Brewer's Grains with Different Pretreatments Used as Bio-Adsorbents for the Removal of Congo Red Dye from Aqueous Solution

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Brewer's grains (BG), a by-product of the beer industry, were first pretreated by sulfuric acid, sodium hydroxide, and white-rot fungus *Coriolus versicolor* for the preparation of bio-adsorbents BGPH, BGPOH, and BGPB, respectively. All bio-adsorbents were rich in hydroxyl groups and could adsorb Congo red dye from aqueous solution, and BGPOH worked better than the others. The order of maximum equilibrium adsorption capacity of bio-adsorbents for Congo red was BGPOH > BGPH > BGPB. The Langmuir, Freundlich, and Temkin adsorption isotherm models all fit well with the experimental data. The negative Gibbs free energy change meant that the adsorption was spontaneous, and lower temperature was useful for the adsorption of Congo red onto the bio-adsorbents. The pseudo first-order and second-order kinetics models fit well with the experimental data, and the second-order kinetics model fit better, which indicated the adsorption was controlled by diffusion phenomena. Brewer's grains with the three pretreatments could be used as efficient adsorbents for the treatment of dye wastewater.

Keywords: Brewer's grains; Pretreatment; Bio-adsorbent; Congo red; Adsorption isotherm; Adsorption thermodynamics; Adsorption kinetics

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INTRODUCTION

Brewer's grains are the main by-product of the beer industry, with a global total of approximately 30 million tons (Mahmood *et al.* 2013). There are two main ways to deal with brewer's grains: to treat it as a waste, which leads to environmental pollution and waste of resources, or to use it as feed (Imaizumi *et al.* 2015; Bougrier *et al.* 2018; Lao *et al.* 2020). Because of the high protein and cellulose in brewer's grains, some researchers have used it in the production of flakes, whole wheat bread, biscuits, and appetizers, but the added amount of brewer's grains was very small (Hassona 1993; Ktenioudaki *et al.* 2013; McCarthy *et al.* 2013; Awolu *et al.* 2016). Brewer's grains are also used for bio-refinery and recovery of polyphenols, but there is still a technical bottleneck for large-scale application (White *et al.* 2008; Mussatto *et al.* 2013; Birsan *et al*. 2019; Rojas-Chamorro *et al.* 2020). The question remains of how to use brewer's grains in large quantities without complicated pretreatment.

Wastewater is a complex issue in the textile and printing and dyeing industries due to the application of a large number of dyes, which are difficult to degrade. The treatment of printing and dyeing wastewater includes physical adsorption, chemical degradation, and biological treatment (Katheresan *et al.* 2018; Dou *et al.* 2020; Li *et al.* 2020; Oliveira *et al.* 2020). Activated carbon adsorption has become the most commonly used method to treat the wastewater, but the cost was too high because of the expensive price of commercial activated carbon. Therefore, many new low-cost adsorbents have been developed such as hardwood, spent diatomaceous earth, fly ash, sewage sludge, orange peel, and spent mushroom substrates (Tsai *et al.* 2004; Wu *et al.* 2018; Chu *et al.* 2019; Godlewska *et al.* 2019; Wu *et al.* 2019; Ahmed *et al.* 2020; Sun *et al.* 2020).

Brewer's grains contain a high level of cellulose and lignin, and they have a porous structure, which has the potential to adsorb some pollutants effectively. Brewer's grains have been used to adsorb cadmium and lead in aqueous solution, and the maximum adsorption capacity reaches 17.3 mg/g and 35.5 mg/g, respectively (Low *et al.* 2000). Brewer's grains were also used to absorb copper and malachite green, and the adsorption results were also good (Chanzu *et al.* 2019; Wierzba *et al.* 2019). Therefore, brewer's grains may be a good adsorbent for wastewater. If brewer's grains could be fully utilized to treat large amounts of printing and dyeing wastewater, the economic and environmental pressure of the printing and dyeing industries could be relieved. However, there are only a few reports on the use of brewer's grains to adsorb dyes.

Pretreated brewer's grains are mostly used in bio-refinery, but seldom used as adsorbent (Zhang and Zang 2016; Lorente *et al.* 2019; Ashman *et al.* 2020). Congo red is a kind of acidic dye, which has been widely used in the cotton dyeing and papermaking industries. The wastewater of Congo red dye can cause cancer and pose possible risk of harm to unborn children, so the wastewater seriously endangers human health (Goswami *et al.* 2020). In this study, the brewer's grains were pretreated by dilute acid, dilute base, and white rot fungus *Coriolus versicolor* in order to prepare them for removal of Congo red dye from aqueous solution, and the adsorption isotherm, thermodynamics, and kinetics were also studied. The brewer's grains adsorbed Congo red could be bio-pretreated again by *C. versicolor* in order to degrade Congo red and reuse the brewer's grains (Wu *et al.* 2018).

EXPERIMENTAL

Preparation of Bio-adsorbents by Pretreatment of Brewer's Grains

Brewer's grains (BG), the residues from saccharification of malt, were pretreated by 0.1 mol/L sulfuric acid (analytical purity) at 121 °C for 20 min; or pretreated by 0.1 mol/L of sodium hydroxide (analytical purity) at 121 °C for 20 min; or pretreated by white-rot fungus *Coriolus versicolor,* which was deposited in the Jiangsu Key Laboratory for Eco-Agricultural Biotechnology around Hongze Lake at 28 °C for 25 days. All brewer’s grains were washed by ultrapure water 2 to 3 times and crushed into 100-mesh particles. The bio-adsorbents BGPH, BGPOH, BGPB were obtained from the brewer's grains with sulfuric acid pretreatment, with sodium hydroxide pretreatment, and with biological pretreatment, respectively.

Fourier Transform Infrared (FTIR) Spectroscopy of Bio-adsorbents

FTIR spectra were determined by Nicolet iS5 FTIR spectrometer (Thermo Scientific, Waltham, MA USA). KBr pellets were prepared with 2 mg of powdered bio-adsorbent in 40 mg of KBr for FTIR spectroscopy. Spectral measurements ranged from 400 cm^{-1} to 4000 cm^{-1} with 0.4 cm^{-1} resolution.

Batch Bio-adsorption of Congo Red

To study the effects of bio-adsorbent usage, temperature, and time on the adsorption of Congo red (99% of purity) onto bio-adsorbents, bio-adsorption was conducted in 250 mL conical flasks with 100 mL of 300 mg/L aqueous solution of Congo red. Batch bio-adsorption conditions were shown in Table 1.

Table 1. Batch Bio-adsorption Conditions

Adsorption conditions	**Level**		
	Usage of adsorbent (g)	*T* (K)	*t* (min)
Usage of adsorbent	0.1, 0.3, 0.6, 0.8, 1.0, 1.3, 1.6, 2	313	150
Adsorption temperature (*T*)	1	303, 308, 313, 318, 323, 328	150
Adsorption time (*t*)	1	313	5, 10, 15, 20, 25, 30, 45, 60, 90, 120, 150

Determination of Dye Concentration

The equilibrium suspensions were centrifuged at 7000 r/min of speed for 10 min, and the concentrations of dye were determined by a UV–vis spectrophotometer (Model 754, Shanghai Sunny Hengping Instrument Co., Ltd., Shanghai, China) with 1 cm of glass cell at 500 nm of wavelength. All data were obtained from three times replicated determinations. The adsorption rate (R%) of Congo red onto bio-adsorbent was calculated by Eq. 1, and the equilibrium adsorption capacity of bio-adsorbent for Congo red, Q_e (mg/g), was calculated by Eq. 2,

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$Q_e = (C_0 - C_e) \times \frac{V}{W} \quad (2)$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of Congo red respectively (mg/L), V is the volume of the experiment solution (0.1L), and W is the amount of bio-adsorbent (g).

Model of Adsorption Isotherm

A single molecule adsorption theoretical model known as the Langmuir model is shown as Eq. 3, and two empirical adsorption models known as the Freundlich and Temkin models are shown in Eqs. 4 and 5,

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L \times Q_m} \quad (3)$$

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (4)$$

$$Q_e = \frac{RT}{b_t} \ln C_e + \frac{RT}{b_t} \ln a_t \quad (5)$$

where C_e is the equilibrium liquid-phase concentration of Congo red (mg/ L), Q_e and Q_m are the equilibrium and maximum adsorbed capacities of Congo red per mass of bio-adsorbent respectively (mg/g), K_L is the Langmuir equilibrium adsorption constant (L/mg) related to the free energy of adsorption, K_F is the Freundlich constant [(mg/g) (L/mg)1/n] related to the strength of the adsorptive bond, 1/n is the adsorption intensity factor or surface heterogeneity, R is the molar gas constant (8.314 J.mol^{-1}.K^{-1}), T is absolute temperature (313 K), and a_t and b_t are the Temkin equilibrium adsorption constants.

Model of Adsorption Thermodynamics

The Gibbs-Helmholtz equation was used as the model of adsorption thermodynamics in Eq. 6, which could be modified as Eq. 7,

$$\Delta G = \Delta H - \Delta S \cdot T \quad (6)$$

$$\ln \frac{C_{Be}}{C_{Ae}} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (7)$$

where C_{Be} and C_{Ae} represent the equilibrium concentrations of Congo red in adsorbent and solution (mg/L), ΔG is the Gibbs free energy change (J.mol^{-1}), ΔH is the adsorption enthalpy change (J.mol^{-1}), ΔS is the adsorption entropy change (J.mol^{-1}.K^{-1}), R is the molar gas constant (8.314 J.mol^{-1}.K^{-1}), and T is absolute temperature (K).

Model of Adsorption Kinetics

The pseudo first-order (Eq. 8) and second-order kinetics (Eq. 9) (Xu *et al.* 2019) were used to evaluate the adsorption kinetics as follows,

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (8)$$

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{k_2 Q_e^2} \quad (9)$$

where Q_e and Q_t represent the adsorption capacities (mg/g) of SSGL at equilibrium and at a particular time t (min), respectively. The first-order and second-order kinetic rate constants are denoted by k_1 (1/min) and k_2 [(g/mg)(1/min)].

RESULTS AND DISCUSSION

FTIR Analysis of Bio-adsorbents

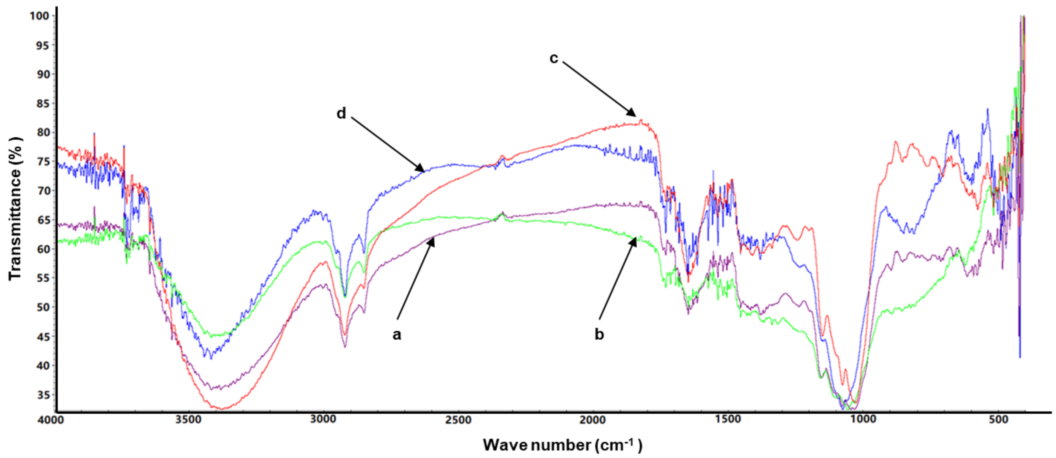

Fig. 1. Fourier transform infrared spectroscopy (FTIR) of bio-adsorbents. Color lines **a**, **b**, and **c** represent that of brewer's grains pretreated by dilute sodium hydroxide (BGPOH), dilute sulfuric acid (BGPH), and white-rot fungus (BGPB); Line **d** represents that of brewer's grains without pretreatment (BG)

The differences in chemical bonds among the adsorbents could be clearly found by FTIR of BG, BGPH, BGPOH, and BGPB which are shown in Fig. 1. They were rich of hydroxyl groups (3400 cm^{-1} band) in BG, which may have been caused by the stretching vibration of the C-OH bond in cellulose and hemicellulose of BG. The peak at 2926 cm^{-1} was caused by the asymmetric stretching vibration of CH_3, and the peaks at 1730 cm^{-1} and 1638 cm^{-1} were from the characteristic stretching vibration of the C=O bond in the carboxyl group or the aldehyde and ketone groups. The stretching vibration of the benzene ring skeleton appeared near 1541 cm^{-1}. The peaks at 1160 and 1081cm^{-1} were mainly attributed to the stretching vibrations of the -Si-O-Cellulose and -Si-O-Si- bonds respectively (Azlinda *et al.* 2016).

When brewer's grains were pretreated by dilute sulphuric acid, the contents of the hydroxyl group and methyl group in BGPH were decreased significantly, which indicated hemicellulose in brewer's grains could be hydrolyzed. However, when brewer's grains were pretreated by sodium hydroxide, the stretching vibration of the benzene ring skeleton in BGPOH was weakened, which indicated the lignin in brewer's grains could be degraded by sodium hydroxide. In addition, when brewer's grains were pretreated by white-rot fungus *Coriolus versicolor*, the stretching vibration of the hydroxyl group in BGPB were enhanced, but the stretching vibration of the benzene ring skeleton was weakened. This indicated that the lignin in brewer's grains was degraded and led to the exposure of cellulose, and the polysaccharide, rich in hydroxyl, which was also produced during biological pretreatment (Wang *et al.* 2019).

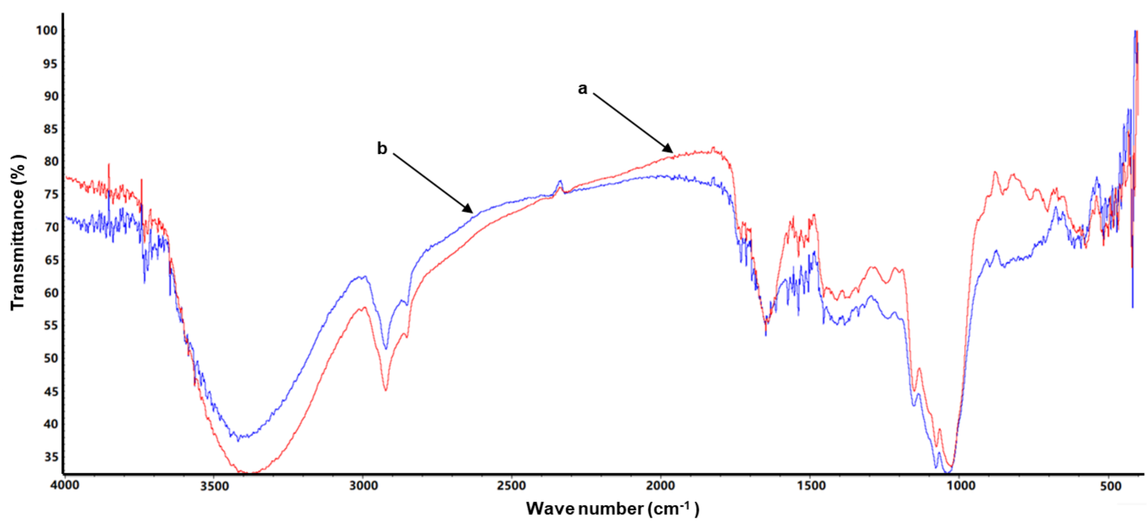

Fig. 2. Fourier transform infrared spectroscopy (FTIR) of BGPB. Line **a** represents that of BGPB; line **b** represents that of BGPB after adsorbing Congo red

Congo red, a kind of acidic dye, was adsorbed in aqueous solution by BGPH, BGPOH, and BGPB, which decreased the concentration of Congo red significantly. The FTIR of the bio-adsorbents with Congo red was also determined, and the FTIR of BGPB with Congo red was shown in Fig. 2. The stretching vibration of the benzene ring was enhanced significantly, which indicated that Congo red should be indeed adsorbed onto the adsorbent as Congo red is rich of benzene ring structure. Because the chemical structure of Congo red contains two molecules of amino groups, which may produce hydrogen bond with the hydroxyl groups on the adsorbents and could have led to the adsorption of Congo red by the adsorbents.

Adsorption of Congo Red by Bio-adsorbents

When the concentration of Congo red was 300 mg/L, the adsorption levels of Congo red onto BGPH, BGPOH, and BGPB increased with the increase of the usage of bio-adsorbents (ranged from 0.1g to 2g), which was shown in Fig. 3a. Especially when the dosages were only 0.1 g, the adsorption reached more than 50%. Further increasing the usages of bio-adsorbents increased the adsorption extents slowly. The equilibrium adsorption capacity (Q_e) of bio-adsorbents for Congo red decreased with the increased usage of bio-adsorbents, as shown in Fig. 3b. The Q_e of adsorbents was quite different at low dosage of bio-adsorbents, and the order for the Q_e of bio-adsorbents was BGPOH > BGPH > BGPB. When the dosage was more than 1.2 g, there was no significant difference among the bio-adsorbents. Therefore, brewer's grains with pretreatments could be used as bio-adsorbents for the removal of Congo red in aqueous solution.

Alkali pretreatment could degrade lignin and make the brewer's grains have a more porous structure, which was more conducive to the adsorption of Congo red onto BGPOH. However, when the pretreatment time of sodium hydroxide was further extended to 2 hours, it was found that the adsorption rate of BGPOH for Congo red was greatly decreased. So, the excessive degradation of lignin in the brewer's grains was not conducive to the adsorption of Congo red. In addition, biological pretreatment could also lead to the degradation and removal of lignin and the porous structure, but it also produced polysaccharides at the same time, which reduced the adsorption of Congo red onto the adsorbent.

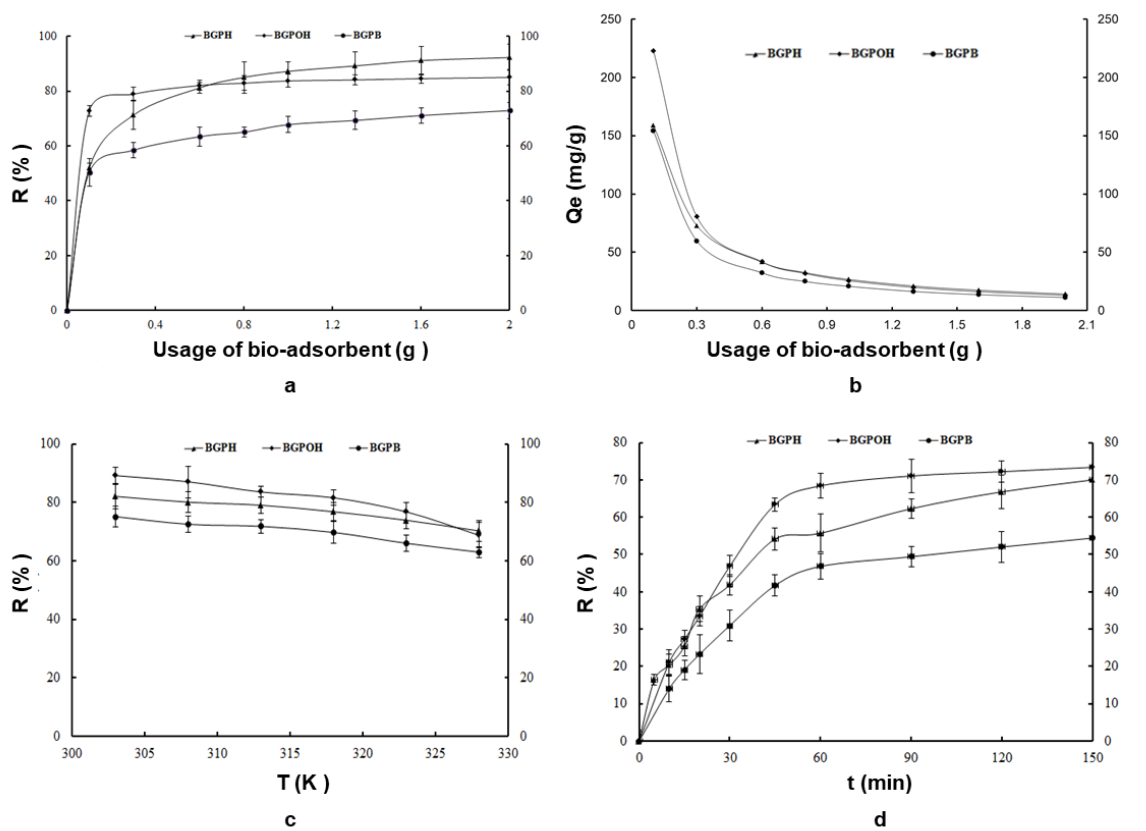

Fig. 3. Effects of usage of bio-adsorbent (a and b), adsorption temperature (c) and time (d) on the adsorption of Congo red dye onto the bio-adsorbents.

As shown in Fig. 3c, increasing the adsorption temperature decreased the adsorption rate of Congo red continually, which indicated that high temperature was not conducive to the adsorption of Congo red onto the bio-adsorbents. It was speculated that the adsorption of Congo red onto bio-adsorbents belonged to physical adsorption, and low temperature would be the better choice to adsorb Congo red using the three bio-adsorbents. Adsorption rates of Congo red increased with increased adsorption time as shown in Fig. 3d. The adsorption rates of Congo red all exceeded 45% during the initial sixty minutes, and then the increased slowly until 150 minutes. Because the time of physical adsorption was relatively short and the time of chemical adsorption was relatively long, along with the observation that high temperature was not conducive to the adsorption of Congo red, it was speculated that the adsorption process of Congo red could be a mixed adsorption process including physical adsorption and chemical adsorption.

From the above adsorption results, the brewer's grains with different pretreatments could all be used as efficient bio-adsorbents for the removal of Congo red in aqueous solutions, and the bio-adsorbent BGPOH should be better.

Analysis of Adsorption Isotherm, Thermodynamics, and Kinetics

The Langmuir, Freundlich, and Temkin models were used to analyze the adsorption isotherm (Araújo *et al*. 2018). The values of (C_e / Q_e) were plotted against C_e in the Langmuir model as shown in Fig. 4a, the values of lnQ_e were plotted against lnC_e in the Freundlich model as shown in Fig. 4b, and the values of Q_e were plotted against lnC_e in Temkin model as shown in Fig. 4c.

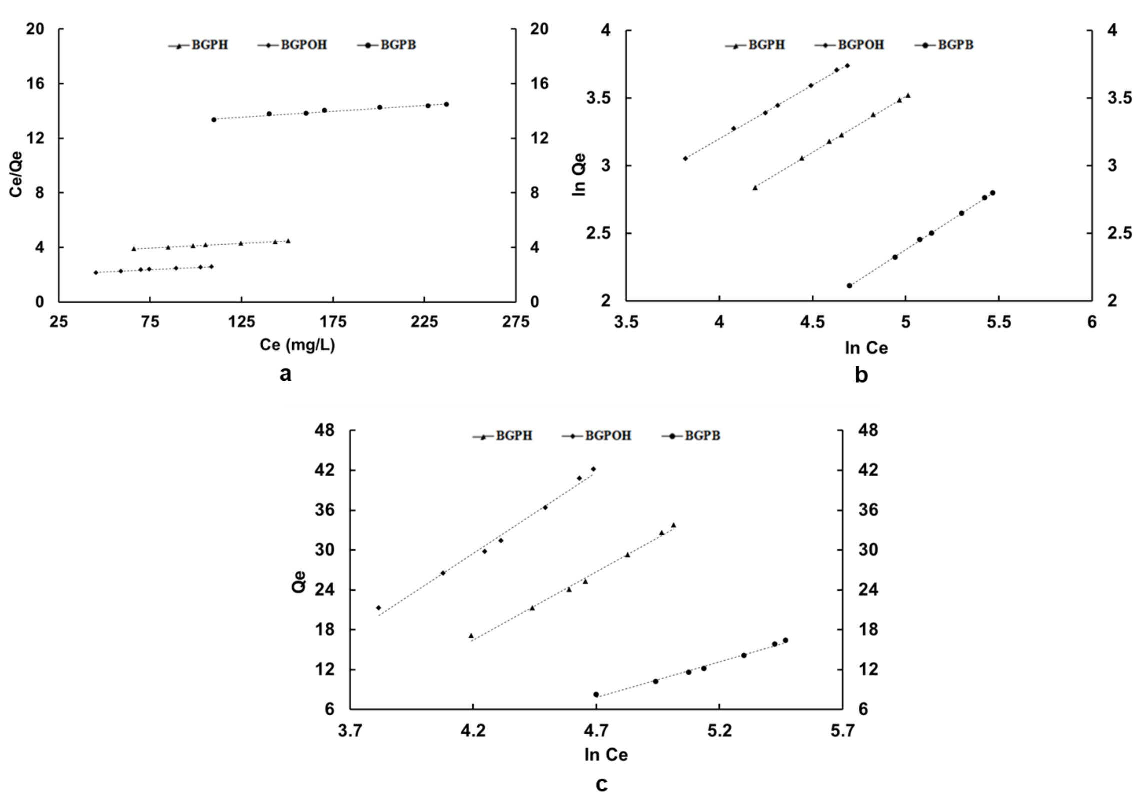

Fig. 4. Plots of Langmuir isotherms (a), Freundlich isotherms (b), and Temkin isotherms (c). The dashed lines were the linearized Langmuir, Freundlich, and Temkin models.

The values of K_L, Q_m, n, K_F, a_t, and b_t were calculated as shown in Table 2 using the slope and intercept of the trend fit lines, respectively. The regression coefficients (R^2) values were used to evaluate the fits of the Langmuir, Freundlich, and Temkin isotherm models to the experimental data.

Table 2. Coefficients of Langmuir, Freundlich, and Temkin Models Fitting for the Adsorption of Congo Red onto Bio-Adsorbents

Bio-adsorbent	Langmuir model				Freundlich model				Temkin model		
	Q_m×10^{-2} (mg/g)	K_L×10^3 (L/mg)	R^2		n	K_F (mg/g) (L/mg)$^{1/n}$	R^2		a_t×10^2	b_t×10^{-2}	R^2
BGPOH	1.49	3.09	0.980		1.27	1.042	0.999		5.03	1.07	0.989
BGPH	1.47	1.98	0.996		1.21	0.530	0.999		3.34	1.27	0.993
BGPB	1.17	0.68	0.965		1.12	0.122	0.999		1.88	2.42	0.988

As shown in Table 2, the maximum adsorption capacities (Q_m) of Congo red onto BGPOH, BGPH, and BGPB obtained from the Langmuir model were 149 mg/g, 147 mg/g, and 117 mg/g, respectively, which indicated that the bio-adsorbents had good adsorption on Congo red, and BGPOH was the best bio-adsorbent. Values of "*n*" obtained from the Freundlich model were all above 1, which indicated that there should be a potential good adsorption of Congo red onto the bio-adsorbents. Based on the alignment of the experimental data with the model lines in Fig. 4a, 4b, and 4c, together with the R^2 in Table 2, the adsorption data of Congo red onto BGPOH, BGPH, and BGPB all fit well with the Langmuir, Freundlich, and Temkin models, and the adsorption of Congo red could take place mainly on the monolayer surface of the bio-adsorbent.

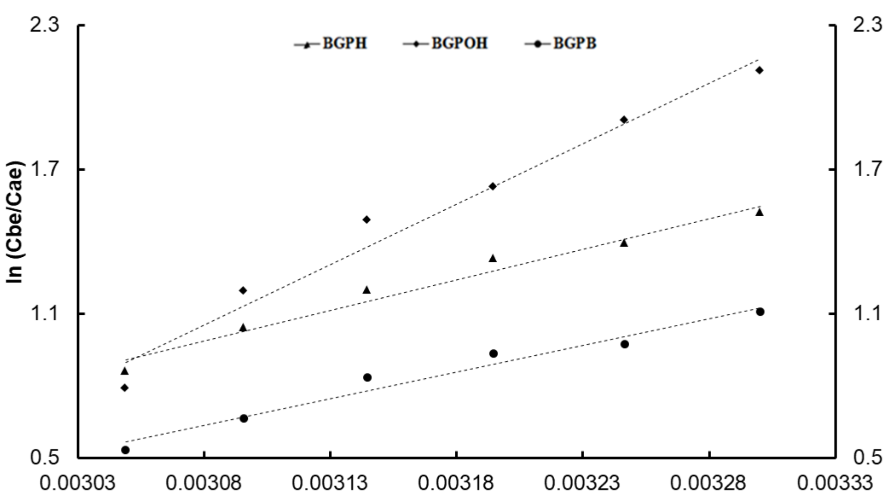

Fig. 5. Plots of adsorption thermodynamics. The dashed lines correspond to the linearized adsorption thermodynamics model

Table 3. Enthalpy and Entropy Changes of Adsorption Thermodynamics Fitting for the Adsorption of Congo Red Onto Bio-Adsorbents

Bio-adsorbent	Δ*H* ×10^{-4} (J.mol^{-1})	Δ*S* ×10^{-1} (J.mol^{-1}.K^{-1})	R^2
BGPOH	-4.17	-11.98	0.974
BGPH	-2.11	-5.69	0.973
BGPB	-1.83	-5.12	0.965

Table 4. Gibbs Free Energy Change of Adsorption of Congo Red onto Bio-Adsorbents at Different Temperatures

Bio-adsorbent	Δ*G* ×10^{-3} (J.mol^{-1})					
	303 K	308 K	313 K	318 K	323 K	328 K
BGPOH	-5.44	-4.84	-4.25	-3.65	-3.05	-2.48
BGPH	-3.90	-3.61	-3.33	-3.04	-2.76	-2.47
BGPB	-2.83	-2.57	-2.32	-2.06	-1.80	-1.55

The adsorption thermodynamics were analyzed by plotting ln (C_{Be} / C_{Ae}) against temperature (T) as shown in Fig. 5, and the values of Δ*H*, Δ*S*, and R^2 are shown in Table 3. The R^2 values of the adsorption thermodynamics model of Congo red onto the bio-adsorbents all exceeded 0.965, which indicated that the model was suitable for the adsorption of Congo red onto the bio-adsorbents. Based on the values of Δ*H* and Δ*S*, the Gibbs free energy change (Δ*G*) was calculated as shown in Table 4. The value of Δ*G* was always negative within the experimental temperature range from 303 K to 328 K, which indicated that the adsorption was spontaneous (Roy and Mondal 2019). The absolute values of the Δ*G* of adsorption for Congo red onto BGPOH were all higher than that of BGPH and BGPB at the same temperature, which indicated that BGPOH could be more easily able to adsorb Congo red dye. The absolute values of Δ*G* decreased when temperature increased, which further indicated that lower temperature was useful for the adsorption of Congo red dye.

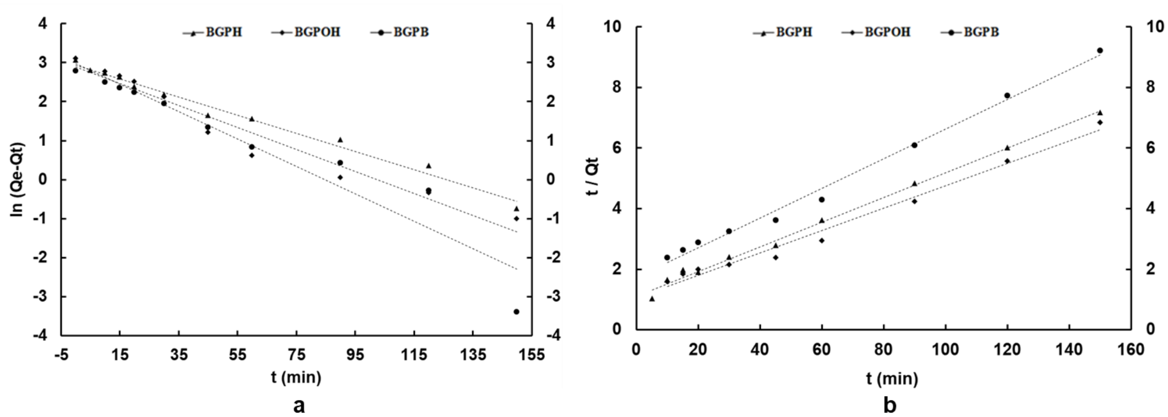

Fig. 6. Plots of first-order (a) and second-order (b) kinetics for Congo red adsorption onto bio-adsorbents. The dashed lines are the linearized first-order and second-order kinetics models.

Table 5. Coefficients of the First and Second Order Kinetic Models Fitted for the Adsorption of Congo Red onto Bio-adsorbents

Bio-adsorbent	First order kinetic model				Second order kinetic model		
	Qe×10^{-1} (mg/g)	k_1×10^2 (1/min)	R^2		Qe×10^{-1} (mg/g)	k_2×10^3 (g/mg)(1/min)	R^2
BGPOH	1.81	2.83	0.954		2.70	1.29	0.984
BGPH	1.89	2.33	0.985		2.46	1.49	0.995
BGPB	1.96	3.51	0.918		2.04	1.39	0.992

Adsorption kinetics can be evaluated by pseudo first-order and second-order kinetics models (Munagapati and Kim 2017). The values of ln(Q_e–Q_t) were plotted against time (t) in a pseudo first order kinetic model, as shown in Fig. 6a, and the values of t/Q_t were plotted against time (t) in a pseudo second order kinetic model as shown in Fig. 6b. The values of k_1, k_2, and Q_e are shown in Table 5. Based on the alignment of the experimental data with the model lines in Fig. 6a and 6b, together with the R^2 in Table 5, the adsorption data of Congo red onto BGPOH, BGPH, and BGPB all fit well with the pseudo first-order and second-order kinetics models, but the second-order kinetics model fit better with an R^2 of 0.984, 0.995, and 0.992, as compared to the first-order kinetics model with an R^2 of 0.954, 0.985, and 0.918, respectively. This indicated that the second-order kinetics model could be more suitable to describe the adsorption kinetics of Congo red onto the bio-adsorbents, and the adsorption of Congo red onto the adsorbents was controlled by diffusion phenomena (Hubbe *et al.* 2019).

CONCLUSIONS

1. Brewer's grains (BG), pretreated by sulfuric acid, sodium hydroxide, and white-rot fungus could be used as bio-adsorbents BGPH, BGPOH, and BGPB, respectively. The 3 adsorbents were rich in hydroxyl groups and could adsorb Congo red dye from aqueous solution, and BGPOH worked better than the others.
2. The Langmuir, Freundlich and Temkin models fit all well with the experimental data. The negative Gibbs free energy change meant the adsorption was spontaneous, and lower temperature was conducive for the adsorption.
3. The pseudo-second-order kinetics model fit with the experimental data better than the pseudo first-order model, indicating that the adsorption was controlled by diffusion phenomena.

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