

# Removal of the Pesticide Pymetrozine from Aqueous Solution by Biochar Produced from Brewer's Spent Grain at Different Pyrolytic Temperatures

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Biochar (BC) produced from brewer's spent grain (BSG) *via* slow pyrolysis at 300, 400, 500, 600, and 700 °C was characterized and investigated as an adsorbent for the removal of the pesticide pymetrozine from aqueous solution. Batch BSG BCs adsorption experiments were carried out under various conditions (such as pH, pymetrozine concentration, and BC dosage) to adsorb the pymetrozine. The BSG BCs adsorption pymetrozine capacities were increased by 21.4% to 55.5% under pyrolysis temperatures of 300, 400, 500, and 600 °C compared to 700 °C with a pyrolysis time of 2 h and by 19.0% to 52.1% at 4 h. At solution pH values of 2, 4, 6, and 8, the adsorption capacities were increased by 9.6% to 39.5% compared with that at pH 10. A similar adsorption tendency was found for the different BCs dosage. In the first 60 min, BC absorbed 70% to 80% pymetrozine. The Langmuir and Freundlich model were highly correlated with BC adsorption. The magnitude of free energy decreased by 32.2% to 47.3% with increasing temperature. The value of the enthalpy change showed the adsorption to be endothermic. The BSG BC had high efficiency in adsorbing pymetrozine and had great potential to prevent the water pollution and reuse the waste of the beer factory.

*Keywords:* Biochar; Pymetrozine; Brewer's spent grain; Contaminants removal; Adsorption

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## INTRODUCTION

Brewer's spent grain (BSG) is one of the most abundant by-products generated by the brewing industry. There are no efficient ways to use BSG based on current technologies, and approximately 30 million tons of BSG is produced *per annum* worldwide (Niemi *et al.* 2012). Thus, BSG is a low-cost material produced throughout the year. Presently, the primary application of BSG has been chiefly tied to animal feeding, favorably combined with green manure or maize silage with a low degradation rate of raw protein in rumen; however, its use has been limited (Santos *et al.* 2003). There is a new approach to using wet BSG as a feedstock for carbonization, whereby biomass is converted into carbonaceous materials, namely biochar (BC) (Baccile *et al.* 2009). Cui *et al.* (2013) also found that four kinds of BCs (bush-, wheat straw-, peanut-, and corn-derived BCs) were highly efficient in adsorbing the Pymetrozine. Poerschmann *et al.* (2014) showed that the BC had a significant sorption rate for functionalized, hydrophilic organic compounds, as well as inorganic species. Therefore, it makes sense, from a manufacturing standpoint, to use BSG as a source for BC.

Biochar is a recalcitrant organic carbon compound that is produced by pyrolysis of biomass under low oxygen concentrations (Yang and Sheng 2003; Chen *et al.* 2008).

Biochar has an abundance of polar functional groups, such as carboxylic, hydroxyl, and amino groups which are favorable for pollutant removal, and has been recognized as a useful amendment for improving plant growth environments (Lehmann and Joseph 2009; Uchimiya *et al.* 2010; Woolf *et al.* 2010; Lehmann *et al.* 2011). In recent years, the adsorption capability of BC has received extensive attention due to its wide availability, low cost, and favorable surface characteristics. Chen *et al.* (2008) reported that pine needle-derived BC effectively adsorbed naphthalene, nitrobenzene, and *m*-dinitrobenzene and can be used as an environmentally engineered adsorbent for the removal of aqueous organic contaminants. In the research of Cao *et al.* (2009), dairy manure BC could effectively remove lead and atrazine simultaneously. Straw-based BC was recognized as a substitute for activated carbon to remove reactive brilliant blue and rhodamine B (Qiu *et al.* 2009). Wheat straw BC has a great sorption capacity for hexachlorobenzene, and its application in soil significantly decreased the dissipation and volatilization of hexachlorobenzene and reduced bioavailability, even for low BC application rates (Song *et al.* 2012).

The constant increase in agricultural production promotes an equivalent increase in the level of insecticide residues in water and soil. To date, the percolation of pesticide waste into groundwater tables and aquifer systems remains an issue with respect to public health and food chain interference (Foo and Hameed 2010). Pymetrozine, 4,5-dihydro-6-methyl-4-(3-pyridylmethylene-amino)-1,2,4-triazin-3(2H)-one (IUPAC), a pyridine azomethine compound, is the first and only substance in the azomethine pyridine group. It is a novel insecticide developed by Novartis Crop Protection, Inc (Canada) with selective activity against homopteran insects (Li *et al.* 2011), and is one of the potential insecticides to replace organophosphates (Nicholson *et al.* 1995). The degradation dynamics of pymetrozine residue in broccoli fields, rice fields, and honey bee ecosystems has been reported previously (Shen *et al.* 2009; Li *et al.* 2011; Abramson *et al.* 2012), but little research has been conducted concerning the elimination of pymetrozine from contaminated solutions. Moreover, the United States Environmental Protection Agency (USEPA) has recently classified pymetrozine as a “likely” human carcinogen (EPA 2000).

The objective of this study was to elucidate the potential of BC prepared from brewer's spent grain, a waste biomass, at different pyrolytic temperatures for the adsorption removal of pymetrozine in solution. The influence of solution pH value, temperature, contact time, particle size, and initial concentration was investigated. Kinetics, isotherms, and thermodynamics of the adsorption process were also evaluated.

## EXPERIMENTAL

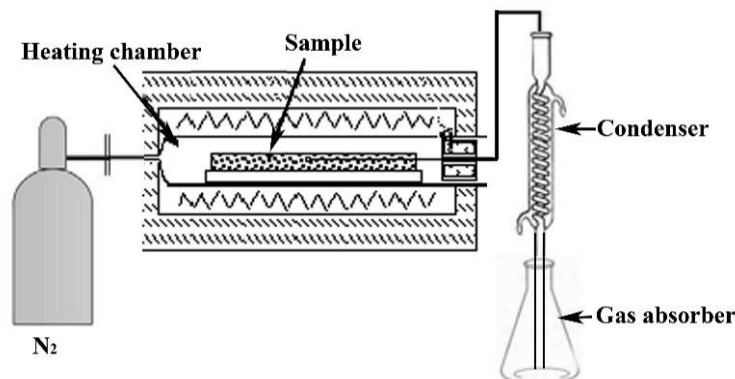
### Materials

#### *Preparation of the Biochar*

The sample of BSG was taken from a factory located in the city of Yancheng, Jiangsu Province, China, and stored at 4 °C until use. Microorganisms in the BSG wastes were killed with a high-pressure steam sterilization, and the BSG was air dried in an oven to prevent decay. When the BSG dried, it was broken in a crusher and passed through a 2-mm sieve.

The BSG BC was produced in a vacuum tube furnace (NBD-O1200, Nobody Materials Science and Technology Co., Ltd.; Henan, China) under a nitrogen atmosphere. An internal quartz tube with an inner diameter of 34.5 mm separates the reaction chamber from the furnace. The samples, with an initial mass of 1 to 5 g, were centrally placed inside the tube. The N<sub>2</sub> flow through the reaction chamber was kept constant at 0.125 MPa (Fig.

1). A linear heating program, with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ , was chosen to heat the samples from room temperature to target temperature in the range of 300 to 700  $^{\circ}\text{C}$ . Temperature was kept constant at the target temperature for 2 h or 4 h to ensure complete pyrolysis. When it was over, the  $\text{N}_2$  was kept flowing until the BC had cooled to room temperature.



**Fig. 1.** Brewer's spent grain (BSG) BC production system

Then, the BC was crushed, ground, passed through 0.83 to 0.15 mm sieves, and analyzed for its basic chemical properties using procedures as Lu (2000) described. The basic properties of different types of BC are listed in Table 1.

**Table 1.** Basic Properties of BC

BCs	pH (H <sub>2</sub> O)	Organic carbon (g kg <sup>-1</sup> )	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Total N (g kg <sup>-1</sup> )	Total P (g kg <sup>-1</sup> )	Total K (g kg <sup>-1</sup> )	CEC (cmol kg <sup>-1</sup> )
300 $^{\circ}\text{C}$	10.25	569.3	5.86	21.15	15.34	21.52	18.46
400 $^{\circ}\text{C}$	10.50	551.6	5.64	20.65	15.42	22.43	19.24
500 $^{\circ}\text{C}$	10.89	489.4	7.35	18.01	16.01	19.56	18.77
600 $^{\circ}\text{C}$	11.50	432.6	10.58	10.52	14.25	25.63	22.31
700 $^{\circ}\text{C}$	12.01	379.2	24.74	9.45	16.54	30.21	30.41

#### *Pymetrozine preparation and characterization*

Pymetrozine was provided by Jiangsu Academy of Agricultural Sciences, Nanjing, China, with a purity of 97%. The chemical name of pymetrozine is (E)-4, 5-dihydro-6-methyl-4-[(3-pyridinylmethylene)amino]-1, 2, 4-triazin-3(2H)-one, and the molecular formula is  $\text{C}_{10}\text{H}_{11}\text{N}_5\text{O}$ . It is composed of colorless crystals, with melting point 217  $^{\circ}\text{C}$ , density (20  $^{\circ}\text{C}$ ) of 1.36, and solubility in water 0.29 g L<sup>-1</sup> (25  $^{\circ}\text{C}$ ). Stock solutions of pymetrozine (200 mg L<sup>-1</sup>) were prepared daily in 30% ethanol solution and kept in the dark at 4  $^{\circ}\text{C}$ . Working solutions were prepared by diluting the stock solution to give the final concentration of pymetrozine in a range of 2 to 40 mg L<sup>-1</sup>. All solutions were protected from light and used within 3 to 6 h to avoid possible decomposition.

## **Methods**

### *Batch adsorption experiments*

The pymetrozine adsorption experiments were performed using a batch equilibration technique. A stock solution of 200 mg L<sup>-1</sup> pymetrozine was prepared by

dissolving 97% pymetrozine in deionized water. To determine the most appropriate pH, adsorption time, and most efficient dosage of the adsorbent, preliminary experiments were done at room temperature (25 °C) with BC dosages of 0.1 to 5 g, particle size of 0.15-0.83 mm, at pH of 2 to 10. Briefly, 0.1 to 1 g BC was transferred into 100 mL transparent plastic bottles. To the bottles, 50 mL of 10 mg L<sup>-1</sup> pymetrozine and BC was added and the pH adjusted using 0.1 N NaOH/HCl solutions and the bottles tightly sealed. All the bottles including controls were transferred into a water bath shaker to equilibrate for 2 h at a reciprocating shaker speed of 180 rpm. At the end of 2 h, the bottle contents were filtered through a 0.45 µm cellulose acetate membrane and from the filtrate the residual amount of pymetrozine in solution was determined colorimetrically using UV spectrophotometer (TU-1901, Persee, Beijing Purkinje General Instrument Co., Ltd, China).

Similar to batch tests, Adsorption kinetics experiments were done using 0.1 g BC in 50 mL of solution. The sorption was investigated at three initial concentrations *i.e.*, 8, 10, 20, and 40 mg L<sup>-1</sup> at a temperature of 298K, 308 K, 318K and contact time ranging from 10 min to 480 min. At predetermined time intervals the samples were taken out and the residual pymetrozine concentrations were determined spectrophotometrically. Blanks filled with pymetrozine solutions, but without BC, were also tested to assess losses of solutes to reactor components during sorption tests. The maximum pymetrozine losses in these blank samples were less than 3% during the experiments, so the missing pymetrozine from the solution phase can be safely considered to be adsorbed into the BC phase. Langmuir and Freundlich models were used to evaluate and compare the adsorption capacities of pymetrozine by BC (Liu *et al.* 2010). The equations for the Langmuir and Freundlich models for adsorption of pymetrozine can be expressed by Eqs. 1 and 2, respectively,

$$Q_e = \frac{C_e \times K_1 \times X_{max}}{1 + C_e + K_1} \quad (1)$$

$$\ln(Q_e) = \ln K_2 + \left(\frac{1}{n}\right) \times \ln(C_e) \quad (2)$$

where  $Q_e$  is the amount of pymetrozine adsorbed *per* unit weight of BC (mg g<sup>-1</sup>),  $C_e$  is the pymetrozine concentration equilibrium of the solution (mg L<sup>-1</sup>),  $X_{max}$  is the maximum adsorption capacity (mg g<sup>-1</sup>),  $K_1$  and  $K_2$  are constants related to the affinity, and  $n$  is an empirical constant. The temperature effect was assessed by equilibrating BC solution containing pymetrozine on a shaker at 25, 35, and 45 °C.

In order to understand the thermodynamic phenomena of pymetrozine adsorption onto the BC, sorption data at a temperature range of 25 to 45 °C were collected after 2 h equilibration time. From the equilibrium data, four parameters—free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), entropy change ( $\Delta S^\circ$ ), and thermodynamics constant—were calculated to confirm the nature of the adsorption process. The thermodynamics of the adsorption processes were estimated using Eqs. 3, 4, and 5,

$$K_e = Q_e / C_e \quad (3)$$

$$\Delta G^\circ = -RT \ln K_e \quad (4)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (5)$$

where  $Q_e$  ( $\text{mg g}^{-1}$ ) is the amount of pymetrozine adsorbed onto the BC from the solution at equilibrium,  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of pymetrozine in the solution,  $R$  is the gas constant ( $8.314 \text{ J (mol K)}^{-1}$ ),  $T$  (K) is the absolute temperature, and  $K_e$  ( $\text{L g}^{-1}$ ) is the adsorption equilibrium constant. By plotting  $\ln K_e$  against  $1/T$ , the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be estimated from the slopes and intercepts, and the values of  $\Delta G^\circ$  can be obtained from the corresponding values of  $\Delta H^\circ$  and  $\Delta S^\circ$  (Liu *et al.* 2009; Yan *et al.* 2010).

### Statistical analysis

All data are expressed as means plus or minus one standard deviation. Differences between the treatments were examined using a two-way analysis of variance (ANOVA), and considered significant when  $p < 0.05$ . All statistical analyses were carried out using SPSS, version 20.0 (SPSS Institute, USA, 2011).

## RESULTS

### Characterization of BC FTIR

The FTIR analysis (Fig. 2) showed that BSG BC had low intensity bands. The intensity in the range  $3600$  to  $3000 \text{ cm}^{-1}$  could be attributed to stretching of hydroxyl (O-H) functional groups due to dehydration of the BSG. The observed peaks in the  $2923 \text{ cm}^{-1}$  could be attributed to aliphatic methyl and methylene groups, especially for  $500^\circ\text{C}$ . The peaks between  $1000$  and  $400 \text{ cm}^{-1}$  indicated C-H stretching within the aromatic rings, and the peak height decreased with temperature increase. The bands in the range of  $2000$  to  $1000 \text{ cm}^{-1}$  indicated that the BC residues uncompleted pyrolysis and produced various oxygen containing species such as  $\text{CO}_3^{-2}$ ,  $\text{PO}_4^{-3}$ , *etc.* The peak at  $1567$  to  $1617 \text{ cm}^{-1}$  was attributed to high aromaticity and corresponded to presence of alkyl and alkene groups (C-H, C-C and C=C) from the stretching of aromatic rings.

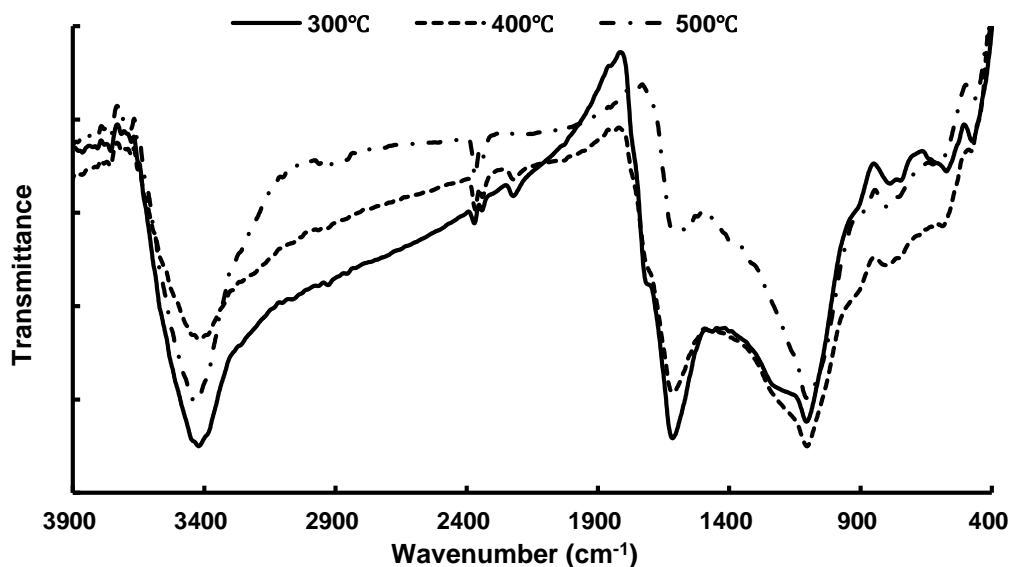


Fig. 2. FTIR spectra of BSG BC at  $300^\circ\text{C}$ ,  $400^\circ\text{C}$ , and  $500^\circ\text{C}$  pyrolysis temperature

### Effects of Pyrolysis Time, Temperature, and Particle Size on Biochar Adsorption of Pymetrozine

The BSG pyrolysis temperature, time, and particle size had significant effects on BC adsorption of pymetrozine (Fig. 3a, b,  $p < 0.05$ ). The adsorption capacities increased by 49.6%, 55.5%, 44.8%, and 21.4% after 2 h of pyrolysis and by 42.5%, 52.1%, 43.0%, and 19.0% after 4 h of pyrolysis for temperatures of 300, 400, 500, and 600 °C compared to that obtained after pyrolysis at 700 °C. The adsorption capacity increased by 9.2% to 17.9% after 4 h compared to that after 2 h. The adsorption capacities increased by 14.7%, 28.2% of particle size in 0.25 to 0.15 mm and <0.15 mm compared to 0.83 to 0.25.

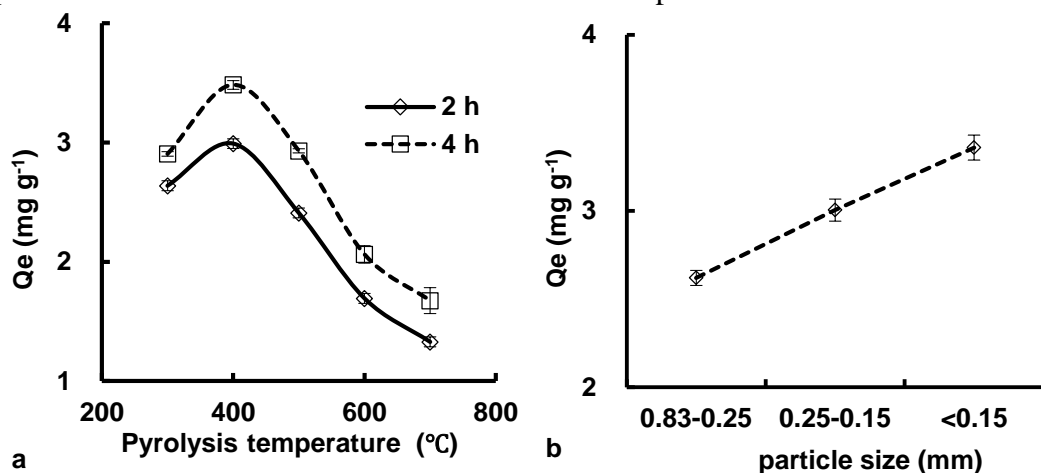


Fig. 3. Effect of pyrolysis time, temperature and particle size on the pymetrozine adsorption capacity of BC. Data presented as the mean  $\pm$  standard deviation

### Effect of Solution pH and BC Dosage

The effects of pH and dosage on BC adsorption of pymetrozine are shown in Fig. 3. The adsorption capacities increased by 9.6%, 39.5%, 25.0%, and 0.5% at solution pH values 2, 4, 6, and 8 compared with that obtained at pH 10 (Fig. 4a). The efficiency rate of BC to remove pymetrozine increased by more than 74%. The adsorption capacity increase scope was slow with dosages greater than 0.1 g 50 mL<sup>-1</sup> (Fig. 4b).

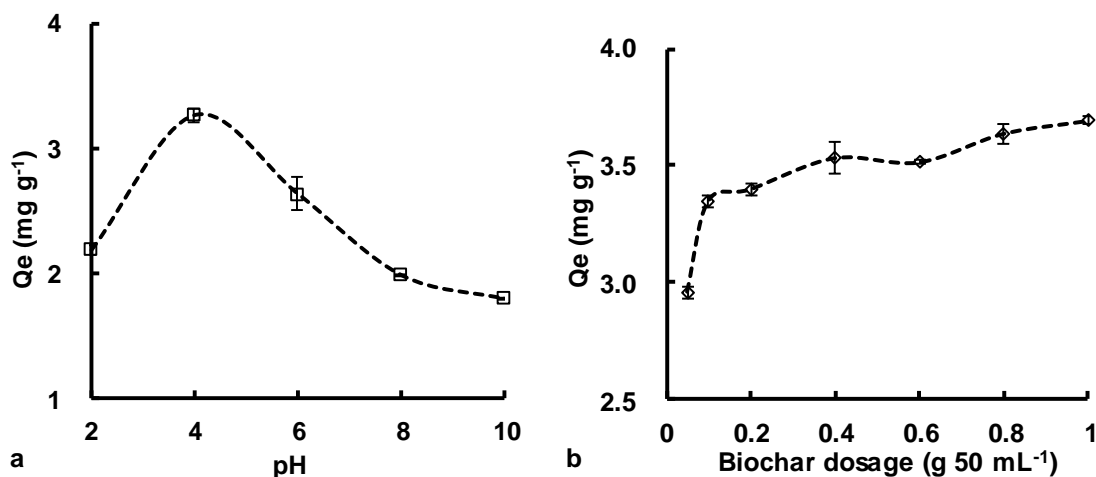
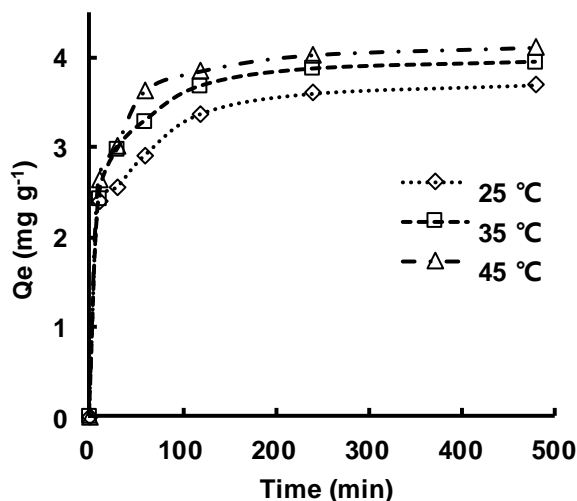


Fig. 4. Effect of (a) pH and (b) BC dosage on the pymetrozine adsorption capacity of BC (pyrolysis time = 4 h). Data presented as the mean  $\pm$  standard deviation

## Adsorption Kinetics

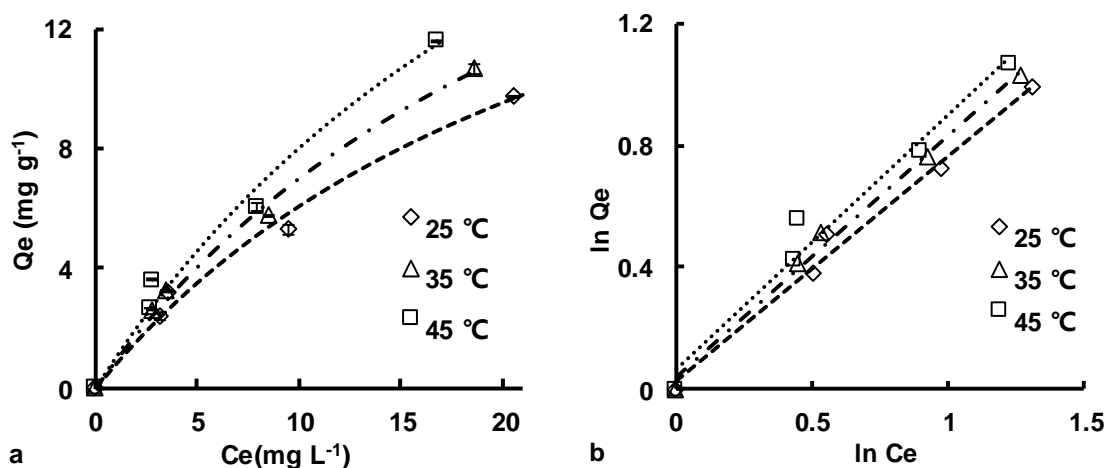
The effects of contact time on pymetrozine adsorption of BC are shown in Fig. 5. The rate of pymetrozine adsorption was fast, with 70 to 80% of the ultimate adsorption occurring in the first 60 min, followed by a slow approach to equilibrium. The pymetrozine adsorption capacities increased by approximately 4% to 7% with a 10 °C increase. The BSG BC, similar to other BC as Cui (2013) described, showed an increasing ability to adsorb pymetrozine with increasing temperature, and the process was endothermic.



**Fig. 5.** Effect of contact time on the pymetrozine adsorption capacity of BC at various temperatures

## Adsorption Isotherms

Pymetrozine adsorption isotherms were studied at different initial pymetrozine concentrations, ranging from 8 to 40 mg L<sup>-1</sup> (Figs. 6a, b). The maximum adsorption capacity of BC for pymetrozine significantly ( $p < 0.05$ ) increased by 18.2% at 35 °C and 43.5% at 45 °C, compared to that at 25 °C. The experimental data was fit with the Langmuir equation ( $r = 0.9945, 0.9975, \text{ and } 0.9925$ ) and the Freundlich model ( $r = 0.9944, 0.9956, \text{ and } 0.9850$ ) at 25, 35, and 45 °C, respectively (Table 2). The data clearly show that adsorption of pymetrozine onto BC was affected by temperature.



**Fig. 6.** Sorption of pymetrozine by BC with (a) the Langmuir model and (b) the Freundlich model. Data presented as the mean  $\pm$  standard deviation

**Table 2.** Parameters of Langmuir and Freundlich Models at Different Temperatures

	T (°C)	Langmuir			Freundlich		
		K1	Xmax	r	K2	n	r
BSG BC	25	0.038	22.020	0.9945	1.058	1.351	0.9944
	35	0.037	26.032	0.9975	1.094	1.261	0.9956
	45	0.034	31.606	0.9925	1.158	1.200	0.9850

### Thermodynamic Studies

The free energy change during the adsorption process was positively correlated with temperature change (Table 3). When the temperature increased, the magnitude of free energy decreased by 47.3% at 25 °C and 32.2% at 35 °C compared to that at 45 °C, suggesting that the adsorption was more spontaneous at high temperatures. The value of the enthalpy change shows the adsorption to be endothermic.

**Table 3.** Thermodynamic Parameters of Pymetrozine Adsorption onto BC

	Temperature T	Thermodynamic parameters		
	(°C)	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J (mol K) <sup>-1</sup> )
BSG BC	25	1.84	2.28	0.43
	35	1.43		
	45	0.97		

## DISCUSSION

The BSG BC production process played an important part in determining the BC characteristics such as pH, surface area, and CEC, among others. The present results showed that as pyrolysis temperature increased, there was higher pH, surface area, and CEC, but lower organic carbon and total nitrogen. Poerschmann *et al.* (2014) also demonstrated that the BSG BC properties were different from the hydrothermal carbonization process BC (brewer's spent grain), insofar as the latter had lower pH (6.9) and organic carbon content (513 g kg<sup>-1</sup>). Additionally, the BSG BC adsorption capacity was also affected by the adsorbent dosage, pyrolysis temperature, and residence time (Sun *et al.* 2012). With increasing pyrolysis temperature, the adsorption capacity first increased, then decreased, with the highest adsorption capacity at 400 °C. This may be due to the presence of fewer organic functional groups in BC as the temperature increased, though the surface area and CEC was increased, implying the function groups can be excluded as the main mechanism for pymetrozine removal by BSG BCs (Mohan *et al.* 2014). The adsorption capacity increased by 9.2% to 17.9% after 4 h of pyrolysis compared to 2 h, which may be due to an improved inner structure and production of more porosity of the carbon matrix with longer pyrolysis time (Mohan *et al.* 2014). Keiluweit *et al.* (2010) reported that BC production processes clearly demonstrate that biomass undergoes dehydration and depolymerization into dissociated lignin and cellulose with an increase in pyrolysis temperature, and the present results also supported this conclusion. With pyrolysis temperature greater than or equal to 700 °C, about 90% of organic carbon in



feedstocks was produced as inorganic carbon in BC, so pyrolysis temperature played a significant role in improving BC characteristics (Lian *et al.* 2011). Compared with the results of Cui *et al.* (2013), the conclusion was that the adsorption of pymetrozine by different BCs was affected by the raw BC materials produced process. In the present work, similar effects on BC removal of the pollution were obtained under the same adsorption conditions. The adsorption capability of BSG BC varied with the pyrolysis temperature in the present study, with 400 °C and a residence time of 4 h optimal.

The results indicated that increasing the mass of the BC from 0.1 to 1 g increased the percentage of pymetrozine removal and equilibrium adsorbed amount onto BC. However, for BC more than 0.1 g, the removal efficiency and adsorbed amount gradually increased slowly, which could be attributed to the increased number of available adsorption sites as the solid mass increases and overlapped of absorbent layers. Similar adsorption studies using BC for  $\text{NH}_4^+$  have reported the same effect (Kizito *et al.* 2015).

Biochar adsorption efficiency decreased as the particle size increased. This result can be linked to the surface area of the adsorbent. Surface area increased with smaller particle sizes and present a better opportunity for pymetrozine to penetrate internal pore structures (Kizito *et al.* 2015). And this explains high absorption at low particle size, so the <0.15 mm size BC was used in the experiment.

The  $\text{H}^+$  concentrations in aqueous solutions are greatly affected by pH, which also affects the functional groups of BC (Lian *et al.* 2014). During the adsorption process, the BSG BC adsorption capacity increased from pH 2 to pH 4, then decreased with increasing pH, probably due to the electrostatic interactions between positive pymetrozine functional groups and negative functional groups of adsorbents (Cui *et al.* 2013). The BC can also decrease the uptake of Cd by plants, which bonded with Cd in interior of BC particles (Bian *et al.* 2014). When rice-straw BC is added in large amounts (10.0% or 40 t ha<sup>-1</sup>), the high alkalinity of ash and solution pH generally controlled the sorption process of pentachlorophenol (Luo *et al.* 2011). Results from this study indicated that BSG BC can act as an effective surface adsorbent to adsorb pymetrozine. This may be attributed to the binding of pymetrozine molecules to functional groups on the active areas on the BC surface, including hydroxyl, carboxyl, methoxyl, and phenolic groups (Hadjittofi *et al.* 2014). Oleszczuk *et al.* (2012) also reported that BC micro-structure was responsible for the enormous adsorption capacity on pymetrozine such as the laminar structure inner fibers and its surface area function groups. At low concentrations, pymetrozine may be located at the outer surface of the BC, while permeating the interior with increasing concentration, so it was very well on fitting Langmuir model and Freundlich model (Liu *et al.* 2009). During the pyrolysis process, the carbonized and non-carbonized functional groups were also play an important role in adsorption process (Cao *et al.* 2009; Xu *et al.* 2012).

The thermodynamic parameters for the pymetrozine adsorption, *i.e.*, the enthalpy ( $\Delta H^\circ$ ), entropy ( $\Delta S^\circ$ ), and Gibbs free energy ( $\Delta G^\circ$ ), were calculated to assess feasibility and define whether sorption was endothermic or exothermic. Higher temperatures significantly ( $p < 0.05$ ) increased pymetrozine adsorption onto BC, indicating that adsorption was an endothermic process. The adsorption capacity increased at higher temperatures of preparation, which may be caused by the enlargement of pore size and activation of the adsorbent surface (Shi *et al.* 2014). The adsorption data have been well fitted by two different isotherm models (*e.g.*, Langmuir and Freundlich). Therefore, on the basis of the observed  $r$  values the Langmuir model fitted the data suggesting that pymetrozine adsorption much occurred by chemisorption within the monolayer. On the other hand, although the  $r$  values from the Freundlich model were over 0.98 suggesting

some level of physical adsorption, the values of  $1/n < 1$ , implied chemisorption was more favorable (Kizito *et al.* 2015). Similar BC adsorption studies have reported that  $\text{NH}_4^+$  adsorption fit both the Langmuir and Freundlich models (Liu *et al.* 2013). From our results, the positive standard enthalpy change ( $\Delta H^\circ > 0$ ) indicated that pymetrozine adsorption process was endothermic. The  $\Delta G^\circ$  for tested temperatures was between 0 and 10  $\text{kJ mol}^{-1}$  during adsorption, and this value was in the range of physical adsorption, showing that pymetrozine adsorption was a physical process and the process was still going on for the  $\Delta G^\circ$  values of BCs greater than 0; this result was the same as that of Cui *et al.* (2013). So before adsorption occurs, the pymetrozine molecules near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state, and the ratio of pymetrozine interacting with the adsorbent will be higher than in the adsorbed state (Lai *et al.* 1992). As a result, the distribution of rotational and translational energy among a small number of molecules will increase with increasing adsorption by producing a positive value of  $\Delta G^\circ$ , and randomness will increase at the solid-solution interface during the process of adsorption (Reddad *et al.* 2002). Entropy ( $\Delta S^\circ$ ) could reflect the degree of freedom of pymetrozine in the BC adsorption system. The positive  $\Delta S^\circ$  values suggested that it was increased disorder and randomness of liquid-solid phase interaction at the BC surface (Hema *et al.* 2007; Xu *et al.* 2013). It is important to note that although the equilibrium and kinetic data suggest chemisorption as the major mechanisms of  $\text{NH}_4^+$  adsorption onto the BC, the thermodynamic parameters point out occurrence of physical adsorption. The conclusion can be made that it was complex process with physical-chemical sorption of pymetrozine in the BSG BC. The results of this study suggest that BSG BC adsorbed pymetrozine was a natural process and could be used as an efficient adsorbent for the removal of pymetrozine in ground-water and even in soil.

## CONCLUSIONS

1. This study investigated the potential use of BC for pymetrozine adsorption in solution. Pyrolysis time, temperature of BSG, pH of the solution, contact time, initial ion concentrations, and temperature of pymetrozine adsorption had significant ( $p < 0.05$ ) effects on adsorption efficiency during this study. The most favorable particle size that in range of  $< 0.15$  mm while maximum absorption was observed to occur at pH 4.0 and significantly decreased at other pH. The BCs produced at pyrolysis temperature of 400  $^\circ\text{C}$ , presenting higher adsorption capacity.
2. The thermodynamic parameters of  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  were calculated. This indicated that the adsorption was an endothermic process and that an increase in the temperature in practice will lead to a higher adsorption capacity.
3. The BC function groups involved chemisorption with bond formation and surface area dependent physical diffusion were the most likely mechanisms of pymetrozine adsorption. The BSG BC is an effective alternative biomass for the removal of pymetrozine in terms of high removal efficiency, natural and abundant raw material, and low cost. The production of BC from BSG is a new way to treat ground water and help resolve BSG waste disposal.

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