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Original Research Paper

Effect of Solution pH on the Kinetic Adsorption of Methylene Blue by Sugarcane Bagasse Biochar Under a Magnetic Field

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ABSTRACT

Sugarcane bagasse, an agricultural waste biomass was used to prepare biochar by pyrolyzing the biomass under oxygen-limited conditions. The prepared biochar was used for the adsorptive removal of a cationic dye methylene blue (MB) under a magnetic field. It was found that the existence of the external magnetic field had significantly enhanced the uptake of MB onto the bagasse biochar. The increased biochar dosage actually declined the uptake of MB while the effect of the magnetic field was still significant. The adsorption kinetics was investigated under different solution pH conditions. The experimental data were simulated using non-linear pseudo-first-order, pseudo-second-order and Elovich kinetic models. The Elovich kinetic model was found to be more suitable to describe the adsorption kinetics. This indicates that the adsorption of MB onto BC400 is a chemisorption process in which the rate-determining step is diffusion in nature. The uptake of MB is mainly attributed to the π–π electron-donor-acceptor interaction and electrostatic attraction.

INTRODUCTION

Agricultural wastes are generated in a huge amount annually. They usually contain a large amount of floristic fibre and functional groups such as carboxyl, hydroxyl and amidogen, which are expected to be responsible for the biosorption process (Han et al. 2006, Gupta et al. 2009). It is well accepted that these agricultural wastes could be utilized as low-cost sorbents. One of the best approaches to utilize these agricultural wastes is to generate biochars, which is capable of solving a series of environmental problems. Biochars offer the right chance to turn bioenergy to carbon-negative industry. Low-temperature pyrolysis with carbon sequestration and gas capture is expected to be a carbon-neutral energy source (Lehmann 2007, Lee et al. 2010). Further, biochar is being used in environmental management including soil improvement, waste management, climate change mitigation and energy production (Ahmad et al. 2014). Low-temperature pyrolysis is usually applied to convert biomass, typically agricultural waste into biochars (Keiluweit et al. 2010, Das et al. 2013). Sugarcane bagasse is a residue from production of sugar and ethanol, which has the potential to be used as an environmentally compatible biosorbent. Some studies have demonstrated its excellent adsorption performance for cationic dyes removal (Zhang et al. 2013).

Interestingly, the magnetic field-exposed method has demonstrated its capability for enhancing the adsorptive removal of pollutants from water as static magnetization is convenient, simple and cost-effective. Basically, the magnetic field is capable of affecting the behaviour and physicochemical properties of water (Patkowski et al. 2014). Nevertheless, the exposure to the magnetic field can impact the adsorbent significantly. Zhang and his co-workers reported that magnetic treatment is capable of enhancing the ζ potential of Ca-rectorite suspensions in the absence of Cu and of reducing that of the suspension in the presence of Cu (Zhang et al. 2004). The static magnetization might be a good alternative to enhance the adsorption capability of biochar.

In this research, the biomass of sugarcane bagasse was firstly pyrolyzed at different temperatures under oxygen-limited conditions. Then the prepared biochars were used for the enhanced adsorptive removal of methylene blue with the aid of an external magnetic field. The effect of the magnetic field was mainly investigated. The adsorption kinetics under different solution pH conditions was investigated and the experimental data were fitted by typical kinetic models. The adsorption mechanism was also discussed.

MATERIALS AND METHODS

Chemicals: Methylene blue (mass fraction >98.5%, chemical pure) was purchased from Tianjin Chemical Reagent Research Institute. The other chemicals used were of analytical grade. Deionized (DI) water was used throughout the study. A pair of permanent magnets (30 mm×19 mm×6 mm, Beijing Fengrui Magnetic Material Factory) was used to provide the magnetic field.

Adsorbent preparation: Sugarcane bagasse (bagasse) was collected from Guangxi province of China. It was washed, dried, crushed and sieved using a 100 mesh sieve. The biochars from bagasse were prepared by pyrolyzing the bagasse biomass at various temperatures under oxygen-limited conditions for 2 h. For demineralization, the resultant bagasse biochars were put in a 4 mol/L HCl solution for 12 h and separated by filtration. Then the residues were rinsed with DI water until neutral solution pH was achieved and then dried in an oven at 80°C overnight. The treated biochars were finally preserved in a desiccator until further use. The prepared bagasse biochars pyrolyzed at 200°C, 400°C and 600°C were designated as BC200, BC400 and BC600.

Batch adsorption studies: Adsorption of methylene blue (MB) onto the bagasse biochar was conducted in a series of cylindrical flasks. The stock solutions of MB (500 mg/L) were prepared in DI water. All working solutions were prepared by diluting the stock solution with DI water to the desired concentration. A desired amount of bagasse biochar (200 mg) was added to a conical flask containing 500 mL of MB solution with a concentration of 10 mg/L. A pair of permanent magnets was set in parallel to the reaction vessels to provide a magnetic field. Constant stirring was maintained by mechanical agitation for 24 h. Finally, samples were collected and filtered through a 0.45 μm pore-size membrane before measurement.

The reaction temperature was controlled at a constant of 25°C. All the solution pH was maintained at neutral pH except for the pH effect study. The solution pH adjustment was conducted by addition of diluted HCl or NaOH solution.

Analysis of MB: The concentration of MB was analysed using an UVmini-1240 spectrophotometer (Shimadzu) by monitoring at the wavelength of maximum absorption (664 nm). The adsorption capacity (q_e and q_t) was calculated by the following equation:

$$q_e = \frac{V \times (C_0 - C_t)}{m} \quad ...(1)$$

$$q_t = (C_0 - C_t)\, V/W \quad ...(2)$$

Where q_e and q_t (mg/g) are the adsorption capacity at equilibrium and t min; C_0 is the initial concentration of MB in solution, while C_e and C_t (mg/L) are the concentrations of MB at equilibrium and t min, respectively; V (L) is the volume of solution, and W (g) is the mass of biochar used.

RESULTS AND DISCUSSION

Effect of pyrolytic temperature and magnetic field on MB adsorption: Effect of pyrolytic temperature on MB adsorption was investigated under a magnetic field, as presented in Fig. 1. At 24 h, the uptake of MB on the BC200, BC400 and BC600 achieved were 10.59, 12.49 and 15.33 mg/g, respectively. As a comparison, under a magnetic field, the uptake of MB on the BC200, BC400 and BC600 achieved were 13.99, 14.62 and 16.36 mg/g, respectively. Apparently, the adsorption performance of bagasse biochars was significantly improved as a result of the magnetic field. Considering the energy cost and the possible dissolution of organics from the prepared biochars, BC400 was used in the following tests.

Effect of biochar dosage on MB adsorption under a magnetic field: Effect of biochar dosage on MB adsorption under a magnetic field was also investigated and the results are illustrated in Fig. 2. Similarly, the uptake of MB at the BC400 dosage of 50, 100 and 200 mg achieved were 27.17, 19.85 and 12.49 mg/g, respectively. As a comparison, under a magnetic field, the uptake of MB at the dosage of 50, 100 and 200 mg reached 38.49, 23.7 and 14.62 mg/g, respectively. The enhancement of the external magnetic field was evident from the above data. In the following test, the dosage of BC400 was fixed at 200 mg in 500 mL solution.

Adsorption kinetics non-linear simulation under different solution pH conditions: The adsorption kinetics was explored at 3.0, 7.0 and 11.0. The experimental data were simulated by non-linear kinetic models including pseudo-first-order, pseudo-second-order and Elovich models. The simulated curves are presented in Fig. 3 and kinetic parameters

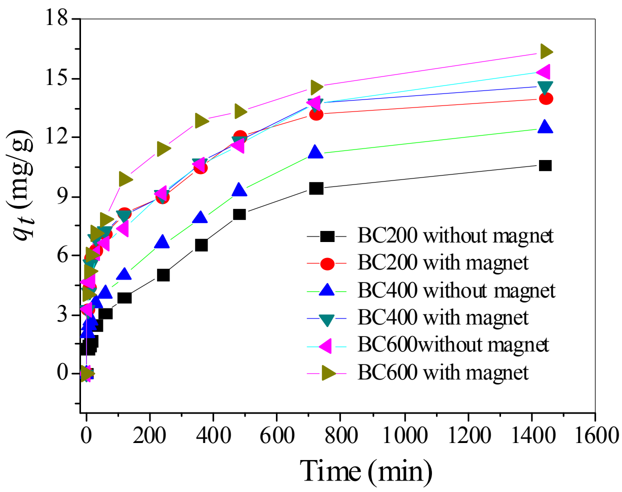

Fig. 1: Effect of pyrolytic temperature on MB adsorption under a magnetic field.

Table 1: Parameters for the kinetic simulation by pseudo-first-order, pseudo-second-order and Elovich models.

Model	Magnet	Parameters	pH=3	pH=5	pH=7	pH=9	pH=11
Pseudo-first-order	no	R^2	0.858	0.863	0.741	0.912	0.886
		q_e	11.82	8.48	11.7	8.71	9.88
		k_1	0.03	0.044	0.019	0.028	0.028
	with	R^2	0.897	0.817	0.817	0.923	0.879
		q_e	13.36	13.08	13.08	10.54	10.67
		k_1	0.03	0.026	0.026	0.03	0.028
Pseudo-second-order	no	R^2	0.934	0.927	0.847	0.969	00.952
		q_e	12.94	9.17	12.97	9.48	10.79
		k_2	0.003	0.006	0.002	0.004	0.003
	with	R^2	0.961	0.909	0.909	0.977	0.948
		q_e	14.52	14.22	14.22	11.41	11.69
		k_2	0.003	0.002	0.002	0.004	0.003
Elovich	no	R^2	0.988	0.983	0.954	0.997	0.996
		a	-0.376	0.558	-0.805	-0.365	-0.331
		k	2.044	1.36	2.03	1.505	1.695
	with	R^2	0.991	0.99	0.99	0.993	0.997
		a	-0.3	-0.058	-0.058	-0.101	-0.506
		k	2.28	2.17	2.17	1.77	1.86

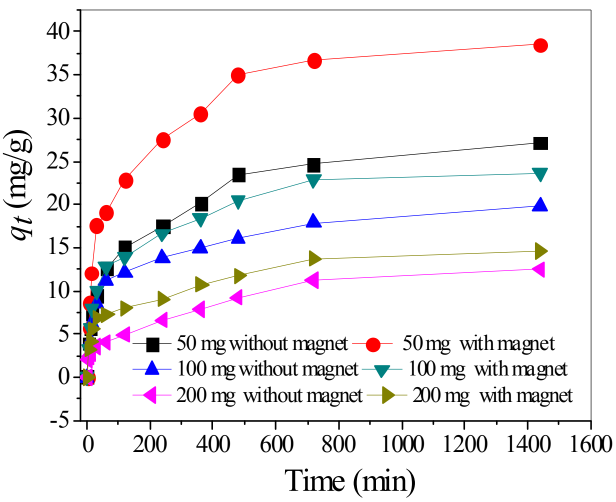

Fig.2: Effect of biochar dosage on MB adsorption under a magnetic field.

are also listed in Table 1.

Pseudo-first-order, pseudo-second-order and Elovich kinetic models were used to fit the experimental data. The mathematical representations of the non-linear models of pseudo-first-order and pseudo-second-order kinetics are given as (Lagergren 1898, Ho & McKay 1999):

$$q_t = q_e(1-e^{-k_1 t}) \quad ...(3)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad ...(4)$$

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad ...(6)$$

Where q_e and q_t are the adsorption capacities (mg/g) of TC at equilibrium and at time t (min), respectively; and k_1 (min^{-1}) and k_2 (g mg/min) are the related adsorption rate constants for pseudo-first-order and pseudo-second-order model, respectively.

The Elovich kinetic model can be written as (Kithome et al. 1988):

$$q_t = a \ln(t) + b \quad ...(7)$$

Where a (g·mg/min) and b (mg/g) are constants.

Typically, the adsorption of MB can be divided into three stages including an initial rapid stage (60 min), a slower second stage (60-180 min) and a slowest equilibrium uptake stage (Vadivelan & Kumar 2005). As illustrated in Fig. 3, the simulated curves at pH 3.0, 7.0 and 11.0 showed the similar behaviour. It was observed that the experimental data are quite in correlation with simulated Elovich curves as the experimental points are closer to the simulated Elovich curves than pseudo-first-order and pseudo-second-order models. Between pseudo-first-order and pseudo-second-order models, the calculated q_e values from pseudo-second-order model are much closer to the experimental data than those of pseudo-first-order model, indicating the pseudo-

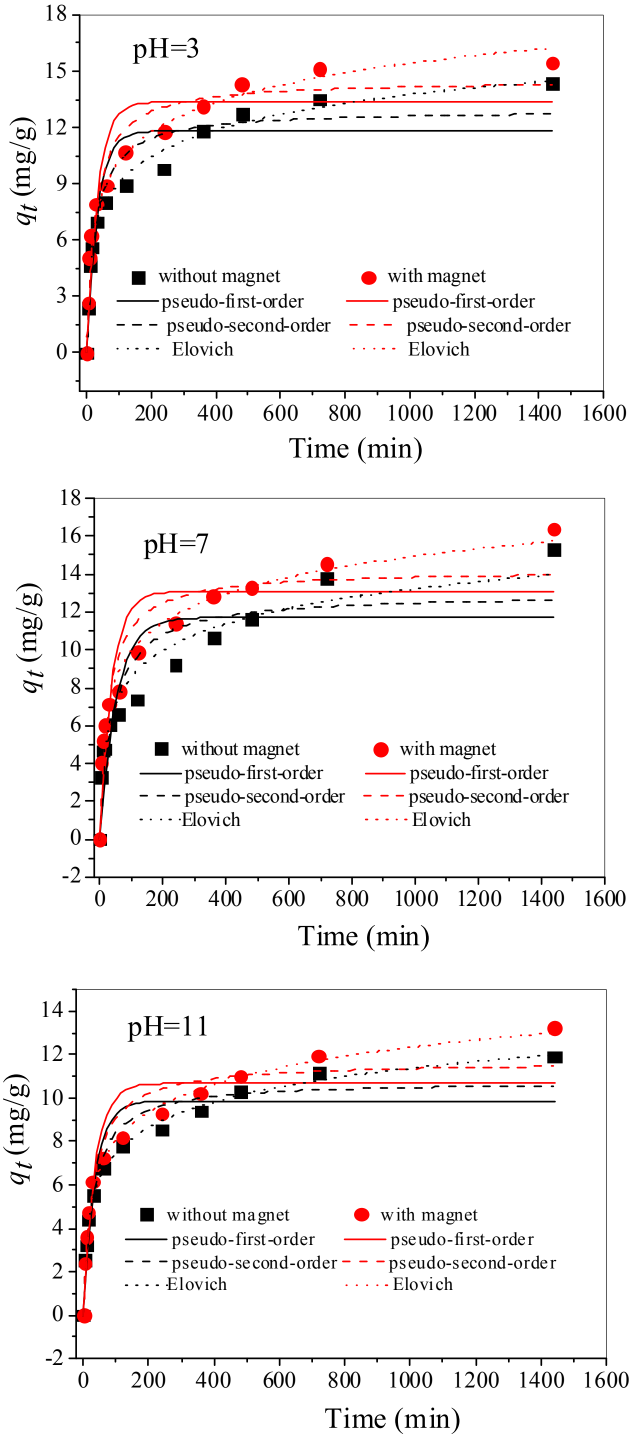

Fig. 3: Simulated curved of the adsorption kinetics at pH 3.0, 7.0 and 11.0.

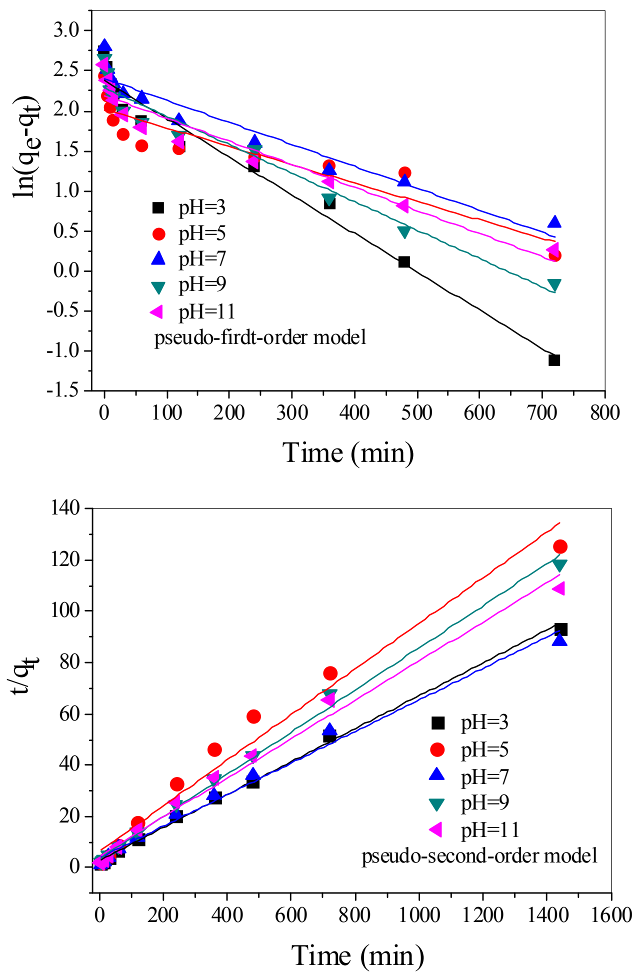

Fig. 4: Linear adsorption kinetic simulation for the pseudo-first-order (a) and pseudo-second-order (b) models.

second-order model was more suitable to simulate the experimental data. Meanwhile, from Table 1, the values of correlation coefficient (R^2) of Elovich model are all higher than those of other models at all the solution pH values. The Elovich model is used to describe chemisorption in which the rate-determining step is diffusion in nature (Aharoni et al. 1991, Pavlatou et al. 1988). Consequently, the adsorption of MB onto BC400 could be a chemisorption process in which the rate-determining step is diffusion in nature.

Additionally, the calculated q_e values from pseudo-second-order model at pH 3.0, 5.0, 7.0, 9.0 and 11.0 are 12.94, 9.17, 12.97, 9.48 and 10.79 mg/g, respectively. Under the magnetic field, these values at pH 3.0, 5.0, 7.0, 9.0 and 11.0 are 14.52, 14.22, 14.22, 11.41 and 11.69 mg/g, respectively. Typically, the highest uptake of MB was achieved under acidic conditions while alkaline conditions were not favourable for the adsorption of MB. On one hand, MB is a cationic dye throughout the pH range examined while biochar BC400 is normally negatively-charged

(Ahmad et al. 2014), which facilitate the uptake of MB onto BC400. On the other hand, the bagasse biochar BC400 possesses more graphitized surfaces, and the surfaces were expected to have higher π–electron density. As MB molecules are regarded as π–electron acceptors and biochar B600 as π–electron donors, a mechanism of π–π electron-donor-acceptor (EDA) interaction might contribute to the uptake of MB as well (Teixidóet et al. 2011, Zheng et al. 2013, Jing et al. 2014). As a consequence, the adsorption of MB is mainly attributed to the EDA interaction and electrostatic attraction.

Adsorption kinetics non-linear simulation under different solution pH conditions: In addition to the non-linear simulation of the adsorption kinetics, the experimental data were also fitted by the linear pseudo-first-order and pseudo-second-order kinetic models, as shown in Fig. 4. Judged from the simulated curves, it is evident that the simulated curve of pseudo-second-order kinetic model is more in correlation with the experimental points than that of the pseudo-first-order model. Meanwhile, at all the pH conditions, the values of correlation coefficient (R^2) of pseudo-second-order model are higher than 0.976, which is apparently higher than those of pseudo-first-order model. The calculated q_e values from pseudo-second-order model are much closer to the experimental data than those of pseudo-first-order model as well. As such, the pseudo-second-order kinetic model is more suitable to describe the adsorption kinetics, indicating the adsorption process is chemisorption as the aforementioned results.

CONCLUSION

Sugarcane bagasse biochar was prepared by pyrolyzing the biomass under oxygen-limited conditions. It was used for the adsorptive removal of a cationic dye methylene blue under a magnetic field. The adsorption performance of bagasse biochars was significantly improved as a result of the external magnetic field. The increased biochar dosage actually declined the uptake of MB while the effect of the magnetic field was still significant. By non-linear kinetic simulation using pseudo-first-order, pseudo-second-order and Elovich kinetic models, it was proved that the Elovich kinetic model was more suitable to describe the adsorption kinetics. This indicates that the adsorption of MB onto BC400 could be a chemisorption process in which the rate-determining step is diffusion in nature. The uptake of MB is mainly attributed to the π–π electron-donor-acceptor interaction and electrostatic attraction.

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