



Sorptive removal of methylene blue from simulated wastewater using biochars derived from pulp and paper sludge



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HIGHLIGHTS

- Fe₂O₃–biochar nanocomposite from pulp and paper sludge.
- Nanocomposite used to remove methylene blue from contaminated synthetic wastewater.
- Excellent methylene blue (MB) removal achieved.
- Activation increased the MB adsorption.

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ABSTRACT

Biochar (BC) and Fe₂O₃–biochar nanocomposite (NC) derived from pulp and paper sludge (PPS) were used to remove methylene blue (MB) dye from synthetic wastewater. Morphology characterization indicated heterogeneous adsorbent surfaces, and textural measurements showed BC and NC possessed pore size in the range 1.7–300 nm. Both these characteristics endowed the adsorbents with good sorption properties for MB. The maximum adsorption capacity of NC (50 mg/g) was higher than of BC (33 mg/g). This was attributed to the hybrid nature of NC where adsorption occurs both on the biochar matrix and Fe₂O₃ nanoparticles. MB adsorption data on BC and NC followed pseudo-second order ($r^2 = 0.958$) and pseudo-first order kinetics ($r^2 = 1.000$), respectively. Isotherm data for BC and NC followed the Freundlich ($r^2 = 0.801$) and Langmuir ($r^2 = 0.948$) isotherm models, respectively. Despite having lower adsorption capacities compared to other adsorbents reported in literature, the use of BC and NC for wastewater remediation is an ingenious way of reducing environmental and health risks associated with the current disposal of PPS while providing remediation of water contaminated with industrial dye effluents.

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1. Introduction

Dye effluents are emitted from a variety of industries including the food industry, tanneries, textile, plastics and pharmaceutical (Musyoka et al., 2014; Chaukura et al., 2016). However, the major source of dye waste water is the textile

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industry, where large quantities of dye are utilized annually. A single dyeing operation can use several dyes from different chemical classes resulting in a complex wastewater. A significant proportion of this amount is lost during the dyeing and printing processes and may be discharged into aqueous environments. Industrial dyes have complex structures, synthetic origin and recalcitrant nature and can be classified as anionic, nonionic and cationic dyes. The major anionic dyes are the acid and reactive dyes, and the most problematic ones are the brightly colored, water soluble acid dyes (Zaharia 2012; Aysan et al., 2016). Owing to their high solubility, non-degradable nature, diversity and often changing speciation in water, dyes cannot be removed through conventional treatment systems (Musyoka et al., 2014; Aysan et al., 2016; Luo et al., 2017). Besides being carcinogenic, small amounts of dye have visual impacts in water, decreasing light penetration and consequently influencing photosynthetic processes and affecting aquatic ecosystems (Jalil et al., 2010; Haque et al., 2011; Gong et al., 2013; Mittal et al., 2014; Musyoka et al., 2014). Therefore, removal of dyes in industrial effluents is critical for safeguarding aquatic ecosystems.

Techniques used for dye removal include sedimentation, filtration and flotation, membrane filtration, photodegradation as well as physicochemical methods such as precipitation and ion exchange (Haque et al., 2011; Musyoka et al., 2014). The major limitations associated with these techniques are that ion exchange, photodegradation and membrane filtration are expensive and have high complexity. Moreover, photodegradation has limited capacity to mineralize dyes, and thus produces toxic residues (Mittal et al., 2014; Musyoka et al., 2014). Adsorption is one method commonly used for dye wastewater remediation. Generally, the adsorption technique does not leave behind by-products, the adsorbent can easily be separated from water, and are exceptionally effective for the removal of dyes (Gong et al., 2013; Mittal et al., 2014; Musyoka et al., 2014; Aysan et al., 2016; Chaukura et al., 2016). Studies investigating the use of adsorption on dye removal focused on the use of adsorbents synthesized from virgin materials, for example zeolites (Aysan et al., 2016), grapheneoxide-based nanocomposites (Heidarizad and Şengör, 2016), metal organic frameworks (Luo et al., 2017), chitosan-based composites (Marrakchi et al., 2016), silica (Russo et al., 2016), and functionalized bakes yeast (Du et al., 2017). Other studies used biowastes such as spent coffee grounds (Jung et al., 2016), fox nutshells (Kumar and Jena, 2016), citrus limetta peel waste (Shakoor and Nasar, 2016). However, compared to adsorbents derived from virgin materials, there are few studies documenting the use of adsorbents derived from waste materials such as pulp and paper sludge. The commonly used adsorbent, commercial activated carbon, is costly and has low removal efficiency for dyes especially at neutral pH and in the presence of interfering pollutants (Kumar and Jena, 2016). The availability of large quantities of biowastes such as sawdust and agro-processing wastes (e.g. finger citron residues, coconut coir dust), provides a compelling case for using biosorbent for dye removal (Macedo et al., 2006; Zaharia, 2012; Gong et al., 2013). Biowastes are either disposed of as garbage or incinerated, causing potential environmental and public health risks. An attractive approach is to valorize the waste for use as an adsorbent. Converting biowastes into carbonaceous material, such as biochar which is cheaper to produce than activated carbon and can achieve dye removal within shorter contact times than raw biomass, may be a plausible approach.

Pulp and paper sludge (PPS), a waste generated from paper mills, has been investigated for the adsorption of a range of pollutants from wastewater including metals, pharmaceuticals, and organics (e.g. Alatalo et al., 2013; Coimbra et al., 2015; Devi and Saroha, 2015). While some work has been done on the synthesis of PPS derived adsorbents for removing organics (e.g. Calisto et al., 2014; Devi and Saroha, 2014), to date few studies have reported the use of adsorbents derived from PPS for the removal of dyes from wastewater. An exception is a recent study showing that a biochar-Fe₂O₃ nanocomposite had a methyl orange (MO) removal that was 52.79% higher than that for biochar derived from PPS (Chaukura et al., 2016). Unlike MO, which is an anionic dye, methylene blue (MB) (Fig. 1) is a monovalent cationic dye with applications in paper coloring, textile dyeing, hair colorant and as an indicator in analytical chemistry. Although MB is not very hazardous, higher concentrations can result in several detrimental health effects that include hypertension, fever, mental disorder, jaundice, and cyanosis (Gong et al., 2013; Mittal et al., 2014; Du et al., 2017). Therefore, to avoid these health risks it is necessary to remove MB from the contaminated water.

The main objective of this study was to evaluate the ability of a biochar (BC) and Fe₂O₃-biochar nanocomposite (NC) synthesized from PPS for the removal of MB from synthetic wastewater. We hypothesized that activation of BC through impregnation of PPS with Fe₂O₃ will increase the MB adsorption capacity compared to the pristine biochar.

2. Materials and methods

2.1. Preparation of adsorbents

Pulp and paper sludge obtained from a paper mill in Kadoma, Zimbabwe was processed according to a procedure described by Chaukura et al. (2016). Briefly, PPS was dewatered and the residue air-dried for 2 days before being oven dried at 70 °C for 24 h. The dried material was divided into two; the first part was tightly packed into a closed steel canister and pyrolyzed at 750 °C for 2 h to produce biochar (BC) (Gwenzi et al., 2014). The other part was soaked in a FeCl₃.6H₂O solution (80% w/v), at a mass-to-volume ratio of 1:3 for 2 h, and dried at 110 °C before being pyrolyzed at 750 °C for 2 h to produce the Fe₂O₃-BC nanocomposite (NC). Both BC and NC were pulverized and sieved with a 250-µm sieve and stored in sealed polyethylene sachets prior to use.

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