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

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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.

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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.

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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 (670,800g). 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

outlined above for single-solute adsorption was then followed using NIP and Norit PAC 200 as adsorbents.

1.5. Pre-loading

Isotherm experiments were also conducted using NIP and Norit PAC 200 that were first exposed to humic acid or wastewater solutions and then subsequently exposed to MB. Fifty milliliters of the 20 mg/L humic acid solution or secondary wastewater effluent was added to 150 mL amber glass bottles. NIP or Norit PAC 200 was added to obtain final concentrations of 0.5 or 0.1 g/L, respectively. The bottles were placed on a shaker table (New Brunswick Scientific Excella E1 Platform Shaker; New Brunswick Scientific Inc.) for 24 hr at room temperature and 200 r/min. Following the 24 hr adsorption period, the samples were centrifuged (Thermo Scientific Sorval Legend RT+; Fisher Scientific) in 50 mL centrifuge tubes for 1 hr at 10,000 r/min (670,800×g). Fifty milliliters of deionized water with MB ranging from 10 to 20 mg/L was added to the centrifuge tubes, and they were shaken to disperse the particles. The solution was then poured into 150 mL amber glass bottles, shaken on a platform shaker for two weeks at room temperature and 200 r/min, and centrifuged, and the centrate was analyzed using UV–visible spectrophotometry.

Pre-loading was conducted for 24 hr because it was not necessary for the pre-loaded adsorbents to be at equilibrium, and 24 hr provided ample time for the initial, fast phase of adsorption to occur, providing competition for the dye added in the second step of experiments.

1.6. Zeta potential

Zeta potential tests were conducted on samples of NIP and PAC 200 alone in water, with humic acid in water, and pre-loaded with humic acid to determine the effect of the humic acid on the surface charge of the particles. A Zeta Meter 4.0 (Zeta-Meter Inc., Staunton, Virginia) was used for zeta potential measurements with a voltage of 300 V. Twenty particle replicates were taken. Tests were conducted at pH 7.

2. Results and discussion

2.1. Adsorbent characterization

NIP, Norit Darco KB-M, Norit PAC 200, and Norit Darco S-51, were studied. The BET surface area, average pore size, total pore volume, micropore volume, mesopore volume, and ratio of micropore volume to mesopore volume for each adsorbent are provided in Table 1. The NIP had the smallest BET surface area of the four adsorbents studied. The NIP also had the smallest ratio of micropore volume to mesopore volume (0.12), meaning that most of their pore volume was contained in larger rather than smaller pores. In contrast, PAC 200, had the highest ratio of micropore volume to mesopore volume (2.87). Generally, a higher surface area enhances adsorption, and a higher micropore volume is favorable for adsorption of micropollutants because micropollutants preferentially adsorb in smaller pores (Newcombe and Drikas, 1997; Pelekani and Snoeyink, 1999, 2000; Newcombe et al., 2002; Ding et al., 2008; Redding and Cannon, 2014).

2.2. Single-solute adsorption

MB was used as a model compound for organic micropollutants. MB is similar in size to many organic micropollutants and is able to penetrate into the same pores and occupy the same adsorption sites. Pelekani and Snoeyink (2000) studied competitive adsorption between MB and atrazine and found that MB was able to compete directly for adsorption sites with atrazine. MB is a good model compound for experiments because it can be measured easily using UV–vis absorbance.

Fig. 1 provides a plot of the adsorption capacity *versus* the initial concentration of MB. The initial MB concentration was plotted instead of the equilibrium liquid phase concentration because the equilibrium liquid phase concentration was constant with changing adsorption capacity, and a plot provided no additional information. This can occur for Langmuir isotherms with high solute concentrations. At high solute concentrations, the particles experience maximum coverage, which cannot increase with increasing solute concentration (Kammerer et al., 2011). Linear trends were observed for all adsorbents when the adsorption capacity was plotted *versus* the initial MB concentration. The percent of MB dye removed remained constant for each of the four adsorbents as the initial concentration was increased, leading to a linear increase in the adsorption capacity with increasing concentration. The adsorption capacities plotted represent the average of three experimental replicates, and the error bars represent the standard deviation. For PAC 200 and Darco KB-M, the error bars were large. Considering that the same procedure was also followed for Darco S-51 and the NIP, and they showed less variability between replicates, the variation is likely due to heterogeneity in the activated carbons themselves.

Referring to Fig. 1, PAC 200 adsorbed the greatest mass of MB per mass of adsorbent, followed by Darco KB-M, Darco S-51, and finally NIP. Theoretically, the adsorbent with the

Table 1 – Adsorbent characterization.						
	BET surface area (m^2/g)	Pore size (Å)	Pore volume (cm^3/g)	Mesopore volume (cm^3/g)	Micropore volume (cm^3/g)	Micropore volume/ mesopore volume
NIP	3.4	73.06	0.0125	0.0112	0.0013	0.12
Darco KB-M	992.7	20.12	0.9989	0.5872	0.4117	0.70
PAC 200	961.8	11.44	0.5502	0.1421	0.4081	2.87
Darco S-51	599.5	25.5	0.7643	0.5041	0.2602	0.52
BET: Brunauer–Emmett–Teller; NIP: non-imprinted polymer.						
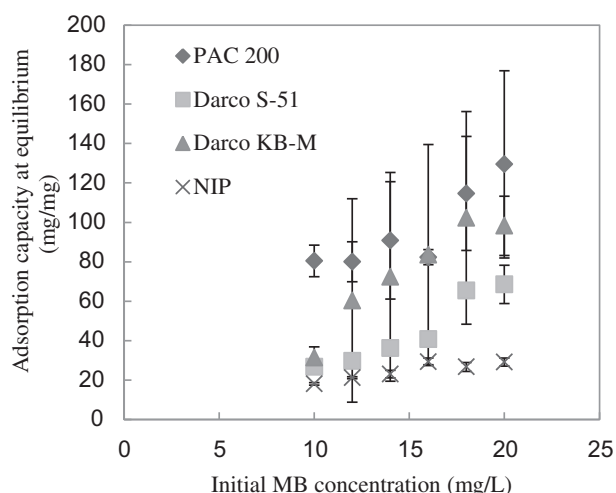
Fig. 1 – Adsorption capacities of activated carbons (Norit PAC 200, Darco KB-M, and Darco S-51), and non-imprinted polymers (NIPs) for varying initial Methylene Blue (MB) concentrations in deionized water.

greatest surface area should have the greatest adsorption capacity, but the distribution of pore sizes is also important. In fact, Wang et al. (2005) found that surface area and pore volume had little effect on MB adsorption by activated carbon, which was instead controlled by the pore size distribution and chemical characteristics. The BET surface area followed the order: Darco KB-M > PAC 200 > Darco S-51 > NIP. On the other hand, the average pore sizes followed the order: PAC 200 < Darco KB-M < Darco S-51 < NIP. The observed performance order followed the order predicted by the pore sizes, with increasing adsorption capacities correlating well with decreasing pore size.

This is important if NIP is to be used as an adsorbent for water and wastewater treatment. The NIP particles were only 292 ± 147 nm in diameter. They have a high surface area on the surface of the particles due to their small size, but it is still not enough to compete with the large surface area possessed by the activated carbons due to their internal porous structure. As provided in Table 1, the NIPs have a surface area of 3.4 m^2/g while the activated carbons had surface areas of 992.7, 961.8, and 599.5 m^2/g for Darco KB-M, PAC 200, and Darco S-51, respectively. The disadvantage posed by the lower surface area is apparent in Fig. 1, where it is clear that all three of the activated carbons have a higher adsorption capacity than the NIP. The large area on the outer surface of the NIP alone does not allow them to compete with activated carbon; they also require a greater pore volume to further increase their surface area and adsorption capacity. The solvent in which the NIPs are created is called a porogen, and the chemistry of the porogen, as well as the amount used, can control the pore morphology and volume (Cormack and Elorza, 2004). Creating NIP particles with a greater specific surface area, smaller average pore size, and greater pore volume should increase adsorption.

2.3. Competitive adsorption with humic acid

NOM, present in natural waters and wastewater, can reduce the adsorption capacity of activated carbons by one or two

orders of magnitude, and can also decrease the rate of adsorption (Pelekani and Snoeyink, 1999). Humic acid represents one fraction of the NOM present in natural waters, typically the larger diameter fraction (Newcombe, 1994). The humic acid used in this study was Suwannee River Humic Acid, chosen because it has been widely characterized. Several researchers have measured the average molecular weight of Suwannee River Humic Acid by number and by mass, and the averages of these recorded values are 1716 ± 478 (by number) and 3303 ± 904 g/mol (by mass) (Perdue and Ritchie, 2003).

The Suwannee River Humic Acid was combined with MB to investigate the competition between humic acid and MB for activated carbon and NIP. PAC 200, the best-performing activated carbon based on single-solute experiments, was studied alongside NIP for competitive experiments.

In general, there are two mechanisms for competition between NOM and micropollutants: direct site competition and pore-blocking. Direct competition typically occurs when the adsorbate and NOM are similar in size and capable of occupying the same adsorption sites. In this case, the humic acid had an average molecular weight of 1716 ± 478 (by number) or 3303 ± 904 g/mol (by mass) whereas MB has a molecular weight of 284 g/mol. It is unlikely that the humic acid would be capable of occupying the small pores energetically preferred by the MB molecules. Ebie (1995) found that volumes of pores ranging from 30 to 100 Å correlated best with adsorption of humic acid. As stated previously, Pelekani and Snoeyink (2000) found that adsorption of MB correlated well with micropore sizes close to 7.5 Å.

Three different adsorption scenarios were investigated to elucidate the competitive mechanisms involved for NIP and activated carbon: (1) single-solute adsorption, where adsorption experiments were conducted in deionized water with no competition from humic acid, (2) simultaneous adsorption experiments, were humic acid and MB dye were adsorbed simultaneously, and (3) pre-loading experiments, where adsorption of MB onto adsorbents that already contained adsorbed humic acid was investigated. Decreased adsorption capacity observed during simultaneous adsorption can be indicative of either direct competition or pore-blocking (Pelekani and Snoeyink, 1999). A further decrease in adsorption performance following pre-loading with NOM, or exposure to NOM prior to exposure to the target adsorbate, is indicative of pore-blocking (Pelekani and Snoeyink, 1999).

A series of t-tests with 90% confidence limits were used to conduct paired comparisons of means for changing initial MB concentrations for single-solute and competitive adsorption scenarios. Fig. 2 shows the adsorption capacity for NIP and activated carbon for single-solute, simultaneous adsorption, and pre-loading scenarios.

For the NIP, adsorption was 27% (p = 0.087) lower with humic acid during simultaneous loading as compared to single-solute adsorption. Interestingly, the pre-loaded sample out-performed the simultaneously exposed sample, and pre-loading with humic acid had no significant effect on adsorption of MB dye. The NIP samples pre-loaded with humic acid performed 26% (p = 0.057) better than those simultaneously exposed to humic acid and MB.
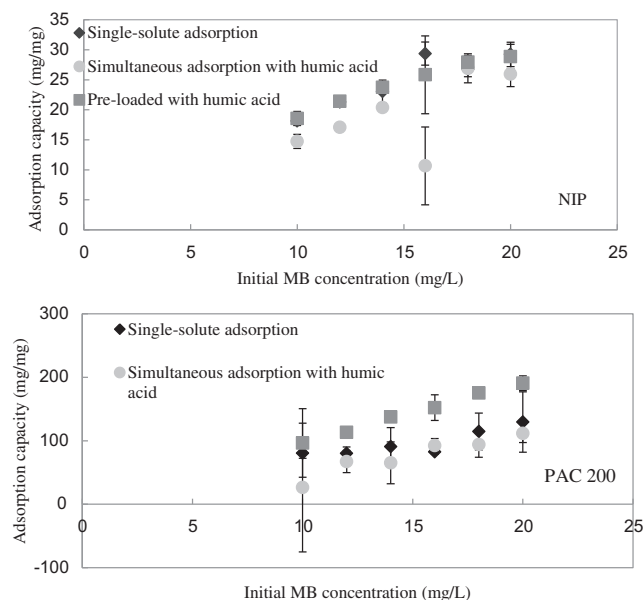
Fig. 2 – Comparison between single-solute adsorption of MB, simultaneous adsorption with humic acid, and pre-loading with humic acid for NIP and PAC 200. The adsorption capacities are averages of three experimental replicates, and the error bars represent the standard deviations.

Pelekani and Snoeyink (2000), observed a similar phenomenon, where adsorption capacity increased for pre-loaded samples. They investigated the adsorption of atrazine for activated carbons pre-loaded with Congo Red dye, which is a much larger molecule than atrazine. They concluded that the increased adsorption was due to desorption of pore-blocking Congo Red dye, where desorption of relatively few molecules can increase performance. The difference could also be caused by interactions between the activated carbon surface, humic acid, and MB. The humic acid contained both carboxyl and phenolic functional groups (International Humic Substances Society, 2015). The MB dye may have interacted with these functional groups and adsorbed onto the humic acid.

Similarly, for PAC 200, adsorption was 29% lower with competition from humic acid during simultaneous loading, but the pre-loaded sample out-performed the simultaneously loaded sample by 66% ($p = 0.0008$). In fact, the pre-loaded PAC 200 subsequently adsorbed 39% ($p = 0.0005$) more MB than was adsorbed during single-solute experiments. This is clearly indicative of interactions between adsorbed humic acid and MB. Humic acids behave as polyelectrolytes in solution and have been shown to change the surface charge of activated carbons, making them more negative (Newcombe, 1994). This could reasonably increase adsorption of a cationic dye such as MB. It does not mean that there was no competition for adsorption sites or pore-blocking, but that the system was too complex to determine the degree of competition. Huang et al. (2016) found that both porosity and surface chemistry of activated carbons were important, additionally, the porosity of the activated carbon could affect the surface chemistry in water.

2.4. Competitive adsorption with wastewater

NOM, present in water and wastewater, can reduce the adsorption capacity of adsorbents by competing for adsorption sites or blocking pores. Competition with humic acid was studied because the sample was well-characterized, and, although the variability was large, the average molecular weight of the humic acid was known. However, humic acid represents only one fraction, typically the larger diameter fraction, of the NOM present in wastewater, and wastewater also contains other components which also compete with MB during adsorption (Newcombe, 1994). Most significantly, it contains smaller molecules capable of accessing smaller pores occupied by MB. Adsorption of MB from wastewater using adsorbents pre-loaded with wastewater was examined to further evaluate competitive effects for NIP and PAC 200.

A series of t-tests with paired comparisons of means were used to compare the amount of MB adsorbed from deionized water, secondary wastewater effluent, and from deionized water using adsorbents pre-loaded with secondary wastewater effluent. Fig. 3 shows the amounts adsorbed for increasing MB concentrations for NIP and PC 200.

For the NIP, there was no significant difference for a 90% confidence limit in performance for simultaneous ($p = 0.14$) or pre-loading ($p = 0.3$) with wastewater in comparison to deionized water. In fact, 20 mg/L of humic acid, which
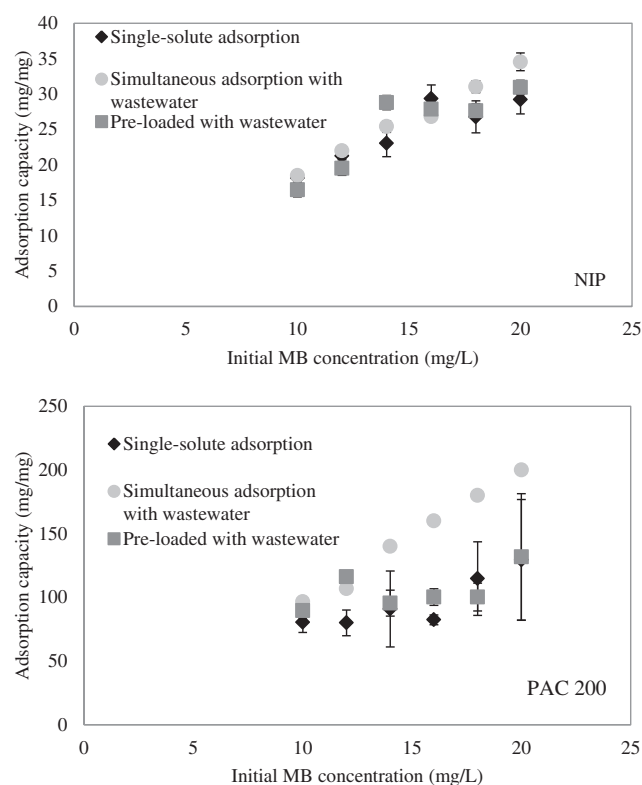
Fig. 3 – Comparison between single-solute adsorption of MB, simultaneous adsorption with wastewater, and pre-loading with wastewater for NIP and PAC 200. Data points are averages of three experimental replicates, and the error bars represent the standard deviations.

decreased the adsorption capacity by 27% ($p = 0.09$) during simultaneous loading, had a more detrimental effect on MB adsorption onto NIP than the wastewater did. Humic acid has been shown to adsorb best in pores ranging from 30 to 100 Å (Ebie, 1995), and the average pore size of the NIP was 73 Å, which is within that range. Competitive adsorption of humic acid onto NIP may have been greater than that of wastewater for that reason. The wastewater contained a greater distribution in molecular size, and thus would have competed for a greater distribution of pore sizes.

For PAC 200, simultaneous adsorption of MB from wastewater was 40% ($p = 0.001$) higher than from deionized water and was significant for a 90% confidence limit. An increase in adsorption in the presence of competition was also seen for humic acid. Adsorption of NOM from wastewater can increase the negative surface charge of the adsorbent (Newcombe, 1994) and increase adsorption of MB, which is a cationic dye. For PAC 200 pre-loaded with wastewater, there was no significant difference in adsorption as compared to deionized water. This could have been due to an absence of competition or enhanced adsorption caused by changes in the surface charge of the adsorbents hiding the negative effects of competition.

It is clear from this work that experiments into competitive mechanisms between micropollutants and NOM cannot ignore the effects of surface chemistry and surface charge. In this case, those effects became clear because the change in surface charge likely enhanced adsorption. However, it is possible for those changes to decrease adsorption instead (Newcombe, 1994), in which case they would be indistinguishable from competitive effects.

2.5. Effect of zeta potential on adsorption performance for NIP and PAC 200

Both NIP and PAC 200 showed significant decreases during simultaneous exposure to humic acid and MB, but there was no significant decrease for NIP pre-loaded with humic acid, and pre-loaded PAC 200 showed a significant increase in performance. These increases may have been due to an increase in the negative surface charge of the adsorbents due to adsorbed humic acid, leading to increased adsorption of MB dye, which was a cationic dye. To further investigate the effect of surface charge on adsorption, the zeta potentials were measured for: (1) NIP and PAC 200 in deionized water; (2) NIP and PAC 200 in 20 mg/L of humic acid; and (3) NIP and PAC 200 pre-loaded with 20 mg/L of humic acid. Fig. 4 shows the zeta potential measurements for each case.

The error bars, indicating the standard deviation, for some of the zeta potential measurements were large because the NIPs were very small and difficult to see with the zeta potential microscope, and the activated carbon did not reflect light uniformly and, although the particles were easily visible, they tended to blink. There was also a noticeable difference in the speed at which individual particles traveled when the voltage was applied, for this reason, 20 replicates were taken.

Although the change was within the range of the error bars, Fig. 4 shows that both the PAC 200 and NIP particles become more negative in humic acid or when pre-loaded with humic acid than in water. Due to the size of the error bars, it is not possible to say conclusively that the particles became
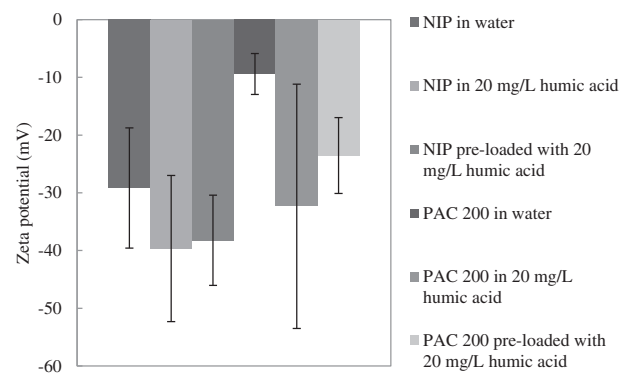
Fig. 4 – Effect of humic acid on the zeta potential of NIP and PAC 200.

more negative, but the zeta potential measurements do support the results obtained during single-solute and competitive adsorption of MB. Humic acid was expected to significantly decrease the performance of both the activated carbon and NIP both during simultaneous adsorption with MB and when pre-loaded. However, although there was a significant decrease for simultaneous adsorption, there was no corresponding decrease for pre-loaded adsorbents. The zeta potential suggests that this may have been because the humic acid increased the negative surface charge of the adsorbents, and increased adsorption of MB. The decrease observed for simultaneous adsorption of MB, and humic acid suggests that the humic acid competed with MB for adsorption sites or by blocking pores, decreasing adsorption, while also potentially increases the negative surface charge, increasing adsorption. For pre-loaded activated carbon, the increase in adsorption caused by the increase in the negative surface charge may have canceled out any competitive effects, leading to no significant difference between competitive adsorption and single-solute adsorption.

3. Conclusion

This study compared NIP with three activated carbons (Norit PAC 200, Darco KB-M, and Darco S-51) for adsorption of MB dye from water. Characterization of the NIP and the three activated carbons revealed that the NIP had a much smaller surface area of 3.4 m^2/g compared to the powder activated carbons which ranged in surface area from 599.5 to 992.7 m^2/g. The NIP also had a smaller ratio of micropores to mesopores. The micropore to mesopore volume was 0.12 for the NIP *versus* 0.52 to 2.87 for the three activated carbons. The lower surface area and micropore to mesopore ratio of the NIP led to decreased adsorption capacity in comparison to the activated carbons. More porous NIP should be created to enhance their adsorption capacity. The NIPs were also compared to Norit PAC 200 for adsorption of MB dye with competition from humic acid and wastewater. The hypothesis was that NIP would be less affected by pore-blocking than activated carbon. Competition occurred either during simultaneous exposure to the humic acid or wastewater and MB dye or pre-loading with humic acid or wastewater followed by subsequent adsorption of MB dye. 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. Interestingly, there was no corresponding decrease, considering a 90% confidence limit, 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% ($p = 0.0005$). This may have been due to an increase in the negative surface charge of the activated carbon caused by adsorbed humic acid. For wastewater, the NIP showed no significant increase or decrease in adsorption capacity during either simultaneous exposure or pre-loading for a 90% confidence limit. 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. The results of this study indicated that more porous NIP should be created by modifying the preparation steps to enhance their adsorption capacity for wastewater treatment applications.

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