Influence of humic acid on adsorption of methylparaben from aqueous solutions onto commercially available granular activated carbons

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Abstract
The adsorption of methylparaben (MP) on Calgon carbon (F400) and Norit-type granular activated carbons (GACs) from aqueous solutions was examined. The influence of humic acid (HA) on the adsorption of MP under different pH conditions was evaluated. The adsorption isotherm results are well described by the Freundlich model. The MP adsorption capacity on F400 and Norit GACs was found to be 150 mg/g. In the presence of 2.357 mg/L HA total organic carbon (TOC), the maximum MP adsorption capacity on F400 GAC at pH 7 was increased to 2.2 folds. The Norit-type GAC had a comparatively higher uptake capacity of MP than F400 GAC. The key mechanism for MP adsorption onto the F400 GAC was through the hydrogen interaction between the –OH functional group of the MP molecules. The MP adsorption capacity on Norit GAC was increased from 5 to 100 mg/g at pH 7.

Keywords: Humic acid, Methylparaben, Adsorption, F400 GAC, and Norit GAC
1. Introduction

Preservatives are organic compounds widely used in food, cosmetics, pharmaceuticals, and personal care products. Because of their wide range usage, preservatives constitute a class of emerging contaminants (ECs), commonly detected in trace amounts (μg/L and ng/L) in surface, sub-surface, coastal, and drinking water [1-3]. Parabens belong to a group of alkyl esters of p-hydroxybenzoic acid. They are most commonly consumed as preservatives due to their broad spectrum of antibacterial activity, good performance in a wide pH range, and low cost [4]. Methylparaben (MP) and propylparaben (PP) are the two most frequently used preservatives among them. The potentially threatening and undesirable effects of parabens on aquatic organisms and human health (such as estrogenic effects and breast cancer) have become an environmental issue and a major concern worldwide [5-7].

Most of the studies on paraben have assessed their side effects on human health [6,8]. Others have focused on paraben detection, modification, and measurement methods at low concentrations in aquatic environments [9-11]. Lincho et al. [4] reviewed several reported results of the detected parabens in different water sources, and influent and effluent of sewage treatment plants from different locations worldwide with concentrations in the range of ngL⁻¹ or greater value around 100 μgL⁻¹. Assessments of paraben removal techniques in wastewater treatment systems indicate that despite parabens degradation, they are still frequently detected in water resources in the range of ng/L concentrations [12]. The average removal efficiency is about 90% for biological treatments, however, the amount of parabens absorbed by the process sludge and other parabens losses are not reported [5]. Considerable paraben amounts are detected in some biological process outlet streams [13-15]. Some chlorinated derivatives are produced from the reactions between parabens and the free chlorine ions present in water, which are even more poisonous and resistant to biodegradation than the parent paraben molecules [16]. This secondary chemical production is the main challenge
for paraben treatments using the application of advanced oxidation processes [17].

Few studies have addressed the adsorption on paraben. β-cyclodextrin based polymer was applied for the adsorption of paraben [18]. Amino-modified magnetic nano-adsorbent was tested for the adsorptive removal of parabens attaining up to 98% removal efficiency [19]. Bernal et al. have found that π-stacking between basic activated carbon and MP molecule functional groups is the main mechanism governing MP adsorption on activated carbon [20]. The adsorption capacity of MP onto three types of activated carbons was evaluated and related to the textural characteristics and the content of surface phenolic and lactonic groups of the activated carbons [21,22]. Equilibrium adsorption experiments of MP and PP with the commercial PAC Pulsorb PWX HA was shown a maximum adsorption capacity in the range of 155 ± 12 mg g⁻¹ for both parabens, while in bicomponent experiments competitive adsorption plays a significant role in decreasing the MP adsorption [23]. A major component of naturally occurring dissolved organic carbons is humic acid (HA). HAs are the fraction of humic substances not soluble at pH lower than 2, but soluble at higher pHs in an aqueous solution [24]. Although coagulation, settling, and sand filtration are the most frequently used drinking water treatment processes, the natural organic matter (NOM) removal efficiency is limited to within 20 to 50% of typically dissolved humic substances [25]. The granular activated carbon (GAC) based adsorption process is an effective treatment for removing NOM and enhancing drinking water quality [26]. Several studies have evaluated the influence of HA on ECs adsorption behavior onto various types of adsorbents [27-30]. The interaction of HA and ECs and their adsorption mechanisms are not well known and the influence of NOM on paraben adsorption is not well investigated. Simultaneous MP and NOM removal through the adsorption process requires experimental assessment to make decisions about potential treatment applications for water treatment plants.

This study examines the adsorption behavior of MP on Calgon carbon (F400) and Norit-type
GACs in HA-containing water to determine an effective treatment method for paraben removal in the presence of NOM in drinking water. These GACs were widely used in many water and wastewater treatment plants and frequently referred to in the literature as the effective adsorbents for the removal of ECs from aqueous media.

2. Materials and methods

2.1. Chemicals, reagents, and granular activated carbons

Analytical reagent (A.R) grade MP with a technical purity of 99.9% was purchased from Sigma-Aldrich, Germany. Solid powdered commercial-grade HA was procured from Sigma-Aldrich, Switzerland. All other chemicals used during the study were of A.R grade and purchased from Merck, Germany. Two types of commercial GACs viz. Filtrasorb-400 (F400) and Norit PK 1-3 (NPK) were purchased. Filtrasorb-400 is a coal-based steam GAC supplied by Calgon Carbon Asia Pte Ltd. and Norit PK 1-3 (NPK) was produced from peat by Norit Americas Inc. (USA) and purchased from Sigma-Aldrich, Germany. The surface properties of these adsorbents are presented in Table 1. The GACs were rinsed several times with deionized (D.I) water to remove dissolved contaminants and fine particles and then dried at 105 °C for 48 h before storage in a desiccator.

2.2. Analytical techniques

The physiochemical properties of the adsorbents are characterized by employing BET surface area, pore size distribution, Fourier-transform infrared spectrometry (FT-IR), and pH_{pzc} value. The Brunauer-Emmett-Teller (BET) surface area analyzer (Microtrac Bel Corp, Model Belsorp mini, Japan) was used to determine the textural parameters such as surface area (S_{BET}), total pore volume (V_{tot}), micropore volume, supermicropore (0.7-2 nm) volume (V_{supermic}), ultramicropore (<0.7 nm) volume (V_{ultramic}) and mesopore volume (V_{meso}). The FT-IR spectrometer (Nicolet-Iso50, Thermo Electron, USA) was applied to identify the GACs surface functional groups. The surface morphology of the GACs was observed by a scanning electron microscope (SEM) (Model
QUANTA200 ESEM, FEI company, USA). The pH drift method was used to determine the pH\textsubscript{pzc} of GACs according to the technique presented by Rivera-Utrilla et al. [31].

### 2.4. Methylparaben and humic acid concentration determination

The MP concentration was measured by using high-pressure liquid chromatography (HPLC) and a chromatograph Alliance Water 2695 separations module equipped with a water 2487 UV detector. Aliquots of 100 μL were injected into the HPLC. The isocratic mobile phase was a mixture of 40:60 (v/v) acetonitrile/D.I water at a flow rate of 1.0 ml/min, and the effluent was detected at 256 nm.

The HA concentration was determined by total organic carbon (TOC) measurement using a Shimadzu V-570 TOC analyzer. To determine the HA concentration in the solutions spiked with both of the pollutants, the solution TOC and MP concentration were measured. Concentration was determined using the results obtained from the HPLC chromatography followed by applying a calibration curve relating the MP TOC to its measured concentration for the MP contaminated solutions. The solution’s HA TOC was obtained by subtracting MP TOC from the solution’s TOC.

### 2.5. Batch adsorption experiments

To prepare the HA stock solution, 0.15 g of HA was dissolved to 1 L of D.I water at the pH value of the solution. The mixture was then ultrasonicated for an hour. The supernatants were filtered through a 0.22 μm PTFE syringe filter to remove the undissolved HA particles and then examined for HA concentration. Methylparaben stock solution (200 mg/L) was prepared by dissolving 0.2 g MP in 1 L of D.I water. A series of 100 mL amber glass bottles containing 0.01 to 0.5 g of GAC per 50 ml of the solution was prepared. The stock solutions were added to each bottle and diluted with a predetermined amount of D.I water to provide 50 ml spiked solutions. The solution's pH was adjusted from 4 to 10 using NaOH (0.1 M) and HCl (0.1 M) and measured using a pH meter (Orion Star Series, Thermo Electron, USA). All bottles were tightly sealed and incubated
(immersed in a thermostatic bath) at 25±1°C and shaken at 100 rpm. The adsorbents were then separated by centrifugation at 8,000 rpm for 10 min. The concentrations of MP and HA at equilibrium were analyzed. The pollutants’ adsorption capacity at equilibrium ($q_e$, mg/L) was calculated as follows [32]:

$$q_e = \frac{(C_0 - C_e)V}{M}$$

(1)

where, $C_0$ (mg/L) and $C_e$ (mg/L) are the initial and equilibrium pollutants’ concentrations, respectively, $V$ is the volume of the solution (L), and $M$ is the mass of the adsorbents (g).

These experiments are categorized into the following three sets, where the effects of the solution pH, GAC type and concentration, initial concentration of MP and HA on the equilibrium adsorption behavior of the pollutants were assessed:

1. Equilibrium monocomponent adsorption assessment of MP and HA from spiked solution onto the GACs.

2. Fractional equilibrium adsorption assessment of MP and HA from the spiked multicomponent solution onto the GACs, simultaneously. The initial concentrations of MP and HA were considered 30 ppm and 2.357 ppm TOC, respectively. This equilibrium set model concentration is addressed as a typical real condition.

3. Competitive equilibrium adsorption assessment at the same TOC concentrations (2.357 ppm) of MP and HA from spiked solution onto the GACs. The fractional adsorption potential of the pollutants was assessed to compare the effect of the pollutants’ nature.

All of the experiments were independently run in duplicate at 25°C and pH 5, 7, and 9. The results from the three assessments provided many insights into the MP adsorption mechanisms for
aqueous solutions in the presence or absence of HA.

3. Results and discussion

3.1. Characterization of granular activated carbons

The respective BET surface areas of F400 and Norit GACs were 1034 and 682 m²/g (Table 1). The total pore volume (0.53809 cm³/g) and mesopore volume (0.18608 cm³/g) of F400 GAC were higher than that of Norit GAC. The F400 GAC and Norit GAC have a $V_{\text{supermic}}$ of 0.2246 and 0.1211 cm³/g, respectively. The ultramicropore volumes were similar for both of the GACs.

Nitrogen adsorption-desorption isotherms at 77 K for GACs are illustrated in Figure 1(a). The isotherms showed that F400 GAC had greater nitrogen adsorption than the Norit GAC. The isotherms can be classified as I–H4 hybrid type isotherms due to the hysteresis cycle characterization, which is associated with capillary condensation inside mesopores and narrow slit pores in the micropore region. The pore size distribution plots of the GACs, obtained using a DFT method are shown in Figure 1(b). The bimodal distribution, related to an intensive peak for the micropores-ultramicropores, and the broader range is related to the mesoporosity of the materials.

The FT-IR spectra of GACs are presented in Figure 1(c). The two spectra exhibit a similar profile for carbonaceous materials. Two distinct broad and intense absorption bands for both F400 and Norit GACs at 3,440 and 3,140 cm⁻¹ confirmed the presence of the hydroxyl (O–H) group. The absorption bands at 2,916 and 2,849 cm⁻¹ indicate the asymmetric and symmetric C-H stretching vibrations of alkane groups -CH₃ and -CH₂- [33]. The absorption bands within the 1,536 to 1,634 cm⁻¹ range can be attributed to the C=C stretching vibration of the aromatic ring structures [34]. An intense peak appears for both GACs at 1,400 cm⁻¹, indicating the C-O and C=O bending absorption of carboxylic groups [35]. The bands within the 1,091 to 1,124 cm⁻¹ range correspond to the C–O
stretching vibration of ether groups [36].

The surface morphology of F400 and Norit GACs was captured by SEM micrograph and the images are shown in Figure 2((a) and (b)) and Figure 3((a) and (b)), respectively. It is observed that the S_BET of F400 GAC is higher than that of Norit GAC.

3.2. Humic acid adsorption kinetics

A kinetic study was performed to assess the time required for achieving HA adsorption equilibrium. The HA adsorption kinetics on F400 GAC is illustrated in Figure 4(a). The kinetics experiment was performed at 0.004 g adsorbent/ml of solution, 2.357 mg/L HA initial concentration, at a pH of 7 and temperature 25°C. Results indicate that equilibrium was achieved after two weeks. The pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models, as follow by Eqs. (2) and (3), respectively, were applied to fit the HA adsorption kinetics data.

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

(2)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}
\]

(3)

where, \(q_e\) is the equilibrium quantity of adsorption and \(q_t\) is the adsorption quantity at time \(t\), and \(k_1\) and \(k_2\) are the apparent PFO and PSO rate constants, respectively. The PFO model was well fitted to the experimental results with a correlation coefficient of \(R^2=0.9831\). This suggests that the adsorption process is diffusion controlled. The obtained value of \(q_e\) from the PFO model was 0.3614 mg g\(^{-1}\) and \(k_1\) was 0.02152 h\(^{-1}\). The \(R^2\) value of the PSO kinetic model was 0.966. The PSO model constants of \(q_e\) and \(k_2\) were 0.432 g mg\(^{-1}\) h\(^{-1}\) and 0.05176 h\(^{-1}\), respectively. The equilibrium adsorption times for MP onto both of the adsorbents were measured at less than three hours. The HA equilibrium adsorption times in the presence and/or absence of MP took two weeks for both of
the GACs.

3.3. Adsorption Isotherm

The adsorption results were fitted to adsorbent dosage modified Freundlich model. Adsorbent dosage modified Freundlich isotherm [37] is an experimental model based on the hypothesis that layers of adsorbate form on an adsorbent heterogeneous surface. It takes into account the binding strength, which reduces the site occupation through enhancement and is expressed by Eq. (4):

$$q_e = K \left( \frac{C_e}{M} \right)^{\frac{1}{n}}$$

(4)

where, $K$ (mg/g)(L/mg)$^{1/n}$ and $n$ are the Freundlich isotherm constants related to the adsorption capacity and adsorption intensity, respectively.

3.3.1. Humic acid adsorption isotherm

The HA adsorption isotherms onto F400 and Norit GACs are presented in Figures 4 ((b) and (c)), respectively. The concentration and adsorbed weights are expressed based on the TOC results. The modified Freundlich isotherm agrees with the HA adsorption results for both GACs at the three different pH levels, indicating multilayer pollutant adsorption. Using the batch equilibrium method [38], the F400 and Norit GACs pH of the point of zero charges ($\text{pH}_{\text{pzc}}$) were measured at 7.8 and 8.4, respectively (Figure A1). The GACs surface ionizable functional groups gain protons, and the surface becomes positively charged at an equilibrium pH less than $\text{pH}_{\text{pzc}}$. The GACs surfaces exhibit negative charges when the solution pH was higher than $\text{pH}_{\text{pzc}}$ [20]. The adsorption capacity of the Norit GAC was more than F400 GAC. The $\text{pK}_a$ of the HA carboxylic group is less than 5. Thus, the HA’s charge was negative in the pH range of this study [39]. The electrostatic attraction/repulsion mechanism between the GACs surface and HA molecule charges could explain the adsorption results within the applied pH range[40]. Kołodziej et al. [41] argued that electrostatic
attraction is mainly responsible for the twice higher removal degree for two different HA fractions for modified ACs. The resulting trends are in accordance with the present findings. The adsorption capacity of HA on F400 GAC is in accordance with those reported in [37]. The modified Freundlich model parameters' values for the three assessed categories' adsorption experiments are tabulated in Table 2. High values of 1/n suggest a high affinity between the heterogeneous GAC sites and the pollutants.

3.3.2. Methylparaben adsorption isotherm

The MP adsorption isotherms at varying pH on F400 and Norit GACs are presented in Figures 5((a) and (b)), respectively. The isotherms' behaviors are described by the modified Freundlich model with a high correlation coefficient. The maximum adsorption capacity of MP on the GACs is in the order of the results achieved by Moreno-Marenco et al. [21] and Bernal et al. [22], however, the physicochemical characteristics of their ACs and the experiment temperature were different than those in the present study.

The pollutant’s hydrophobicity is a common mechanism in adsorption operation(s). The MP’s octanol/water partition (log $k_{ow}$) logarithm is 1.96. Based on the hydrophobicity classification [42], the MP hydrophobicity was low, therefore, the hydrophobic mechanism was not a concern. In this study, the main MP adsorption mechanism for F400 GAC was hydrogen bonding. The adsorbent and adsorbate -OH functional group has the potential for hydrogen bonding. A decrease in pH enhances hydrogen bonding, while it weakens the $\pi-\pi$ interaction. A schematic diagram of the MP adsorption mechanism on F400 GAC is presented in Figure 6.

The main mechanism for MP adsorption onto Norit GAC was the $\pi-\pi$ type interaction. This adsorption process mechanism has already been reported in other work [43]. An increase in pH enhances the $\pi-\pi$ interaction. The MP ionization percentage for a particular pH solution was
calculated using Eq. 5 [44].

\[
\text{Ionization} \%= \frac{100}{1 + 10^{(pK_a - pH)}}
\]  

(5)

The MP molecular type was about 96% below a pH of 7. Methylparaben adsorption decreases beyond pH 7 when the MP ionization increases (see Table 3). The repulsive force or and the less intend of the ionized species for adsorption onto the Norit GAC was responsible for the decreased adsorption capacity. Bernal et al. [20] observed that a commercial AC decreased the MP adsorption capacity due to the higher percentage of ionization and higher equilibrium pH than the adsorbent’s pH_{pzc}.

3.4. Simultaneous adsorption of methylparaben and humic acid

The simultaneous adsorption isotherms of MP and HA onto F400 GAC are presented in Figures 7 ((a) and (b)). The electrostatic force was the main factor in explaining the pH effect on the adsorption results for F400 GAC, which indicates a decrease in pH value and an increase in HA and MP adsorption. The MP deprotonates at a pH greater than a $pK_a$ of 8.17, while it protonates at a pH lower than the $pK_a$ value.

The GAC surface’s repulsive electrostatic force of the maximum negative charge corresponds to the HA adsorption capacity decrease at a pH of 9. The GAC’s available sites for MP adsorption were high at this pH and its capacity was higher than pH 7. The MP molecules were either directly adsorbed onto the GAC surface or indirectly adsorbed on already-adsorbed HA surface layers. Humic acid’s negative charge and MP’s positive charge within the studied pH range show that HA acting as a bridge between the GACs surface and MP molecules. It was expected that the MP adsorption capacity of the GACs under these conditions was greater than that of aqueous systems only contaminated with MP.

Humic acid’s physicochemical properties including the presence of different oxygen-
containing functional groups, aromaticity, and hydrophobic interactions, contributed to its aggregation extent. The presence of HA aggregates provides an additional hydrophobic domain for partitioning that enhances MP removal. Though, the steric blocking of GACs surfaces may inhibit its reduction to some extent [45]. The effect of GACs steric blocking was comparatively lower at the HA concentration in the present study.

In the presence of HA, a threefold increase in MP adsorption at 1 mg/L TOC and pH 7 was observed. The average increase across all MP in solution with a pH of 7 was approximately 2.2-fold. Similar behavior was reported the HA effect on ciprofloxacin removal, which facilitates the adsorption process [46]. No significant increase in the MP adsorption capacity was observed under acidic conditions as the result of electrostatic repulsion force between HA and MP molecules at pH lower than 5. Delgado et al. [47] observed significantly negative HA presence on ibuprofen and atenolol adsorption for two commercial GACs due to competition for adsorption sites and the pharmaceutically active compounds. The GAC’s pore blockage was caused by HA, while Li et al. [30] claim that HA was not effectively removed in competition with metaldehyde on a powdered activated carbon. The different HA effects on ECs adsorption onto AC-type adsorbent could be attributed to different experimental conditions.

The MP’s equilibrium adsorption onto Norit GAC in the presence of HA indicates that there does not exist any detectable MP in the liquid phase at pH 5, 7, and 9 and all of the initial MP content was adsorbed. A comparison of these results with the MP adsorption results (Figure 5(b)) indicates that most of the MP molecules were adsorbed onto the HA molecules’ surface. Although the initial HA molecule count was less than the MP molecule count, some HA molecules remain in the liquid phase at equilibrium conditions, while all of the MP molecules were adsorbed. The Norit GAC revealed a greater adsorption capacity for both the HA and MP molecules compared to the F400 GAC. The F400 GAC’s higher specific surface area and porosity properties cannot explain
the behavior of these results. The HA adsorption isotherm onto the Norit GAC presented in Figure 7(c) was fitted to the modified Freundlich model. At pH less than 9, the MP molecules were protonated, which neutralizes a part of the HA molecules’ electron cloud and leads to a reduction in HA and GACs adsorption interactions. A schematic presentation of the MP adsorption mechanism on F400 GAC in the presence of HA is illustrated in Figure 8.

3.5. Competitive adsorption of methylparaben and humic acid

Methylparaben and HA competitive adsorption assessments were performed at the same TOC concentration. The MP and HA isotherms at varying pH values are presented in Figures 9((a) and (b)). The results were fitted to the modified Freundlich isotherm model. In this experimental set, the MP concentrations for lower aggregates may become more significant [48] and lead to a presence of the weaker π-stacking interactions between the electrons in the MP aromatic rings, basic GAC functional groups, and the adsorption hydrophobicity. The organic carbon/water partition coefficient ($k_{oc}$) was applied to estimate the adsorbed MP values according to the Karickhoff empirical equation [49]:

$$\log k_{oc} = \log D - 0.21$$

(6)

where, log$D$ is expressed through a modified criterion of the effect of pH on the log $k_{ow}$. An explanation of their relationship can be found in [50]. This criterion is defined as the equilibrium concentration ratio of the ionized and non-ionized forms of the pollutant in the octanol phase to the same species in the water phase. The MP percent of hydrophobicity and ionization at the assessed
pHs are tabulated in Table 3. The MP adsorption results were explained by the variation of $k_{oc}$ with pH.

As depicted in Figure 9(b), HA’s adsorption capacity onto the F400 GAC was the same at both the competitive adsorption condition and different pH values. The number of specific affinity sites for the F400 GAC was high at low initial MP and HA concentrations.

No detectable amount of MP was measured in the solution at equilibrium conditions in the competitive adsorption experiment with Norit GAC. The amount of overall MP and HA adsorption onto the Norit GAC is shown in Figure 9(c). The MP molecules were protonated at pH less than 9, which neutralizes a portion of the HA negative charges and reduces the effect of the electron cloud between GAC and HA molecules. The HA adsorption increases as the pH decreases.

4. Conclusions

The adsorption of MP and HA onto two commercial GACs was investigated in different pH aqueous solutions. The results indicate that the MP adsorption capacity onto both the F400 and Norit GACs was high (~150 mg/g). The main MP adsorption mechanism onto the F400 GAC was the hydrogen interaction between –OH functional groups from the MP molecules and the adsorbent. The fractional adsorption potential of the pollutants was assessed to compare the effects of the pollutants. The fractional adsorption capacity of MP and HA in a bicomponent solution was dependent on the pH of the solution, and the initial concentrations of pollutants. The charge interactions among pollutants molecules and the GAC surface were responsible for interpreting the complex adsorption behavior at different pH. The MP adsorption capacity increased to nearly 2.2-fold in the presence of HA molecules and at a pH of 7 for both GACs. The experimental results were well fitted to the adsorbent dosage modified Freundlich isotherm. Both of the GACs have the potential to enhance drinking water quality from MP and HA contamination by applying a pre or post adsorption
Acknowledgments

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Conflicts of interest

Authors have no potential conflict of interest.

References

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**Figure Captions**

**Figure 1.** (a) N\textsubscript{2} adsorption-desorption isotherms at 77 K, (b) Pore size distributions obtained using the DFT method, (c) FTIR spectra of F400 and Norit GACs.

**Figure 2.** SEM micrographs of the surface from F400 GAC at (a) 10000× and (b) 1000× magnifications.

**Figure 3.** SEM micrographs of the surface from Norit GAC at (a) 10000× and (b) 1000× magnifications.

**Figure 4.** (a) HA adsorption kinetics onto the F400 GAC at 0.04 g of adsorbent/ml, HA initial TOC 2.357 ppm, pH 7, and 25 °C, (b) adsorption isotherms of HA onto the F400 GAC at pH 5, 7, and 9, (c) adsorption isotherms of HA onto the Norit GAC at pH 5, 7, and 9.

**Figure 5.** (a) MP adsorption isotherms onto the F400 GAC at pH 5 and 7, (b) MP adsorption isotherms onto the Norit GAC at pH 5, 7, and 9.

**Figure 6.** The schematic diagram of the MP adsorption mechanism on F400 GAC.

**Figure 7.** (a) MP adsorption isotherms onto F400 in presence of HA at pH 5, 7, and 9, (b) HA adsorption isotherms onto F400 in presence of MP at pH 5, 7, and 9, (c) HA adsorption isotherms onto Norit GAC in presence of MP at pH 5, 7, and 9.

**Figure 8.** The schematic presentation of the MP adsorption mechanism on F400 GAC in the presence of HA.

**Figure 9.** Competitive adsorption isotherms of (a) MP on F400 GAC in presence of HA at pH 5, 7, and 9, (b) HA on F400 GAC in presence of MP at pH 5, 7, and 9, and (c) overall adsorption isotherms of HA and MP on Norit GAC at pH 5, 7, and 9.

**Figure A1.** The pH\textsubscript{pzc} results of the studied GACs.
Table Captions

Table 1. GAC BET area and pore volumes.

Table 2. Adsorbent dosage modified Freundlich model parameters for the three studied adsorption categories.

Table 3. MP hydrophobicity and percent ionization.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8
Figure 9
Appendix A

The results of pH$_{pzc}$ measurement of the studied GACs through the pH drift method are presented in Figure A1.

![Figure A1](image-url)
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<th>S\textsubscript{BET} m\textsuperscript{2}/g</th>
<th>V\textsubscript{tot} (cm\textsuperscript{3}/g)</th>
<th>V\textsubscript{supermic} (cm\textsuperscript{3}/g)</th>
<th>V\textsubscript{ultramic} (cm\textsuperscript{3}/g)</th>
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<td>Simultaneous adsorption of MP and HA</td>
<td>F400/HA</td>
<td>1.3266</td>
<td>0.6894</td>
<td>0.9357</td>
<td>0.9702</td>
<td>0.7326</td>
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<td></td>
<td>F400/MP</td>
<td>233.96</td>
<td>0.8601</td>
<td>0.94</td>
<td>549.88</td>
<td>1.0282</td>
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<td></td>
<td>Nori/HA</td>
<td>2.8517</td>
<td>0.6182</td>
<td>0.8573</td>
<td>2.2417</td>
<td>0.6765</td>
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<tr>
<td>Competitive adsorption of MP and HA</td>
<td>F400/HA</td>
<td>1.4536</td>
<td>0.6693</td>
<td>0.9831</td>
<td>1.4617</td>
<td>0.6343</td>
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<td></td>
<td>F400/MP</td>
<td>77.871</td>
<td>1.1069</td>
<td>0.9994</td>
<td>58.868</td>
<td>0.9443</td>
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<tr>
<td></td>
<td>Nori/HA+MP</td>
<td>39.241</td>
<td>0.704</td>
<td>0.9639</td>
<td>32.229</td>
<td>0.7658</td>
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<tr>
<td>pH</td>
<td>Ionization percent</td>
<td>logD</td>
<td>( \log k_{ac} = \log D - 0.21 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>--------------------</td>
<td>------</td>
<td>----------------------------------</td>
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<td></td>
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</tr>
<tr>
<td>5</td>
<td>0.03979</td>
<td>-1.44</td>
<td>-1.65</td>
<td></td>
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<tr>
<td>7</td>
<td>3.8287</td>
<td>0.543</td>
<td>0.333</td>
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<td>9</td>
<td>79.92</td>
<td>1.263</td>
<td>1.053</td>
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</tbody>
</table>
Biographies

Ali Reza Solaimany Nazar is currently an associate professor in the Chemical Engineering Department at the University of Isfahan, Iran. He received his Ph.D. in Chemical Engineering from Amirkabir University of Technology, Iran. His current research interests are mainly on the application of nanomaterials in oil flow assurance, convection heat transfer, and water and wastewater treatment fields. His specific research topic is emerging organic compounds removal from the aqueous phase by adsorption technique and advanced oxidation process. He has published about one hundred research articles in well-known peer-reviewed scientific journals.

Mayur Bharat Kurade has acquired his Ph.D. at Shivaji University, Kolhapur, India and he is currently working as Research Associate Professor at the Department of Earth Resources and Environmental Engineering, Hanyang University, Seoul, South Korea. He has demonstrated experience in the field of bioenergy generation with specialization in biofuels production, anaerobic digestion of waste organic resources, mass cultivation of 3rd generation biomass, and its pre-treatment and fermentation technologies. His specific interests include biological wastewater treatment, sludge treatment, organic waste management, and emerging organic compounds removal from wastewater. The developed technologies with an integrated approach to wastewater treatment and bioenergy generation have been aimed at ‘zero waste biofuel generation.’ Dr. Kurade has published ~80 research articles in well-known peer-reviewed international journals of high repute along with 3 book chapters and 1 patent focusing on wastewater pollution control technologies.
Moonis Ali Khan received his Ph.D. in Applied Chemistry from Aligarh Muslim University, Aligarh, India, in 2009. From 2009 to 2011, he had worked as a Post-Doctoral Researcher at Yonsei University, South Korea, and University Putra Malaysia, Malaysia. In 2011, he joined the Chemistry Department at the King Saud University (KSU), Saudi Arabia as an Assistant Professor. Currently, he is working as an Associate Professor at KSU. He is an interfacial chemist, and his research is focused on the synthesis and development of novel materials for energy and environmental remediation applications. To date, he has guided two doctoral students for their respective degrees. He has published more than a hundred (research and review) articles and has two U.S. patents to his credit.

Byong-Hun Jeon is a professor at the Department of Earth Resources and Environmental Engineering at Hanyang University, South Korea. He holds a B.Sc. degree in Mineral and Petroleum Engineering from Hanyang University, and M.Sc. & Ph.D. degrees in Civil & Environmental Engineering from Pennsylvania State University, USA. His current research interests include environmental biotechnology, bioremediation, anaerobic digestion, fermentation, and environmental biogeochemistry. His research group is primarily working on organic waste management through bioenergy production and soil and water pollution control using biological and chemical tools. His current specific emphasis has been on the meta-omics studies of the environmental microbiota using state-of-the-art high throughput sequencing methods. His in-depth research on these topics has yielded him more than 300 research articles in well-known, international peer-reviewed journals. Some of his highlighted research has appeared in Nature Communications, Energy and Environmental Sciences, Coordination Chemistry Reviews, Trends in Biotechnology, Progress in Energy Combustion Science.