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Removal of methylene blue from aqueous solution by sewage sludge-derived biochar: Adsorption kinetics, equilibrium, thermodynamics and mechanism

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ABSTRACT

In this study, biochar was produced from municipal sludge and was characterized by Surface area and porosity analysis, Scanning Electron Microscope–Energy Dispersive Spectrometer (SEM-EDS) and Fourier Transform Infrared Spectroscopy (FTIR). The effect factors including adsorbent dosage, contact time, pH, temperature on the adsorption properties of methylene blue (MB) from aqueous solution onto sludge-derived biochar were investigated in batch experiments. The adsorption kinetics, isotherm, thermodynamic and mechanism were also studied. The results showed that the adsorption kinetics of MB on biochar was accurately described by a pseudo-second-order model, indicating that liquid film diffusion, intra-particle diffusion and surface adsorption coexisted during MB adsorption on the biochar. The equilibrium adsorption data were well represented by the Langmuir isotherm equation ($R^2 > 0.99$). As the initial MB concentration and temperature increased, the adsorption amount also increased and the adsorption was favorable. The thermodynamic analysis showed that MB adsorption onto sludge-derived biochar was spontaneous and endothermic. The desorption and reusability experiment indicated that sludge-derived biochar had the potential to be a reusable adsorbent for MB removal.The adsorption mechanism appeared to be related to electrostatic interaction, ion exchange, hydrogen bond interaction, n-π interaction, etc. Thus, sludge-derived biochar can be used as an effective absorbent to remove dyes from wastewater. As a beneficial by-product of sludge, sludge-derived biochar also can mitigate the environmental burden of sewage sludge.

1. Introduction

At present, wastewater from textile, leather, paper, plastics and other industries were largely produced, especially methylene blue wastewater which may pose potential risks to human and animals [1]. In addition to large wastewater yield, the dyeing industry produces effluent that is characterized by high concentrations of aromatic pollutants, dark color, alkaline properties, weakly biodegradable components and multiplicate complex substance [2]; thus, unexpected or accidental dyeing industries discharge effluent into the rivers or lakes and could cause serious pollution. So, the treatment of dyeing wastewater is the focus of considerable water treatment research and one of the difficult challenges.

The conventional used treatment methods of dyeing wastewater involve advance chemical oxidation technology, photo-degradation, membrane treatment, biological treatment and adsorption treatment, among others [3]. Due to higher efficiency, lower cost, ease and simplicity of operation and lower sensitivity to toxic pollutants, adsorption method (typically using commercial activated carbon) has been considered superior to other treatment techniques. Nevertheless, cost considerations and complicated technology have limited the widespread application of adsorption treatment. Recently, value-added material or modified waste material has become more commonly used in the treatment of dyeing wastewater [4–6].

Nowdays, large amount of sludge that is produced during biological wastewater treatment represents a serious burden on ecological health and society. In general, the typical techniques for sludge treatment include incineration, composting, aerobic digestion, disposal in landfills and land application, among others. Resource utilization has become an important means by which to

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derive value from sludge and preparations to transform sludge into activated carbon is an important pathway of sludge resource utilization. Through physical, chemical or physicochemical activation, highly active and highly adsorbent sludge-derived adsorbent can be obtained [7–9].

Recently, due to the functions in soil improvement, greenhouse gases reduction, waste water pollutant control, solid waste resource utilization, much research on biochar has been performed [10–19]. The main raw materials of biochar preparation have been forestry waste, agricultural residue and the organic fraction of municipal solid waste, among others. The typical raw materials for biochar include agricultural waste [20], manure [21], municipal sludge [22]. Compared with sludge-derived activated carbon, sludge-derived biochar lacks an activation process and was prepared at relative lower temperatures when compared with activated carbon. Therefore, the preparation process for sludge-derived biochar is relatively simple and inexpensive. Sludge-derived biochar has a large potential for transforming sludge as a value-added waste material into a resource to be utilized in pollutant control field.

Currently, the application of sludge-derived biochar to treat dyeing wastewater has been rarely reported, especially the interaction mechanism between sludge-derived biochar and MB solution. Therefore, municipal sludge was used to prepare biochar at 550 °C in this research. The sludge-derived biochar was used to adsorb methylene blue (MB), a typical component of dyeing waste water. The objectives of this study were to: 1) observe the effect of biochar mass, adsorption time and pH on MB adsorption; 2) investigate the kinetics and isotherm of MB adsorption on sludge-derived biochar; 3) characterize the mechanism of MB adsorption on sludge-derived biochar. This research should provide a reference for sludge resource utilization and application of sludge-derived biochar in dyeing waste water treatment.

2. Materials and methods

2.1. Preparation of sludge-derived biochar

Air-dried sludge (moisture content 8.06 ± 0.29%) was obtained from the dewatering stage of a domestic wastewater treatment plant. The wastewater treatment process consisted of an oxidation ditch treating 180,000 $m^3 d^{-1}$. To prepare biochar, a specified amount of sludge was put into a crucible with a lid. The crucible was put into a stainless steel cylinder. The air in the cylinder was removed by nitrogen gas to ensure an oxygen-free atmosphere. Then, the cylinder was put into the furnace and the furnace temperature was programmed to increase at a rate of 10 °C min^{-1} until it reached at 550 °C and kept for 2 h. After natural cooling, the yield rate of the sludge-derived biochar was determined gravimetrically, and pH of biochar was determined using the 24 h-equilibrated solution of biochar and deionized water with a solid/liquid ratio of 1:10(w/w). The yield rate was 43.61% and the pH was 7.50. Sludge-derived biochar was ground and passed through a 100-mesh sieve. The sample was saved for further adsorption experiment.

All chemicals used in this study were of analytical grade. The batch experiments were duplicated and only the average values were reported.

2.2. Characterization

The textural property of the sludge-derived biochar was analyzed with a surface area and porosity analyzer (Micromeritics, Tristar II 3020) at 77 K. The surface area, pore volume and average pore size were calculated using the nitrogen adsorption isotherms. The multipoint Brunauer–Emmett–Teller method was employed to calculate surface area.The pore volume and average pore siz were obtained from desorption isotherms using the Barrett–Joyner–Halenda method.

Scanning Electron Microscopy (SEM, S-4800, Hitachi, Japan)-Energy Dispersive Spectrometer (EDS, X-Max, Oxford Instruments, Britain) analysis was carried out on the sludge-derived biochar to investigate the surface morphology and element distribution before and after MB adsorption.

Fourier Transform Infrared (FTIR, Nicolette is50, Thermo Fourier, USA) analysis was applied on the sludge-derived biochar to characterize the surface functional groups, and the spectrum was recorded in the wave number range of 400–4000 cm^{-1}. The production of sample pellet was mixed with KBr at a ratio 1:100 w/w.

The concentration of released metals (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) from the sludge-derived biochars in the supernatant of the equilibrium solution were analyzed by Inductively Coupled Plasma (iCAP 6300 Series, Thermo Fourier, USA). Meanwhile, the corresponding release of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} from the biochars with deionized water was served as control. The net metal release was calculated by the difference of the values obtained from the equilibrium solution and those of the control experiment (background control for normalization).

2.3. Effect of operational parameters on MB adsorption

Adsorption experiments were conducted using 50 mL centrifuges tubes with same volume of 20 mL, and MB concentration of 100 mg L^{-1}.Different mass of biochar was added to adjust the varying solid-to-liquid ratios. Different dosages of biochar were added to achieve liquid-solid ratios between 2 and 50 g L^{-1} (biochar mass effect). Sub-samples were collected at pre-determined times during the 24 h of oscillation (contact time effect).1 mol L^{-1} HCl or NaOH was added to the MB solution to adjust the pH in the range of 2–11 (pH effect).Meanwhile, the raw MB solution without pH adjustment was used as a control treatment. The samples were placed in an oscillating shaker operated at 180 rpm and 25 °C for 24 h.Then, the samples were filtered through a 0.45 μm membrane and the absorbance of the filtrate was measured by spectrophotometer (the wavelength was set at 665 nm, 722S, Shanghai Precision, Shanghai, China). The absorbance of the filtrate was measured by a spectrophotometer (1 cm pathlength cuvettes was used). The ultrapure water was used to zero calibration. The MB removal efficiency and amount adsorbed were calculated using Eqs. (1) and (2), respectively.

$$\text{Removal efficiency } (\%) = (C_0\text{-}C_e)/C_0 \times 100\% \quad (1)$$

$$\text{Adsorption amount } (mg \cdot g^{-1}) = (C_0\text{-}C_e) \times (V/m) \quad (2)$$

In Eqs. (1) and (2), C_0 is the initial MB concentration (mg L^{-1}); C_e is the equilibrium MB concentration (mg L^{-1}); V is the volume of MB solution (L); and “m” is the weight of adsorbent (sludge-derived biochar, g).

2.4. Adsorption kinetics

Based on the above experimental parameters, a certain amount of biochar was added to a 500-mL Erlenmeyer flask containing 250 mL MB solution having an initial concentration of 50 mg L^{-1}, 100 mg L^{-1} or 150 mg L^{-1}. The experiment was conducted at 25 °C, 35 °C and 45 °C. Sub-samples were collected at pre-determined times and were determined. The adsorption amount of MB was calculated by:

$$q_t = (C_0\text{-}C_t)/C_0 \times V/m \quad (3)$$