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Competitive effects of humic acid and wastewater on adsorption of methylene blue dye by activated carbon and non-imprinted polymers

*Audrey Murray, Banu Örmeci**

Department of Civil and Environmental Engineering, Carleton University, Ottawa, ON K1S 5B6, Canada

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ABSTRACT

Natural organic matter (NOM), present in natural waters and wastewater, decreases adsorption of micropollutants, increasing treatment costs. This research investigated mechanisms of competition for non-imprinted polymers (NIPs) and activated carbon with humic acid and wastewater. Three different types of activated carbons (Norit PAC 200, Darco KB-M, and Darco S-51) were used for comparison with the NIP. The lower surface area and micropore to mesopore ratio of the NIP led to decreased adsorption capacity in comparison to the activated carbons. In addition, experiments were conducted for single-solute adsorption of methylene blue (MB) dye, simultaneous adsorption with humic acid and wastewater, and pre-loading with humic acid and wastewater followed by adsorption of MB dye using NIP and Norit PAC 200. Both the NIP and PAC 200 showed significant decreases of 27% for NIP ($p = 0.087$) and 29% for PAC 200 ($p = 0.096$) during simultaneous exposure to humic acid and MB dye. There was no corresponding decrease for NIP or PAC 200 pre-loaded with humic acid and then exposed to MB. In fact, for PAC 200, the adsorption capacity of the activated carbon increased when it was pre-loaded with humic acid by 39% ($p = 0.0005$). For wastewater, the NIP showed no significant increase or decrease in adsorption capacity during either simultaneous exposure or pre-loading. The adsorption capacity of PAC 200 increased by 40% ($p = 0.001$) for simultaneous exposure to wastewater and MB. Pre-loading with wastewater had no effect on MB adsorption by PAC 200.

Introduction

Micropollutants released into the environment in wastewater effluent, contaminate freshwater resources and are harmful to humans and the environment (Ashby et al., 1997; Gillesby and Zacharewski, 1998; Bögi et al., 2003; Segner et al., 2003; Yang et al., 2006; Helfman, 2007; Bergman et al., 2013; Rochester, 2013). Micropollutants are present in wastewater at very low concentrations, typically in the order of parts per billion or parts per million. Treatment of micropollutants is challenging because wastewater effluents typically contain natural organic matter (NOM) at concentrations several orders of magnitude higher than that of the micropollutants. A significant fraction of the capacity of various treatment methods implemented to target micropollutants is consumed treating NOM instead.

Abbreviations: NOM, Natural organic matter; NIP, Non-imprinted polymer; MIP, Molecularly imprinted polymer; BET, Brunauer–Emmett–Teller; MB, Methylene blue dye.

* *Corresponding author*. E-mail: banu.ormeci@carleton.ca (Banu Örmeci).

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Molecularly imprinted polymers (MIPs) are specific, polymeric adsorbents. MIPs are designed to specifically target a one of a group of micropollutants and are able to remove micropollutants with high efficiency despite the presence of competition in natural waters (Meng et al., 2005; Zhongbo and Hu, 2008; Hajizadeh et al., 2010; Deng et al., 2009; Luo et al., 2011; Guo et al., 2011; Li et al., 2009; Yu et al., 2008; Lin et al., 2008; Krupadam et al., 2010; Le Noir et al., 2007a, 2007b; Fernández-Alvarez et al., 2009; Randhawa et al., 2007; Xie et al., 2011; Huang et al., 2015; An et al., 2008). Non-imprinted polymers (NIPs) are non-specific polymeric adsorbents typically prepared alongside MIP as a control.

Because NIPs are non-specific, they do not have the advantage of being able to specifically target a single compound and may experience competition from NOM in natural waters the same way that activated carbons do. Without the template possessed by MIP, NIPs are essentially sub-micron or nano-sized polymeric adsorbents, and their advantages are due to their small size, and large external surface area. Xie et al. (2011) found that NOM in river water and lake water interfered with adsorption of bisphenol A less for NIP than activated carbon, and Murray et al. (2011) found that NIP could reduce ammonia, total organic carbon, and chemical oxygen demand concentrations in wastewater without reduced adsorption of 17β estradiol. This suggests that NIP may possess an advantage over activated carbon in natural waters, however, further study is needed to understand this advantage.

NIPs are synthetic polymers, and their properties can be controlled by varying the monomer, cross-linker, or the amounts of each added (Sellergren, 1999; Masqué, 2001) as well as the temperature of polymerization (Ensing and De Boer, 1999; Yan and Row, 2006). An understanding of the differences between activated carbon and NIP, as well as the characteristics that lead to enhanced adsorption, can provide the information necessary to create NIP with better adsorption capabilities. If NIP indeed out-perform activated carbon in the presence of NOM, they could be used as adsorbents in their own right. If not, knowledge gained from this study could enhance the design of MIP. This research investigated the adsorption of methylene blue (MB) dye, similar in size to many micropollutants, from water containing humic acid and from wastewater with both NIP and activated carbon in an attempt to elucidate which characteristics of the NIP are important, and how to better design NIP for micropollutant removal.

1. Materials and methods

1.1. Materials

Three powder activated carbon samples were obtained from Cabot Norit: Norit PAC 200, Darco KB-M, and Darco S-51 (Marshall, TX). Functional monomer methacrylic acid (Sigma-Aldrich; Oakville, Canada) and cross-linker ethylene glycol dimethacrylate (Sigma-Aldrich; Oakville, Canada) were dissolved in a porogen with a molar ratio of 1:8:6.7 (Wei et al., 2006). The porogen was composed of 40 mL of 1:3 (V/V) acetone (Fisher Scientific; Ottawa, Canada), and acetonitrile (Fisher; Ottawa, Canada). Two percent (W/W) of 2-isobutyronitrile was added as the initiator (Sigma-Aldrich; Oakville, Canada). The mixture was mixed with a vortex mixer (Fisher Scientific Vortex Mixer, USA), deoxygenated with nitrogen for 5 min, and then placed in a 60°C hot water bath for 24 hr (Isotemp 220, Fisher, USA). The resulting polymer particles were dewatered using a centrifuge (Thermo Scientific Sorval Legend RT+, Fisher Scientific) at 10,000 r/min, air dried at room temperature, and ground manually.

BET (Brunauer–Emmett–Teller) surface area, average pore size, pore volume, and mesopore volume were measured by Engineering Performance Solutions (Jacksonville, FL). Quenched Solid Functional Theory and Barret–Joyner–Halenda analyses were performed using a NOVA BET surface analyzer.

A Suwannee River Humic Acid sample (Suwanee River Humic Acid II) was purchased from the International Humic Substances Society (St. Paul, Mn).

1.2. Wastewater

Secondary wastewater effluent was collected from the Robert O. Pickard Environmental Centre in Ottawa, Ontario. It was stored in the refrigerator and then left at room temperature overnight prior to use.

1.3. Single-solute adsorption

Adsorption isotherm tests were conducted to evaluate removal of MB dye from deionized water using NIP, Norit PAC 200, Darco KB-M, and Darco S-51. One hundred fifty milliliter amber glass bottles were filled with 50 mL of deionized water spiked with 10, 12, 14, 16, 18 or 20 mg/L of MB dye. Fifty gram per liter solutions were prepared for the NIP and three activated carbons at pH 7, and sonicated (Vibracell Sonics, Sonics and Materials Inc., Newtown Connecticut) for 15 min to disperse the particles. One milliliter of the NIP solution or 0.1 mL of each activated carbon solution was then added to each sample bottle to obtain final concentrations of 0.1 g/L for the activated carbons and 0.5 g/L for the NIP. The samples were mixed on a shaker table (New Brunswick Scientific Excella E1 Platform Shaker, New Brunswick Scientific Inc) for two weeks. They were then centrifuged (Thermo Scientific Sorval Legend RT+, Fisher Scientific) for 1 hr at a speed of 10,000 r/min (670,800*g*). Following centrifugation, the centrate was poured into 15 mL centrifuge bottles and analyzed with a UV–visible spectrophotometer (Cary 100, Varian) using a scan from 200 to 800 nm. Peaks for MB dye were identified at 663, 291, and 246 nm and calibration curves were created for these three wavelengths. A wavelength of 663 nm was selected for experiments because there were no corresponding peaks from either wastewater or humic acid at this wavelength. Blank samples were created with the adsorbents in the sample waters, and all values were zero for 663 nm.

1.4. Simultaneous loading

Isotherm experiments were conducted using MB in a 20 mg/L humic acid solution and secondary wastewater effluent. Samples were adjusted to pH 7 using sodium hydroxide and hydrochloric acid prior to addition of MB. The procedure

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