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Highly efficient adsorption of cationic dye by biochar produced with Korean cabbage waste

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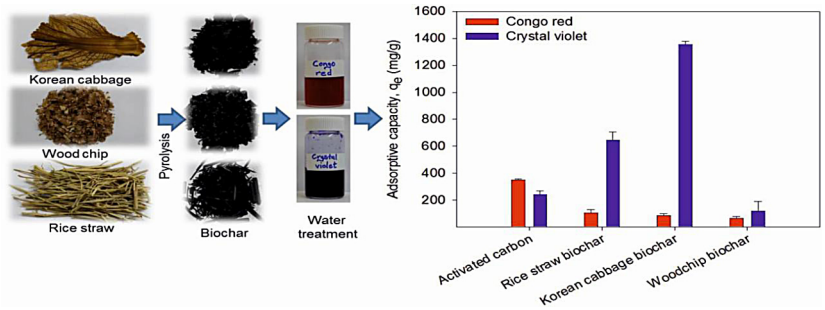
HIGHLIGHTS

- Biochars were produced from rice straw, wood chip, and Korean cabbage.
- The adsorptive performance of the biochars was compared with activated carbon.
- Congo red (anionic) and crystal violet (cationic) were used as model dyes.
- Ash content and functional group control crystal violet adsorption onto biochars.
- Korean cabbage biochar adsorbs crystal violet 4.8 times more than activated carbon.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar was produced from Korean cabbage (KC), rice straw (RS) and wood chip (WC) and the use as alternative adsorbents to activated carbon (AC) in wastewater treatment was investigated. Congo red (CR) and crystal violet (CV) were used as a model anionic and cationic dye, respectively. Initial solution pH had little effect on CR and CV adsorption onto all biochars except for AC on CR. The isotherm models and kinetic data showed that adsorption of CR and CV onto all biochars were dominantly by chemisorption. All biochars had lower adsorption capacity for CR than AC. KC showed higher Langmuir maximum adsorption capacity (1304 mg/g) than AC (271.0 mg/g), RS (620.3 mg/g) and WC (195.6 mg/g) for CV. KC may be a good alternative to conventional AC as cheap, superb and industrially viable adsorbent for removal of cationic dyes in wastewater.

1. Introduction

Biochar, the solid carbonaceous product of biomass carbonization in the presence of little or no oxygen has received much attention due to its carbon sequestration, waste recycling, soil management, and energy production (Lehmann, 2007; Tan et al., 2016; Woo et al., 2016). Aside the above, biochar also has a great potential as adsorbent in water and wastewater treatment facilities for handling a wide variety of organic and inorganic contaminants as a result of its porous nature, surface area and abundant surface functional groups (Mohan et al., 2014). Biomass feedstock for biochar production can be sourced from agricultural waste, forestry waste and animal manure (Reddy and Lee, 2014). Amongst the waste biomass feedstock, rice straw accounts for about 731 million tons globally (90% in Asia alone) (Elumalai et al., 2016). Cabbage and wood chip/saw dust are particularly abundant in South Korea accounting for 3 million tons (30% as waste) and 2.4 million tons (in the form of furniture waste) (Choi et al., 2002; Kim et al., 2012) respectively. Conventional cost-effective approach to handling these wastes has been to resort to in-field burning which creates numerous undesirable environmental and

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health issues. Biochars produced from this abundant waste feedstock in Korea are expected to exhibit different physicochemical properties since the quality and economic applicability of the biochar is feedstock dependent.

Dye-laden wastewater effluents occur predominantly in the textile, paper, rubber and plastic industries. The coloring effect of dyes in water are readily visible even at very low concentrations (Oladipo and Gazi, 2014). Synthetic dyes pose numerous environmentally-oriented drawbacks when released into receiving natural water bodies (Yagub et al., 2014). Congo red (CR), anionic, and crystal violet (CV), cationic, are both harmful synthetic dyes that are carcinogenic and mutagenic to living organisms including humans. CR is a benzidine-based azo dye – with a complex structure – released from textile industries with about 15% ending up in wastewaters after dyeing operations (Chatterjee et al., 2010). CV is a mitotic poison and belongs to the triphenylmethane group and used as a biological stain and in textile operations for dyeing applications (Saeed et al., 2010). The harmful effects of CR and CV have therefore heightened the need to effectively rid industrial wastewater of these dyes before discharge into receiving water bodies.

Conventional dye removal techniques from wastewater are coagulation, precipitation, membrane filtration and adsorption amongst many other physical, chemical and biological treatment methods (Güzel et al., 2014). Adsorption has been one of the most effective means of ridding wastewater of its color to within permissible dye concentrations in wastewater (Angın et al., 2013). Examples of the benefits of using adsorption are the ease of operation, high efficiency, and simplicity of design, comparative low cost of operation (Li et al., 2013) and wide-ranging availability (Chatterjee et al., 2009). Activated carbon is the major adsorbent that finds application in most adsorption units of industries but is in limited use due to the problems of cost – on the basis of efficacy – and regeneration (Patil et al., 2011). For this reason, the search for cheaper but effective adsorbents as alternatives to activated carbon have been on the rise (Yagub et al., 2014) nevertheless many of these adsorbents are still inferior to activated carbon (Chatterjee et al., 2009).

Dyes have been removed from aqueous solutions with biochar produced from bamboo (Yang et al., 2014), pine wood (Lonappan et al., 2016) and hornbeam sawdust (Ates and Un, 2013). For instance, biochar from rice straw has been successfully used to remove a cationic dye, malachite green dye from aqueous solution with a performance of 148.74 mg/g (Hameed and El-Khaiary, 2008). The successful removal of dyes by biochar from woodchip/-sawdust has also been reported. For example, Ates and Un (2013) reported up to 71% of disperse orange 30 dye removal with biochar from hornbeam sawdust. However, there has been no report on the use of biochar from waste cabbage as adsorbent in wastewater treatment.

In light of the above reasoning, this study sought to investigate the alternative source of biochar for an adsorbent derived from cheaper and readily available and accessible biomass feedstock in Asia. Korean cabbage (KC), rice straw (RS), and woodchip (WC) biochar were produced by pyrolysis and used as adsorbents together with commercially-obtained activated carbon (AC) from unwashed lignite carbon for the removal of CR and CV from aqueous solutions. The physicochemical properties of the produced biochars and AC were determined via characterization studies. The effects of initial solution pH, concentration and contact time on the sorption performance of KC, RS, WC and AC were investigated.

2. Materials and methods

2.1. Materials

CR, CV, and AC from unwashed lignite carbon (Darco®, 20–40 mesh, granular, Sigma #242268) used in this study were obtained from Sigma Chemical Co., USA. Hydrochloric acid (HCl, 35.0–37.0%) and sodium hydroxide (NaOH, 98.0%) were purchased from Samchun Pure Chemicals Co., Ltd., Korea. The raw biomass sources – RS, KC, WC – obtained from a local farm in Daejeon, Korea were collected and oven-dried at 105 °C for 24 h after which they were stored in dry air-tight glass jars at room temperature.

2.2. Preparation of biochar from biomass

The raw biomass feedstock was each pyrolysed in a fixed bed pyrolysis reactor system; cylindrical heater with 20 cm height × 17 cm outer diameter and a hollow inner (15.2 cm height × 7 cm diameter) with a 3 cm width lagged area. A cylindrical quartz reactor (26 cm height × 6 cm diameter) was charged with 15 g of the biochar precursor and the system run under nitrogen gas (N_2) at 200 mL/min. The heater temperature was increased steadily for 50 min at a rate of 10 °C/min and allowed to cool (within 150–180 min) still under N_2 flow to room temperature after being held at 500 °C for 60 min. The volatiles (bio-oil) were condensed by means of a water thermostat circulator connected to the condenser. The bio-oil and biochar were collected and their masses determined for yield computation. The biochars produced from each biomass (RS, KC and WC) and AC were ground with a mortar and pestle and sieved to within 300 μm to 710 μm size range. The sieved biochars were collected and kept in air tight 70 mL borosilicate glass vials and used for all successive adsorption experiments as well as in the biochar characterization.

2.3. Characterization of adsorbents

Characterization of the adsorbents before adsorption studies were analyzed for Brunauer-Emmett-Teller (BET) surface area (Micromeritics, Tri Star™ II 3020, USA), and porosity, pore volume and average pore area using a porosimeter (Micromeritics, Auto Pore IV 9520, USA). Surface functional group was analyzed by using a Fourier transform and infrared (FTIR) spectrophotometer (Thermo, Nicolet 6700, USA). Biochar and AC samples prior to FTIR analysis were finely ground to below 75 μm and mixed homogeneously with KBr. Images of the surface morphology were obtained using a scanning electron microscopy (SEM) instrument by Joel Ltd., model JSM-6390, USA. The surface elemental compositions were determined by using an energy dispersive spectroscopy (EDS) instrument by Oxford, ISIS (USA) coupled with the SEM analysis instrument. Total carbon, hydrogen and nitrogen in the biochars and AC were determined on dry ash-free basis using an elemental analyzer (Thermo Flash 2000, UK) and the oxygen content computed from the difference. Proximate analysis was conducted following the American Society for Testing and Materials (ASTM) standard – ASTM D1762-84 Chemical Analysis of Wood Charcoal – after modifications were effected to make room for biochar (Enders et al., 2012; Joseph et al., 2009). A muffle furnace (model SH-MF-C, Samheung energy, Korea) was rather used for the proximate analysis. The pH of biochar and AC were determined following the IBI Biochar Standards Version 2.0 using the Test Category A test methods. More specifically, 0.5 g each of AC and biochars were measured into different 20 mL borosilicate glass vials with 10 mL of deionized water [1:20 (w/v)] for a 90 min shaking incubating period (150 rpm; 30 °C). The pH determination was performed in two replicates.

2.4. Batch adsorption studies

Batch adsorption studies were performed with RS, KC, WC and AC for the removal of CR and CV from aqueous solutions. Specific dye concentrations of either CR or CV were prepared via dilutions of a previously prepared standard stock solution (10,000 mg/L) of