo-first-order, the pseudo-second-order, and the Elovich kinetic models are shown in Table 4. The coefficient of determination value (R^2) for the pseudo-second-order model was significantly higher than that of the pseudo-first-order kinetic model. In other words, the equilibrium adsorption capacity calculated by pseudo-second-order was better, which was consistent with other research results (Cheng *et al.* 2018; Ren *et al.* 2018; Wang *et al.* 2018; Fu *et al.* 2019).

		Pseudo-First-Order			Pseud	o-Second-Orc	ler	Elovich		
C_0	$q_{ m e, exp}$	Kinetic Model			K	inetic Model		Kinetic Model		
(mg/L)	(mg/g)	k_1	q e, cal	R ²	<i>k</i> ₂	q e, cal	R ²	а	b	R ²
		(1/min)	(mg/g)		(g/mg∙min)	(mg/g)		(mg/g∙min)	(g/mg)	
400	941.31	1.54×10 ⁻²	54.43	0.9776	6.05×10 ⁻⁴	909.09	0.9999	4.06759E + 26	6.89×10 ⁻²	0.9738
450	990.07	2.21×10 ⁻²	57.67	0.9742	6.25×10 ⁻⁴	1000.00	0.9999	3.88885E + 25	6.27×10 ⁻²	0.9821
500	1043.81	2.40×10 ⁻²	50.60	0.8597	7.69×10-4	1000.00	0.9999	2.38826E + 38	8.82×10 ⁻²	0.9246
550	1062.07	2.05×10 ⁻²	67.74	0.9450	4.76×10 ⁻⁴	1111.11	0.9999	2.08282E + 22	5.12×10 ⁻²	0.9891
600	1113.90	7.60×10 ⁻³	55.60	0.9008	4.26×10 ⁻⁴	1111.11	0.9997	2.36270E+36	7.94×10 ⁻²	0.9361
650	1148.25	1.22×10 ⁻²	45.90	0.9487	6.23×10 ⁻⁴	1111.11	0.9999	3.82905E+40	8.49×10 ⁻²	0.9179
700	1229.26	1.98×10 ⁻²	145.53	0.9679	2.20×10 ⁻⁴	1250.00	0.9998	1.58368E+11	2.27×10 ⁻²	0.9711

Table 4. Kinetic Parameters of the Three Kinetic Models

Furthermore, the $q_{e, cal}$ values obtained by the pseudo-second-order kinetic equation were closer to the $q_{e, exp}$ values. This indicated that the pseudo second-order model was more suitable for describing the MB adsorption process of NBFC-800. It was shown recently that when adsorption data fit well to the pseudo-second-order rate equation, this can be taken as evidence supporting a diffusion-controlled mechanism (Hubbe *et al.* 2019). The R² value for the Elovich kinetic model was also high. And the valence force shared by the electrons between the hydrophilic edge position of the NBFC-800 and the MB solution for chemisorption. Compared to the *b* values, the higher *a* values at the different initial concentrations of this model confirmed that this adsorption process had irreversible properties (Mahida and Patel 2016).

The linear fit of the intraparticle diffusion model is the most common method for detecting complex and continuous adsorption processes, which included the transfer of solutes, the diffusion of particles and the adsorption of surface active sites. The linear fit plots showed the amount of MB adsorbed (q_t) versus $t^{0.5}$ at different initial concentrations and was shown in Fig. 6a. The adsorption process could be divided into three distinct stages. The first stage (0 min to 60 min) had a higher slope than the other stages for all concentrations, indicating that adsorption process included instantaneous adsorption on external surfaces. The decreasing slope during the second linear stage (60 min to 360 min) indicated an intraparticle diffusion process occurred. The last stage was the equilibrium process, which was due to the decreasing concentration of the solution. This indicated that as the time allowed for adsorption became high the intraparticle diffusion was mitigated and that equilibrium was achieved. In order to further predict the actual slow step involved in the adsorption process, the kinetic data were analyzed *via* the Boyd model. The linear fit plots of the B_t values versus time (t) are shown in Fig. 6b. It was obvious that the line did not pass the origin and that the fit was irregular, which indicated that the film diffusion was the rate-limiting step for the adsorption of MB by NBFC-800 (Chen et al. 2016).



Fig. 6. Plots of the intraparticle diffusion (a) and the Boyd (b) models for the MB adsorption of NBFC-800 at different initial concentrations

Adsorption isotherms

Adsorption isotherms are very important for providing information about the interactions of NBFC-800 with the MB, the adsorption properties of NBFC-800 and the design of the adsorption system. To understand the MB adsorption mechanisms of NBFC-

800, the Langmuir isotherm model, the Freundlich isotherm model, and the Temkin isotherm model were used for this study, and the isotherm parameters were shown in Table 5. It was found that the R^2 value were 0.99568, 0.94372, and 0.92938, corresponding to the Langmuir, Freundlich, and Tempkin isotherm models, respectively. This indicated that the adsorption isotherm properties were in agreement with the Langmuir model, which is based on the assumption that adsorbate molecules can occupy energetically equivalent sites with no interaction between them (Fan *et al.* 2011). Furthermore, the adsorption capacity calculated according to the Langmuir isotherm model was 1111 mg/g, which was closest to the experimental data (1114 mg/g). This further confirmed that the MB adsorption isotherms of NBFC-800 was well fit to the Langmuir isotherm model.

Langmuir Isotherm Model			l Iso	Freundlich therm Mo	ı del	Temkin Isotherm Model			
Q _m (mg/g)	<i>K</i> _L (L/mg)	R ²	<i>K</i> ⊧ (mg/g)	n	R ²	Kτ	b⊤	R ²	
1111.11	0.0702	0.99568	652.680	9.22	0.94372	117.38	21.51	0.92938	

Table 5. The Isotherm Parameters for MB Adsorption on NBFC-800

Adsorption thermodynamics

The thermodynamics parameters include the change in enthalpy (ΔH^0), the change in entropy (ΔS^0), and the change in Gibbs free energy (ΔG^0), which are important for the evaluation of the effects of the temperature during the adsorption process and helpful for understanding the adsorption mechanism and properties. The thermodynamics parameters (as shown in Table 6) were calculated according to the plot of the distribution coefficient values (K_d) versus temperatures, as shown in Fig. 7.



Fig. 7. Regression plot of the thermodynamic parameters

The ΔH^0 value was 5.51 kJ/mol, which indicated that the MB absorption of NBFC-800 was endothermic. The positive value of ΔS^0 (35.0 J/mol·K) indicated that the randomness of the solid-solution interface increased during the fixation of the adsorption process and the presence of possible structural changes or interactions between the adsorbent and the adsorbate (Xiao *et al.* 2015). Furthermore, the negative values of ΔG^0 (- 4.89, -5.29, and -5.59 kJ/mol at 298 K (25 °C), 308 K (35 °C), and 318 K (45 °C), respectively) indicated the spontaneous nature of the adsorption. The ΔG^0 value decreased with an increase in temperature, which suggested that the MB adsorption process of NBFC-800 was more feasible at higher temperatures (Rangabhashiyam *et al.* 2015).

CONCLUSIONS

- 1. The NBFCs were synthesized through a simple simultaneous activation and carbonization method. Sample NBFC-800 had the greatest adsorption capacity and the highest removal efficiency, due to the characteristics of its pores and the functional groups on the surface.
- 2. The adsorbent dosage, the pH of the solution, the absorption temperature, and the contact time had major effects on the MB adsorption abilities of NBFC-800. The optimal adsorbent dosage was 0.8 g/L, the optimal adsorption temperature was 25 °C, the optimal initial concentration of the MB solution was 700 mg/L, and the optimal pH of the solution was 9.0. Under the optimum absorption parameters, the adsorption capacity and the removal efficiency of NBFC-800 was 816.0 mg/g and 93.3%, respectively.
- 3. The pseudo second-order model was most suitable for describing the MB adsorption process of NBFC-800. The adsorption process included instantaneous adsorption or external surface adsorption, intraparticle diffusion, and an equilibrium process.
- 4. The MB adsorption isotherms of NBFC-800 fit well to the Langmuir isotherm model.

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REFERENCES CITED

- Abbad, B., and Lounis, A. (2014). "Removal of methylene blue from colored effluents by adsorption onto ZnAPSO-34 nanoporous material," *Desalination and Water Treatment* 52(40-42), 7766-7775. DOI: 10.1080/19443994.2013.836991
- Angelova, R., Baldikova, E., Pospiskova, K., Maderova, Z., Safarikova, M., and Safarik, I. (2016). "Magnetically modified *Sargassum horneri* biomass as an adsorbent for organic dye removal," *Journal of Cleaner Production* 137, 189-194. DOI: 10.1016/j.jclepro.2016.07.068
- Apul, O. G., and Karanfil, T. (2015). "Adsorption of synthetic organic contaminants by carbon nanotubes: A critical review," *Water Research* 68, 34-55. DOI: 10.1016/j.watres.2014.09.032
- Auta, M., and Hameed, B. H. (2011). "Optimized waste tea activated carbon for

adsorption of methylene blue and acid blue 29 dyes using response surface methodology," *Chemical Engineering Journal* 175, 233-243. DOI: 10.1016/j.cej.2011.09.100

- Bayramoğlu, G., Celik, G., and Arica, M. Y. (2006). "Biosorption of reactive blue 4 dye by native and treated fungus *Phanerocheate chrysosporium*: Batch and continuous flow system studies," *Journal of Hazardous Materials* 137(3), 1689-1697. DOI: 10.1016/j.jhazmat.2006.05.005
- Borah, L., Goswami, M., and Phukan, P. (2015). "Adsorption of methylene blue and eosin yellow using porous carbon prepared from tea waste: Adsorption equilibrium, kinetics and thermodynamics study," *Journal of Environmental Chemical Engineering* 3(2), 1018-1028. DOI: org/10.1016/j.jece.2015.02.013
- Boyd, G. E., Myers, L. S., Jr., and Adamson, A.W. (1947). "The exchange adsorption of ions from aqueous solutions by organic zeolites. III. Performance of deep adsorbent beds under non-equilibrium conditions," *JACS* 69(11), 2849-2859. DOI: 10.1021/ja01203a067
- Cao, Y., Huang, J., Li, Y., Qiu, S., Liu, J., Khasanov, A., Khan, M. A., Young, D. P., Peng, F., Cao, D., *et al.* (2016). "One-pot melamine derived nitrogen doped magnetic carbon nanoadsorbents with enhanced chromium removal," *Carbon* 109, 640-649. DOI: 10.1016/j.carbon.2016.08.035
- Chen, C., Xu, G., Wei, X., and Yang, L. (2016). "A macroscopic three-dimensional tetrapod-separated graphene-like oxygenated N-doped carbon nanosheet architecture for use in supercapacitors," *Journal of Materials Chemistry A* 4(25), 9900-9909. DOI: 10.1039/C6TA04062D
- Cheng, M., Zeng, G. M., Huang, D. L., Lai, C., Liu, Y., Zhang, C., Wang, R. Z., Qin, L., Xue, W. J., Song, B., Ye, S. J., and Yi, H. (2018). "High adsorption of methylene blue by salicylic acid-methanol modified steel converter slag and evaluation of its mechanism," *Journal of Colloid and Interface Science* 515, 232-239. DOI: 10.1016/j.jcis.2018.01.008
- Deng, H., Li, G., Yang, H., Tang, J., and Tang, J. (2010). "Preparation of activated carbons from cotton stalk by microwave assisted KOH and K₂CO₃ activation," *Chemical Engineering Journal* 163(3), 373-381. DOI: 10.1016/j.cej.2010.08.019
- Elovich, S. Y., and Zhabrova, G. M. (1939). "Mechanism of the catalytic hydrogenation of ethylene on nickel. I. Kinetics of the process," J. Phys. Chem. 13, 1761-1764.
- Fan, J., Zhang, J., Zhang, C., Ren, L., and Shi, Q. (2011). "Adsorption of 2,4,6trichlorophenol from aqueous solution onto activated carbon derived from loosestrife," *Desalination* 267(2-3), 139-146. DOI: 10.1016/j.desal.2010.09.016
- Feng, J., Qiao, K., Pei, L., Lv, J., and Xie, S. (2015). "Using activated carbon prepared from *Typha orientalis* Presl to remove phenol from aqueous solutions," *Ecological Engineering* 84, 209-217. DOI: 10.1016/j.ecoleng.2015.09.028
- Feng, Y., Dionysiou, D. D., Wu, Y., Zhou, H., Xue, L., He, S., and Yang, L. (2013). "Adsorption of dyestuff from aqueous solutions through oxalic acid-modified swede rape straw: Adsorption process and disposal methodology of depleted bioadsorbents," *Bioresource Technology* 138, 191-197. DOI: 10.1016/j.biortech.2013.03.146
- Foo, K. Y., and Hameed, B. H. (2011). "Microwave assisted preparation of activated carbon from pomelo skin for the removal of anionic and cationic dyes," *Chemical Engineering Journal* 173(2), 385-390. DOI: 10.1016/j.cej.2011.07.073
- Freundlich, H. M. F. (1906). "Over the adsorption in solution," J. Phys. Chem. A 57, 385-471.

- Fu, J., Chen, Z., Wang, M., Liu, S., Zhang, J., Zhang, J., Han, R., and Xu, Q. (2015).
 "Adsorption of methylene blue by a high-efficiency adsorbent (*polydopamine microspheres*): Kinetics, isotherm, thermodynamics and mechanism analysis," *Chemical Engineering Journal* 259, 53-61. DOI: 10.1016/j.cej.2014.07.101
- Fu, J. W., Zhu, J. H., Wang, Z. W., Wang, Y. H., Wang, S. M., Yan, R. Q., and Xu, Q. (2019). "Highly-efficient and selective adsorption of anionic dyes onto hollow polymer microcapsules having a high surface-density of amino groups: Isotherms, kinetics, thermodynamics and mechanism," *Journal of Colloid and Interface Science* 542, 123-135. DOI: 10.1016/j.jcis.2019.01.131
- Fujishige, M., Yoshida, I., Toya, Y., Banba, Y., Oshida, K., Tanaka, Y., Dulyaseree, P., Wongwiriyapan, W., and Takeuchi, K. (2017). "Preparation of activated carbon from bamboo cellulose fiber and its use for EDLC electrode material," *Journal of Environmental Chemical Engineering* 5(2), 1801-1808. DOI: 10.1016/j.jece.2017.03.011
- Ghaedi, M., Ansari, A., Habibi, M. H., and Asghari, A. R. (2014). "Removal of malachite green from aqueous solution by zinc oxide nanoparticle loaded on activated carbon: Kinetics and isotherm study," *Journal of Industrial Engineering Chemistry* 20(1), 17-28. DOI: 10.1016/j.jiec.2013.04.031
- Ghaedi, M., Ghaedi, A. M., Abdi, F., Roosta, M., Vafaei, A., and Asghari, A. (2013). "Principal component analysis-adaptive neuro-fuzzy inference system modeling and genetic algorithm optimization of adsorption of methylene blue by activated carbon derived from *Pistacia khinjuk*," *Ecotoxicology and Environmental Safety* 96, 110-117. DOI: 10.1016/j.ecoenv.2013.05.015
- Ghosh, S. K., and Bandyopadhyay, A. (2017). "Adsorption of methylene blue onto citric acid treated carbonized bamboo leaves powder: Equilibrium, kinetics, thermodynamics analyses," *Journal of Molecular Liquids* 248, 413-424. DOI: 10.1016/j.molliq.2017.10.086
- Guo, J., Li, B., Liu, L., and Lv, K. (2014). "Removal of methylene blue from aqueous solutions by chemically modified bamboo," *Chemosphere* 111, 225-231. DOI: 10.1016/j.chemosphere.2014.03.118
- Gong, R., Ye, J., Dai, W., Yan, X., Hu, J., Hu, X., Li, S., and Huang, H. (2013).
 "Adsorptive removal of methyl orange and methylene blue from aqueous solution with finger-citron-residue-based activated carbon," *Industrial & Engineering Chemistry Research* 52(39), 14297-14303. DOI: 10.1021/ie402138w
- Hameed, B. H., Din, A. T. M., and Ahmad, A. L. (2007). "Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies," *Journal of Hazardous Materials* 141(3), 819-825. DOI: 10.1016/j.jhazmat.2006.07.049
- Ho, Y. S., McKay, G. (1999). "Pseudo-second order model for sorption processes," *Process Biochem.* 34(5), 451-465. DOI: 10.1016/S0032-9592(98)00112-5
- Hubbe, M.A., Azizian, S., and Douven, S. (2019). "Implications of apparent pseudosecond-order adsorption kinetics onto cellulosic materials: A review," *BioResources* 14(3), 7582-7626.
- Jiao, Y., Wan, C., and Li, J. (2016). "Synthesis of carbon fiber aerogel from natural bamboo fiber and its application as a green high-efficiency and recyclable adsorbent," *Materials & Design* 107, 26-32. DOI: 10.1016/j.matdes.2016.06.015
- Lagergren, S. (1898). "Zur Theorie der sogenannten Adsorption geloster Stoffe," *Kungliga sven. Vetenskapsakad Handl.* 24, 1-39. DOI: 10.1007/BF0150133

- Langmuir, I. (1918). "The adsorption of gases on plane surfaces of glass, mica and platinum," *J. Chem. Phys.* 40, 1361-1403. DOI: 10.1021/ja02242a004
- Li, H., An, N., Liu, G., Li, J., Liu, N., Jia, M., Zhang, W., and Yuan, X. (2016).
 "Adsorption behaviors of methyl orange dye on nitrogen-doped mesoporous carbon materials," *Journal of Colloid and Interface Science* 466, 343-351. DOI: 10.1016/j.jcis.2015.12.048
- Liu. Y., Kang, Y., Mu, B., and Wang, A. (2014). "Attapulgite/bentonite interactions for methylene blue adsorption characteristics from aqueous solution," *Chemical Engineering Journal* 237, 403-410. DOI: 10.1016/j.cej.2013.10.048
- Lorenc-Grabowska, E., Gryglewicz, G., and Diez, M. A. (2013). "Kinetics and equilibrium study of phenol adsorption on nitrogen-enriched activated carbons," *Fuel* 114, 235-243. DOI: 10.1016/j.fuel.2012.11.056
- Luo, P., Zhao, Y., Zhang, B., Liu, J., Yang, Y., and Liu, J. (2010). "Study on the adsorption of neutral red from aqueous solution onto halloysite nanotubes," *Water Research* 44(5), 1489-1497. DOI: 10.1016/j.watres.2009.10.042
- Mahida, V. P., and Patel, M. P. (2016). "Removal of some most hazardous cationic dyes using novel poly (NIPAAm/AA/N-allylisatin) nanohydrogel," *Arabian Journal of Chemistry* 9(3), 430-442. DOI: 10.1016/j.arabjc.2014.05.016
- Ni, H., Li, Y., and Fu, S. (2018). "Morphological structure and properties of bamboo shell fiber," *Journal of Natural Fibers* 15(4), 586-595. DOI: 10.1080/15440478.2017.1349710
- Peydayesh, M., and Rahbar-Kelishami, A. (2015). "Adsorption of methylene blue onto *Platanus orientalis*, leaf powder: Kinetic, equilibrium and thermodynamic studies," *Journal of Industrial and Engineering Chemistry* 21, 1014-1019. DOI: 10.1016/j.jiec.2014.05.010
- Postai, D. L., Demarchi, C. A., Zanatta, F., Melo, D. C. C., and Rodrigues, C. A. (2016). "Adsorption of rhodamine B and methylene blue dyes using waste of seeds of *Aleurites moluccana*, a low cost adsorbent," *Alexandria Engineering Journal* 55(2), 1713-1723. DOI: 10.1016/j.aej.2016.03.017
- Rangabhashiyam, S., and Selvaraju, N. (2015). "Evaluation of the biosorption potential of a novel *Caryota urens*, inflorescence waste biomass for the removal of hexavalent chromium from aqueous solutions," *Journal of the Taiwan Institute of Chemical Engineers* 47, 59-70. DOI: 10.1016/j.jtice.2014.09.034
- Ren, B., Xu, Y. I., Zhang, L. H., and Liu, Z. F. (2018). "Carbon-doped graphitic carbon nitride as environment-benign adsorbent for methylene blue adsorption: Kinetics, isotherm and thermodynamics study," *Journal of the Taiwan Institute of Chemical Engineers* 88, 114-120. DOI: 10.1016/j.jtice.2018.03.041
- Roosta, M., Ghaedi, M., Daneshfar, A., and Sahraei, R. (2014). "Experimental design based response surface methodology optimization of ultrasonic assisted adsorption of safaranin O by tin sulfide nanoparticle loaded on activated carbon," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 122, 223-231. DOI: 10.1016/j.saa.2013.10.116
- Shaibu, S. E., Adekola, F. A., Adegoke, H. I., and Ayanda, O. S. (2014). "A comparative study of the adsorption of methylene blue onto synthesized nanoscale zero-valent iron-bamboo and manganese-bamboo composites," *Materials* 7(6), 4493-4507. DOI: 10.3390/ma7064493
- Temkin, M. J., and Pyzhev, V. (1960). "Recent modifications to Langmuir isotherms," *Acta Physic. USSR* 12, 217-222.

- Tong, M., Liu, D., Yang, Q., Devautour-Vinot, S., Maurin, G., and Zhong, C. (2013).
 "Influence of framework metal ions on the dye capture behavior of MIL-100 (Fe, Cr) MOF type solids," *Journal of Material Chemistry A* 1(30), 8534-8537. DOI: 10.1039/C3TA11807J
- Wang, K., Fu, J. W., Wang, S. M., Gao, M., Zhu, J. H., Wang, Z. W., and Xu, Q. (2018). "Polydopamine-coated magnetic nanochains as efficient dye adsorbent with good recyclability and magnetic separability," *Journal of Colloid and Interface Science* 516, 263-273. DOI: 10.1016/j.jcis.2018.01.067
- Weber, W. J., and Morris, J. C. (1963). "Kinetics of adsorption on carbon from solution," J. Sani. Eng. Division 89(2), 31-60.
- Wu, Z., Zhang, L., Guan, Q., Ning, P., and Ye, D. (2014). "Preparation of α-zirconium phosphate-pillared reduced graphene oxide with increased adsorption towards methylene blue," *Chemical Engineering Journal* 258, 77-84. DOI: 10.1016/j.cej.2014.07.064
- Xiao, X., Zhang, F., Feng, Z., Deng, S., and Wang, Y. (2015). "Adsorptive removal and kinetics of methylene blue from aqueous solution using NiO/MCM-41 composite," *Physica E: Low-dimensional Systems and Nanostructures* 65, 4-12. DOI: 10.1016/j.physe.2014.08.006
- Zhang, J., Cai, D., Zhang, G., Cai, C., Zhang, C., Qiu, G., Zheng, K., and Wu, Z. (2013). "Adsorption of methylene blue from aqueous solution onto multiporous palygorskite modified by ion beam bombardment: Effect of contact time, temperature, pH and ionic strength," *Applied Clay Science* 83-84, 137-143. DOI: 10.1016/j.clay.2013.08.033
- Zhang, J. M., Zhong, Z. W., Zhu, D. P., Lin, L. M., Wang, Q. J., Tang, Q. Y., Luo, Z. M., and Ye, L. Y. (2014a). "Application of bamboo shoot shell in color removal from methylene blue solution," *Applied Mechanics and Materials* 675-677, 489-492. DOI: 10.4028/www.scientific.net/AMM.675-677.489
- Zhang, S., Wang, X., Li, J., Wen, T., Xu, J., and Wang, X. (2014b). "Efficient removal of a typical dye and Cr(VI) reduction using n-doped magnetic porous carbon," *RSC Advances* 108, 63110-63117. DOI: 10.1039/C4RA10189H
- Zhang, Y., Xing, Z., Duan, Z., Li, M., and Wang, Y. (2014c). "Effects of steam activation on the pore structure and surface chemistry of activated carbon derived from bamboo waste," *Applied Surface Science* 315, 279-286. DOI: 10.1016/j.apsusc.2014.07.126
- Zhao, Y., Fang, F., Xiao, H., Feng, Q., Xiong, L., and Fu, S. (2015). "Preparation of pore-size controllable activated carbon fibers from bamboo fibers with superior performance for xenon storage," *Chemical Engineering Journal* 270, 528-534. DOI: 10.1016/j.cej.2015.02.054

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