Journal of Molecular Liquids 223 (2016) 335–342

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Adsorption characteristics of Direct Red 23 from aqueous solution by biochar

Na Liu [a], Meiling Zhu [a], Hang Wang [a], Huiqiang Ma [a,b,*]

[a] Key Laboratory of Groundwater Resources and Environment, Ministry of Education, College of Environment and Resources, Jilin University, Changchun 130021, China
[b] College of Chemistry, Chemical Engineering, and Environmental Engineering, Liaoning Shihua University, Fushun 113001, China

ARTICLE INFO

Article history:
Received 26 April 2016
Accepted 18 August 2016
Available online 20 August 2016

Keywords:
Direct Red 23
Biochar
Effective diffusion coefficient
Liquid film diffusion coefficient
Adsorption equilibrium

ABSTRACT

Biochar, produced by the pyrolysis of pig manure at 800 °C, was characterized and investigated as an adsorbent for the removal of Direct Red 23 from aqueous solution. The adsorption kinetics was best described by a modified Freundlich model and intra-particle diffusion models. The value of the apparent adsorption constant k (modified Freundlich model) decreased from 0.133 to 0.076 L/(g·min$^{1/m}$), when the amount of biochar increased from 1 to 8 g/L. Values of effective particle diffusion coefficient (D_p) and liquid film diffusion coefficient (D_f) were calculated to further determine the rate-limiting step of the adsorption process. The value of activation energy 5.558 kcal/mol indicates that the adsorption is a physical process controlled by film diffusion and the adsorption process is endothermic. When pH < pH_{ZPC} (8.71),the surface of biochar is positively charged; the positive charge promoted the anionic dyes attracted onto the biochar by electrostatic force; and a hydrogen band was formed with the protonated —OH functional groups on the active sites. The adsorption equilibrium study indicates that the adsorption was in a multilayer mode, and the maximum adsorption capacity was 2.19×10^{-5} mol/g, at pH 2.20 and temperature 25 °C. Considering the widely availability and high removal efficiency, biochar is deserved further investigations for applications in more hazardous substances removal.

1. Introduction

Azo dyes, contained in textile and printing industry wastewaters, are hard to be degraded due to chemical stability. The dyes also have been proven to be carcinogenic to humans and harmful to aquatic organisms [1–3]. Considering the threaten that dyeing wastewater has caused to the environment, many technologies have been used to remove dyes from wastewater. The technologies include advanced oxidation processes (AOPs), biological treatment and adsorption. AOPs are commonly used for the destruction of azo dye molecules using acute-oxidation radicals, for example hydroxyl radicals (OH•) and sulfate radicals ($SO_4^{-\bullet}$). Target pollutants in water can be removed efficiently and fast by the radicals [4–6]. However, when chemicals that affect the production of radicals (OH•or$SO_4^{-\bullet}$) exist in the water, the degradation efficiency can be reduced [7]. Although chemical oxygen demand can be effectively removed through biological treatment process, the color cannot be completely eliminated [8].

Adsorption is another regular method used in removing dyes from aqueous solutions because of its simplicity, economy, high efficiency, and environmental-friendly properties [9]. The selection of proper adsorbent is very important and the efficiency, cost and reliability should be taken into account. Biochar is a carbonaceous material obtained by pyrolysis of biomass under an oxygen limited condition [4]. The chemical (for example, abundance of functional group on biochar surface) and physical (for example, porosity, surface charge and specific superficial area) properties of biochar have been the focus of previous studies [10,11]. Biochar has been widely used in the removal of pollutants from gas, solid and aqueous phase. Most biochars are prepared from agricultural residues, such as animal manures and plant stalks. Biochar are commonly applied in the improvement of soil fertility, and in the removal of heavy metals and organic pollutants from wastewaters [12–14]. Although dyes in aqueous solutions have been removed by various biochars [15,16], detailed chemical equations are required to explain the mechanism. Meanwhile, few studies have been reported for Direct Red 23 (2-azo dye; DR23) adsorption by biochars.

In this study, biochar (prepared from pig manure) was used to remove DR23, which is difficult to be degraded and plays an important role in textile and printing industries. Batch experiments were conducted to study the adsorption capacity of the biochar under different key parameters, including adsorption time, pH, temperature and ionic strength. To better understand the adsorption process, adsorption kinetics and equilibrium studies were performed. A multilayer adsorption model was applied to fit the results of isotherm data. Studies on the adsorption of DR23 by biochar in this research will promote further application of biochar on removing dyes from wastewater.

* Corresponding author at: Key Laboratory of Groundwater Resources and Environment, Ministry of Education, College of Environment and Resources, Jilin University, Changchun 130021, China.
E-mail address: mahuiqiang0921@126.com (H. Ma).

http://dx.doi.org/10.1016/j.molliq.2016.08.061
0167-7322/

2. Materials and methods

2.1. Materials

The pig manure was obtained from the rural area of Jilin Province, China. DR23 (SIGMA-ALDRICH, Co., product in China) is an anionic diazo dye with chemical formula as $C_{35}H_{25}N_7Na_2O_{10}S_2$, molecular weight as 813.72 g/mol and maximum wavelength as 504 nm. Molecular structure of DR23 is presented in Fig. 1. Chemicals used in this study were analytical grade. A stock solution was prepared by dissolving DR23 into distilled water.

2.2. Biochar preparation and characterization

The pig manure was air-dried for 14 days to remove moisture and then pyrolyzed slowly in a muffle furnace (SXZ-8-13, Shanghai Yi-feng Electric co., Ltd) under oxygen-limited condition at 800 °C for 2 h, using a similar method described by Zhang et al. [17]. The diameter of biochar used in this study was <0.6 mm.

The morphologies and basic components of the biochar were characterized by a scanning electron microscopy (SEM) instrument equipped with energy dispersive X-ray spectroscopy (EDS) (JSM-6700F; JEOL, Japan). The specific surface area (SSA), average pore radius and total pore volumes of the biochar were determined by a SSA-4200C physical and chemical adsorption analyzer (Beijing Aude Electronic Technology, China) with Brunauer-Emmett-Teller (BET) method [18]. The phases and functional groups of the biochar was determined by X-ray diffraction (XRD) (DX2700, Dandong Square-Round Instrument Company) and Fourier Transform Infrared spectroscopy (FTIR) (Nicolet Avatar 370DTGS, Thermo Fisher Scientific, USA). The XRD analysis was performed by a diffractometer equipped with a Cu Ka radiation source and was operated at 40 kV and 126 mA. The range of scanning angle was $5° \le 2\theta \le 70°$ with increments of 0.05°. A particle size analyzer (Bettersize 2000, Dandong Baxter Instrument Co., LTD, China) was used to characterize particle size. The measuring conditions are follows, refractive index of sample: 1.630–0.1001, optical model: Mle, refractive index of medium: 1.333.

The pH values of biochar were determined by mixing the biochar with de-ionized water at a 1:5 w/w ratio [19] after 5 min shaking using a pH meter (PHS-3C, Rex Electric Chemical, Shanghai, China). To determine the pH of zero point of charge (pH_{ZPC}) of the biochar, 0.01 M NaCl was prepared and the suspension pH was adjusted within the range 2.0–12.0 using 0.1 M NaOH and HCl. Then 50 mL different pH of 0.01 M NaCl solution was taken into a conical flask containing 0.2 g biochar. The mixtures were shaken for 48 h [20], and then the final pH was measured.

2.3. Adsorption experiment

2.3.1. Kinetic studies

DR23 adsorption experiments were carried out by varying time and temperature for studying the kinetic and activation energy. Effect of time on adsorption experiments was conducted to determine equilibrium time. 0.1 g of biochar (1 g/L) was added into a series of 100 mL 1.0×10^{-4} M DR23 solutions with ionic strength (NaCl) as 0.01 M and pH as 2.20. The mixtures were shaken at 115 r/min for 3 h at 25 °C. 5 mL of the solution was extracted at the preset-time intervals and filtered through a 0.45-μm membrane filter. The residual DR23 concentration was determined in the supernatant with a spectrophotometer (Hach DR3900, USA). The previous procedures were repeated with different biochar amount (2, 4, 6, and 8 g/L). The activation energy of DR23 adsorption was investigated by maintaining the adsorption condition (pH, ionic strength, DR23 concentration and amount of biochar) and varying the temperature (5, 15, 25, 35, 45 °C).

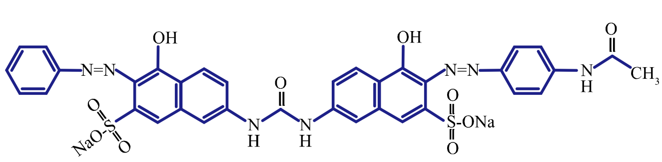

Fig. 1. Molecular structure of Direct Red 23.

The amount of DR23 adsorbed onto biochar was calculated as follows (Eq. (1)):

$$q_t = \frac{(C_0 - C_t)}{w} \tag{1}$$

where q_t (mol/g) is the amount of DR23 adsorbed onto biochar; C_0 (mol/L) and C_t (mol/L) are initial DR23 and residual concentration of DR23 at the time t; w (g/L) is the amount of biochar added into solution.

2.3.2. pH effect

A series of adsorption experiments was conducted to study the effect of pH on DR23 adsorption. The experimental procedures were as follows: (1) 2 L 1.0×10^{-4} M DR23 solution was prepared with the ionic strength as 0.01 M NaCl; (2) 100 mL of the solution was added to polyethylene bottles; (3) the pH of the solutions was adjusted in the range of 2.0–12.0 using HCl or NaOH solution; (4) same amount of biochar (5.0 g/L) was added into each solution; (5) the mixtures were shaken at 115 r/min for 12 h; (6) after shaking, each sample was immediately filtered through a 0.45-μm membrane filter and the pH values was immediately measured.

2.3.3. Adsorption isotherms

To investigate the isotherms of the biochar produced in different pyrolysis temperature, a single factor variable method was used. The experiments were conducted by changing the pyrolysis temperature (450, 550, 650, 800 °C) of biochar and adding the same amount of different biochar above in experiments, and keeping other conditions constant. The following procedures are similar to the (5) and (6) in Section 2.3.2.

2.3.4. The effect of ion strength on adsorption

The effect of ion strength on adsorption was taken into consideration, and conducted by changing the ion strength of the solution (0, 0.005, 0.01, 0.02, 0.05 M), by keeping other conditions constant. And the procedure are the same as (5) and (6) in Section 2.3.2.

3. Results and discussion

3.1. Biochar characterization

The characteristic properties of the biochar are presented in Table 1. The SSA of the biochar was 15.58 m^2/g with a total pore volume of 0.01 m^3/g and an average aperture as 16.64 Å. The pH value of biochar was 8.94 indicating that it was an alkaline material. The pH_{ZPC} of biochar was 8.71 (Fig. 2) and less than its pH 8.94. It was reported that the relations between materials pH and pH_{ZPC} would influent the surface charge of material [21]. When $pH < pH_{ZPC}$, material is positively

Table 1
Properties of biochar.

Parameters	Value	Elements	Content (% as mass)
Particle size (mm)	<0.6	C	51.33
Specific surface area (m^2/g)	15.58	O	31.56
Total pore volume (cm^3/g)	0.01	P	1.67
Pore size (Å)	16.64	Ca	1.39
pH	8.94	Si	10.87
pH_{ZPC}	8.71	K	2.16
		Mg	1.02