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1 Perspective

# Influence of sodium dodecyl sulfate coating on adsorption of methylene blue by biochar from aqueous solution

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#### ABSTRACT

Biochar is regarded as a promising new class of materials due to its multifunctional character and the possibility of effectively coupling different properties. With increasing introduction into the environment, environmental chemicals such as surfactants will load onto the released biochar and change its physicochemical characteristics and adsorption behavior toward pollutants. In this study, sodium dodecyl sulfate (SDS), as one type of anionic surfactant, was coated onto biochar with different loading amounts. The influence of SDS loading onto biochar's physicochemical properties were investigated by Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, zeta potential and Brunauer-Emmett-Teller (BET) surface area and pore size distribution analysis. Results showed that the pore size of the biochar decreased gradually with the increase of SDS loading because of the surface-adsorption and pore-blocking processes; the pH of the point of zero charge (pH<sub>PZC</sub>) decreased with increasing SDS loading. Although surfacecoating with SDS decreased the pore size of the biochar, its adsorption capacity toward methylene blue (MB) significantly increased. The biochar-bound SDS introduced functional groups and negative charges to the biochar surface, which could thus enhance the adsorption of MB via hydrogen bonding and electrostatic interaction. The results can shed light on the underlying mechanism of the influence of anionic surfactants on the adsorption of MB by biochar.

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#### 50 Introduction

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52 Biochar is a carbon-rich aromatic material produced by 53 pyrolyzing biomass through various thermochemical processes (i.e., pyrolysis, hydrothermal carbonization, flash carboniza- 54 tion, and gasification) under oxygen-limited conditions and 55 at relatively low temperatures (<700°C) (Tan et al., 2017). 56 The specific properties of biochar include high specific 57 surface area, porous structure, and copious amounts of 58

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surface functional groups (Safaei Khorram et al., 2016; Wang 59 et al., 2017). Although its specific surface area and micropore 60 volume are much lower than that of activated carbon, biochar 61 is still regarded as a good replacement for commercial 62 activated carbon because of its abundant functional groups 63 and lower cost (Zhou et al., 2016). Recently, biochar has been 64 65 used widely as an effective adsorbent for removal of heavy metals and organic compounds from wastewater (Chen et al., 66 67 2008; Guo et al., 2014; Jiang et al., 2017a, 2017c; Pan et al., 2013; 68 Shen et al., 2017; Zafar et al., 2017). Among these pollutants, much attention has been paid to the adsorption of dyes by 69 70 biochar due to their toxic effects and high concentrations in 71 wastewaters. For instance, Nautiyal et al. (2016) used Spirulina platensis algae to prepare biochar which exhibited excellent 72 73 adsorption performance toward Congo red. Ding et al. (2016) 74 investigated the simultaneous adsorption of methyl red and methylene blue onto woody biochar in different concentra-75 tion combinations. Sewu et al. (2017) examined the adsorp-76 77 tion ability of crystal violet onto biochar produced from Korean cabbage, and the Langmuir maximum adsorption 78 79 capacity was as high as 1304 mg/g.

80 Surfactants, as a key component of industrial and household waste, are routinely deposited in numerous ways on land 81 82 and into water systems (Emmanuel et al., 2005; Metcalfe et al., 83 2008). These commonly are organic substances with amphiphilic 84 structures, indicating that they contain both hydrophobic groups 85 and hydrophilic groups, which allow them to adsorb various 86 pollutants such as heavy metal ions and organic molecules 87 (Flores et al., 2017; Gamba et al., 2017; Shah et al., 2017; Stofela 88 et al., 2017; Zhang et al., 2017). As reported, surfactants can 89 interact with geosorbents and impact their adsorption behavior toward pollutants (Koh and Dixon, 2001; Park et al., 2011; 90 Richards and Bouazza, 2007; Xi et al., 2010). Surfactants also 91 92 can bind to released nanomaterials, change their physicochemical characteristics, and then affect their adsorption mechanism 93 94 (Liu et al., 2014; Rajesh and Ramagopal, 2016). It was reported that a surfactant (i.e., cetylpyridinium chloride) can coat onto 95 activated carbon and mineral substances to improve their 96 97 removal performance for heavy metals from water (Choi et al., 2009; Lin et al., 2011; Sánchez-Martín et al., 2008). Furthermore, 98 several papers have demonstrated that dissolved surfactants 99 100 could impact the adsorption of organic pollutants by biochar. 101 For example, Han et al. (2013) reported the influence of a cationic surfactant on pentachlorophenol adsorption by 102 biochar; and the cationic surfactant cetyltrimethyl ammoni-103 um bromide could be coated onto the biochar surface via 104 ion-exchange with abundant exchangeable cations, such as 105 106 Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>, and then impacted the pentachlorophenol 107 adsorption.

Considering its increasing production and application, 108 109 biochar has inevitably been released into the environment. 110 Understanding the adsorption behavior of biochar toward toxic dye in the presence of surfactant has multiple important 111 environmental implications, including assessing (i) the feasi-112 bility of using biochar as an adsorbent in engineered treatment 113 of toxic dye, (ii) the fate and transport of toxic dye by biochar in 114 115 the environment, and (iii) the potential environmental and health risks of biochar-adsorbed toxic dye in ecological systems. 116 In this work, therefore, the physicochemical characteristics of 117 biochar with surfactant coating such as sodium dodecyl sulfate 118

(SDS) were investigated. In addition, the effect of the presence of 119 SDS on the adsorption behaviors of methylene blue (MB) onto 120 biochar was also examined. 121

#### 1. Material and methods

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The biomass used in this work was peanut shell obtained 125 locally from the farms in Changsha City, Hunan Province, 126 China. MB (3,7-bis{dimethylamino}-phenazathionium chlo- 127 ride,  $C_{16}H_{18}CIN_3S\cdot 3H_2O$ , molecular weight 373.9) was ob- 128 tained from Tianjin Hengxing Chemical Reagent Co., Ltd. 129 (Tianjin, China). SDS was purchased from Shanghai Yabang 130 Chemical Reagent Co., Ltd. (Shanghai, China). All other 131 chemicals including HCl, NaOH and NaCl were provided by 132 Guangdong Xilong Chemical Co., Ltd. All chemicals employed 133 in this experiment were analytical reagent grade and used 134 without any further purification. The water used in this work 135 was Milli-Q water (18.25 M $\Omega$ /cm) obtained from a Millipore 136 Milli-Q water purification system.

1.2. Preparation of adsorbent

The biochar was prepared as described by a previously published 139 paper (Jiang et al., 2015). Briefly, 10-g biomass was added to 140 a 250-mL beaker with 100-mL Zn(NO<sub>3</sub>)<sub>2</sub> solution (1 mol/L). 141 Then, the mixture was stirred continuously in a temperature- 142 controlled water bath shaker at 40°C for 24 hr. After being 143 dried, the mixture was pyrolyzed by a lab-scale tubular reactor 144 (SK-G08123K, China) in a N2 environment (400 mL/min) at 550°C 145 for 1 hr. After cooling, the resulting biochar was washed with 146 water, and dried in an oven at 65°C. After that, 1 g of prepared 147 biochar was added into 100 mL of SDS solution (3, 1 and 0.6 mg, 148 respectively). The mixture was also shaken in a temperature 149 controlled water bath shaker at 120 r/min for 24 hr. Then 150 the SDS-coated biochar was collected by filtration and dried 151 at 65°C for 12 hr. The products were named 0.6 SDS-biochar, 152 1 SDS-biochar, and 3 SDS-biochar, respectively. Finally, the 153 prepared samples were stored in a desiccator for further use 154 (Mi et al., 2016). 155

#### 1.3. Adsorbent characterization

Fourier transform infrared (FT-IR) spectroscopy measurements 157 were performed using a Fourier Transform Infrared Spectrometer 158 (Nicolet 5700 Spectrometer) using the KBr pellet technique in 159 the range of 4000-400/cm. The Brunauer-Emmett-Teller (BET) 160 surface area and the pore size distribution were determined 161 by using N<sub>2</sub> adsorption-desorption (Quantachrome, USA) at 77 K 162 over a relative pressure range from 0.0955 to 0.993. C, H O, Q6 N and S contents of samples were determined using an ele- 164 mental analyzer (Elementar, Vario EL III). Thermal analysis of 165 the precursor was done by thermogravimetry-differential scan- 166 ning calorimetry (TG-DSC) on a Netzsch STA 449C instrument 167 (conditions: air atmosphere, temperature ramp from 25 to 900°C, 168 rate 20°C/min). The zeta potential of samples was obtained 169 using a zeta potential meter (Zetasizer Nano-ZS90, Malvern) by 170 adjusting the solution pH from 2.0 to 11.0. 171

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