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# Activated Carbon for Pharmaceutical Removal at Point-of-Entry

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**Abstract:** Pharmaceuticals are an increasing problem in waterways due to improper disposal and lack of removal at wastewater treatment plants. Long-term exposure impacts to humans are unknown but have been observed in model organisms (i.e., fish), impacting reproduction, changing temperament, and causing organ damage. The application of activated carbon (AC) for organic contaminant removal is widespread and applied successfully for water treatment. The objective of this study is to rapidly adsorb ibuprofen using AC to determine the feasibility as a point-of-entry treatment option for removal of pharmaceuticals in the toilet. AC factors analyzed include type of AC raw material, adsorbent particle size, contact time, and competitive adsorption of ibuprofen and common toilet bowl cleaner components such as chlorine and methylene blue dye. A coconut-based AC with a high surface area adsorbed the highest quantity of ibuprofen. There was no significant impact to ibuprofen adsorption upon the introduction of other compounds to the solution, thus demonstrating rapid adsorption and the potential for application at the point-of-entry.

**Keywords:** activated carbon; ibuprofen; surface area; surface chemistry; raw materials; adsorption kinetics; adsorption capacity



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## 1. Introduction

Up until October 2016, the Food and Drug Administration (FDA) was recommending that unused medication be disposed of in the toilet or sink. Since then, the FDA has re-written their statement recommending that unused medication be taken to a Drug Enforcement Administration (DEA) authorized collector [1]. However, with human urine excreting more than 70% of pharmaceuticals ingested, municipal wastewater discharge is contaminated with trace amounts of unwanted pharmaceuticals originating from urine excretion [2]. These trace contaminants are not routinely monitored in wastewater streams because of the limit of detection, cost, and analysis time required. However, chemo-sensors provide a rapid solution [3].

The pharmaceuticals found in waste streams include, but are not limited to, non-steroidal and anti-inflammatories (i.e., ibuprofen, diclofenac, naproxen, and ketoprofen), which have been detected at very low concentrations (ng/L and µg/L) in surface waters [4]. Adverse developmental patterns have been observed in aquatic species in the presence of low concentrations of pharmaceuticals such as ibuprofen, diclofenac, the antidepressant fluoxetine, and steroids like oestrogens and progestogens [5]. Negative effects include impacts on the reproductive system, changes in temperament, and organ damage. The toxicological impact to the human body is still unclear after an extended period of exposure to low concentrations of pharmaceuticals [6–8]. Some of these low-dosage impacts may include obesity, neurobehavioral disorders, infertility, and immune dysfunctions [9,10].

There are currently no state or national level regulations in the United States limiting the concentration of pharmaceuticals in wastewater effluent. Therefore, upon the discharge of the water into lakes and aquifers, pharmaceuticals have been studied to be ingested or accumulated by plants and animals within the ecosystem [11]. Pharmaceuticals in

liquid streams are most effectively removed by advanced filtration or chemical removal processes which are not typically employed in conventional wastewater treatment plants (WWTP) [12]. An important aspect of WWTP removal of pharmaceuticals is the ability for water reuse back into the drinking water system, a process many cities with limited water supply are looking to implement. Many counties are in the process of implementing such practices, and specifically in Florida, Manatee County is exploring direct reuse practices that would require pharmaceuticals to be removed from the WWTP discharge [13].

Wastewater reuse is an untapped available water source requiring less energy-intensive treatments. In water-scarce areas, water resource planning is necessary to comply with regulatory policies, address the need for reliable and cost-effective water, and reduce the use of existing freshwater as a potable water resource [14]. The "fit-for-purpose" framework is an example of redistributing effluent water in a more sustainable way to reduce cost and energy consumption [15]. For example, the state of California had a net energy savings of 0.7 to 1 Terawatt hours per year from wastewater reuse as of 2012 [16]. The current barriers for implementation are choosing the appropriate technology for wastewater reuse and design decisions. As the demand for drinking water increases, the need for specific end-uses for wastewater may become more apparent with drinking water treatment options still very costly.

The techniques for removal of pharmaceuticals in potable drinking water treatment plants include membrane technologies, ozonation, ultraviolet radiation, and adsorption. Some of these processes have been implemented at WWTPs [17]. However, some compounds are not affected by these technologies and remain in the effluent at high concentrations. Studies by Gros et al. suggested that this is due to high half-lives observed in the majority of pharmaceuticals, and that new technologies should be implemented to aid in the removal of these compounds [18]. The complexity of wastewater and variability from one WWTP to another increases the robustness to achieve high levels of removal. Addressing pharmaceutical removal at the point-of-entry (i.e., the toilet) provides a logical approach to remove pharmaceuticals prior to them reaching a WWTP and can be achieved through the use of activated carbon.

Activated carbon has a wide range of applications for water and air purification [19–21]. It is typically the adsorbent of choice for water and wastewater treatment and can be applied in various forms, for example, powdered, granular, or pelletized [22,23]. It has been described as a non-graphitic form of carbon, having porosity enclosed by carbon atoms, and an extended interparticle surface area [24]. Coal-based activated carbon can be derived from lignite, sub-bituminous, bituminous, and anthracite coal. Activated carbon can also be produced from materials such as wood, peanut shells, coconut shells, etc. While the resulting activated carbons from these numerous raw materials have often been described as similar, recent research suggests the raw material used to produce activated carbon can have a significant impact on adsorption, specifically for contaminants whose adsorption mechanism will be more driven by chemi- versus physi-sorption [25].

Activated carbon is a very robust technology and has been demonstrated to efficiently remove several types of organic and inorganic compounds from wastewater treatment systems due to its high rates of absorption and adsorption [26,27]. Recent studies have focused on the application and optimization of biomass-derived biochar as a cost-effective solution for accomplishing pollutant removal [28,29]. When removing organic micropollutants from wastewater, removal rates using activated carbon were as high as 99%, whereas ozonation treatment removed a maximum of 80% [29–31].

Since WWTPs are not conventionally equipped to remove pharmaceuticals from wastewater, these concentrations can instead be removed at the source: the toilet bowl. The focus of the work herein is rapid adsorption kinetics of pharmaceutical compounds, specifically ibuprofen as a model pharmaceutical, with activated carbon. This can lessen the concentrations of pharmaceuticals in wastewater by treating the water at the source. The method in which carbon is introduced to the toilet is not addressed herein, but the concept would be that with each flush of a toilet, carbon is introduced perhaps concurrently

with toilet bowl cleaner from the water tank. Therefore, competitive adsorption from the presence of toilet bowl cleaner and impact from chlorine on the activated carbon are important to understand. While the FDA recommends against discarding pills down the toilet, a reality is this wide-spread practice is still likely, and hence was assumed.

## 2. Materials and Methods

### 2.1. Adsorbates

The compounds selected to observe competitive adsorption to the carbon surface are ibuprofen-sodium, methylene blue, and sodium hypochlorite. Ibuprofen is a hydrophobic compound, requiring an alcohol to dissolve the salt (unless at a concentration below the solubility limit in water) [32,33]. Previous literature has demonstrated that activated carbon can preferentially adsorb alcohols (i.e., methanol) [34,35]. To avoid interferences by the solvent, ibuprofen-sodium (Sigma Aldrich) was used to increase the solubility of ibuprofen and allow for the use of only water as the solvent [36].

Ibuprofen (molecular size of 1.3 × 0.6 nm) is typically used as a model molecule in experiments of controlled drug release, due to its stability and applicability. This makes it easy to compare the drug adsorption and capacity of sorbents with different pore sizes. A concentration of 1 g/L was selected to roughly model the concentration of 25 pills at 200 mg of ibuprofen per pill being discarded in a standard United States toilet. A standard toilet uses about 1.6 gallons (6.5 L) per flush. Analysis with ibuprofen pills was not explored to avoid further complication of the system by introducing competitive adsorption with the pill binder constituents. Additionally, accurate ibuprofen concentration cannot be expected from drug store pills. Methylene blue (Acros Organics) was selected at 3 mg/L to simulate the dye frequently used by toilet bowl cleaner companies. Sodium hypochlorite (TCI America) was selected at 100 mg/L to represent the chlorine bleach concentration also used by toilet bowl cleaner companies.

### 2.2. Activated Carbons

The commercially available carbons were dried at 150 °C and sized to less than 45 µm for dosing, unless denoted otherwise, and stored in a desiccator prior to experimental analysis. One of the highest-performing activated carbons at 48-h contact time (AC-Coco-1) was further crushed to the following mesh sizes to determine the impact of particle size: 2.0 mm × 1.0 mm, 1.0 mm × 850 µm, 850 µm × 500 µm, 500 µm × 212 µm, 212 µm × 75 µm, 75 µm × 45 µm, and 45 µm × 20 µm.

### 2.3. BET Surface Area, Total Pore Volume, and Average Pore Size

Porosity characteristics of all sorbents were analyzed using nitrogen adsorption/desorption via a Quantachrome NOVA 2200e instrument (Boca Raton, FL, USA). Each sample was held at 110 °C under vacuum overnight prior to analysis. The activated carbons were analyzed with Ultra-High purity nitrogen gas (NexAir) under a liquid nitrogen bath maintained at a constant temperature of approximately −196 °C. The volume of adsorbed nitrogen gas was plotted against the relative equilibrium pressure to determine the total pore volume.

Assuming all pore spaces of the activated carbon are filled with the adsorbate, total pore volume was measured from the amount of gas adsorbed at the limiting pressure, $P/P_0 = 0.99$. The surface area of each sample was analyzed in duplicates and calculated by the Brunauer–Emmett–Teller (BET) equation at a $P/P_0$ of 0.01 to 0.3 [37]. The C constant of the isotherm was calculated from the slope and y-intercept and ensured to be a positive value for the multipoint BET calculation to hold valid. A best-fit set of five data points was used in the multipoint BET calculation. The average pore size is estimated from the pore volume, distributed over various pore sizes.

### 2.4. Analytical Methods and Calibration Curve

The concentrations of ibuprofen-sodium and methylene blue were analyzed on an ultraviolet-visible (UV) spectrophotometer (Hach DR 6000) using a 1 cm quartz cuvette.

The following methods were adapted from previous literature [31]. Wavelength scans from 200–400 nm were conducted for the solutions to obtain the peak absorbance. The peak absorbance was used to calculate the unknown concentration in a sample. A calibration curve was developed for ibuprofen-sodium with increasing concentrations from 0.0, 50.0, 250.0, 500.0, 750.0, and 1000.0 mg/L at 224 nm ($y = 1.3484x + 0.0019$). The calibration curve for methylene blue included the following concentrations: 0, 1, 2, 3, 5, 7, 10 mg/L at 664 nm ($y = 0.1992x - 0.0047$). For the calibration curves, the coefficient of determination ($R^2$) was greater than 0.98.

### 2.5. pH Measurements

Measurements for solution pH and ORP were taken using an Accumet AP-55 (pH) and SensION 5057 ORP electrode (ORP) connected to an Orion Star portable pH meter. Prior to use, the pH meter was calibrated using a pH 4.01, pH 7.0, and pH 10.0 buffer. Contact pH of the carbon samples is a modified procedure of ASTM D3838 [38]. It was measured by adding 1.0 g of powdered activated carbon (dried at 150 °C overnight and cooled in a desiccator) sized to less than 45 µm to 10.0 mL of deionized water. This solution was rotated for 30 min and then analyzed for contact pH.

### 2.6. Adsoroption Experimental Design

Batch tests were conducted to evaluate the adsorption of ibuprofen-sodium with and without methylene blue and chlorine by commercial activated carbons to simulate the simultaneous removal of ibuprofen in the presence of a toilet bowl cleaner. The impact of background water was determined using a natural water (Gainesville, FL, USA) spiked with 1 g/L ibuprofen-sodium salt. In order to evaluate equilibrium uptake, the samples were agitated for 48-h whereby 200 mg of an overnight dried carbon (150 °C) was added to 40 mL of a 1.0 g/L ibuprofen-sodium salt solution. An aliquot was collected and filtered through a 0.45 µm syringe and analyzed using a UV spectrophotometer.

To evaluate the impact of particle size on adsorption, a coconut-based AC was grinded and sieved, giving seven different particle sizes ranging from 20 µm–2 mm. After drying overnight at 150 °C, 1000 milligrams of each carbon sample were added to 100 mL of a 1.0 g/L ibuprofen-sodium salt solution and stirred at 300 RPM for 30 min. The mixture was then syringe-filtered with a 0.45 µm nitrocellulose filter and analyzed using a UV spectrophotometer to determine the final ibuprofen concentration for each particle size.

The residence time in a toilet bowl is much shorter than equilibrium; therefore, the kinetics of adsorption were explored. An amount of 45 µm powdered samples were dried overnight at 150 °C; ~100 milligrams of a coconut-based, a bituminous-based, and lignite-based ACs were added to 30 mL of a 1.0 g/L ibuprofen-sodium salt solution and stirred at 300 RPM for 1, 5, 10, and 15 min. The mixture was filtered through a 0.45 µm syringe and analyzed using a UV spectrophotometer for each time interval of each carbon.

## 3. Results

### 3.1. Characterization of Materials

The activated carbons (labeled based on the raw material (e.g., Bit = bituminous, Lig = lignite, and Coco = coconut) were characterized for physical properties and water contact pH (Table 1). The BET surface areas ranged from about 400 to 1500 $m^2/g$, and the surface areas for similar raw materials are relatively comparable except for the wood-based ACs. As a result, the chemically activated carbons have a much higher surface area than the physically activated wood-based carbon. There is also a distinction in the water contact pH; the chemically activated wood carbons have a lower water contact pH because of the acid used to increase porosity while the physically activated wood carbon used steam to develop the surface area. Water contact pH can provide an indication to the acidic and basic nature of the activated carbon. Here, the water contact pH varied from about 3.25 to 11.8. Overall, the activated carbons have vastly different surface areas, pore sizes, pore

size distributions, and water contact pH, providing a sample set to evaluate whether these variables alone impact ibuprofen adsorption and/or competitive adsorption.

**Table 1.** Physcial characterization and water contact pH for commercially available ACs.

| Carbon ID | BET Surface Area ($m^2$/g) | Average Pore Size (Å) | Total Pore Volume (cc/g) | Micro-Pore Volume (cc/g) | Water Contact pH |
|---|---|---|---|---|---|
| **AC-Bit-1** | 784 | 20.1 | 0.39 | 0.27 | 9.78 |
| **AC-Bit-2** | 797 | 24.2 | 0.48 | 0.27 | 10.3 |
| **AC-Coco-1** | 1139 | 16.9 | 0.48 | 0.40 | 10.9 |
| **AC-Coco-2** | 1252 | 13.9 | 0.59 | 0.53 | 11.3 |
| **AC-Coco-3** | 1008 | 17.0 | 0.42 | 0.35 | 9.57 |
| **AC-Coco-4** | 1184 | 17.7 | 0.52 | 0.42 | 10.8 |
| **AC-Lig-1** | 689 | 41.5 | 0.71 | 0.18 | 3.25 |
| **AC-Lig-2** | 427 | 51.0 | 0.54 | 0.12 | 11.8 |
| **AC-Lig-3** | 440 | 42.5 | 0.47 | 0.20 | 9.65 |
| **AC-Lig-4** | 461 | 42.6 | 0.49 | 0.20 | 11.4 |
| **AC-Sub Bit-1** | 1072 | 25.0 | 0.67 | 0.35 | 9.24 |
| **AC-Wood-1** | 1450 | 33.9 | 1.23 | 0.41 | 5.41 |
| **AC-Wood-2** | 426 | 25.6 | 0.27 | 0.18 | 9.17 |
| **AC-Wood-3** | 1529 | 31.2 | 1.19 | 0.45 | 3.08 |

### *3.2. Activated Carbon Removal of Ibuprofen at Equilibrium*

The carbon capacity for ibuprofen was determined using batch equilibrium tests for each carbon sample at a contact time of 48 h, as seen in Figure 1. Interestingly, although the surface areas and water contact pH for the activated carbons varied substantially, percent removal was similar for most of the activated carbons (e.g., about 55%). The final concentration of ibuprofen was reduced by more than half (except with AC-Wood-2) regardless of the different BET surface areas (Table 1).

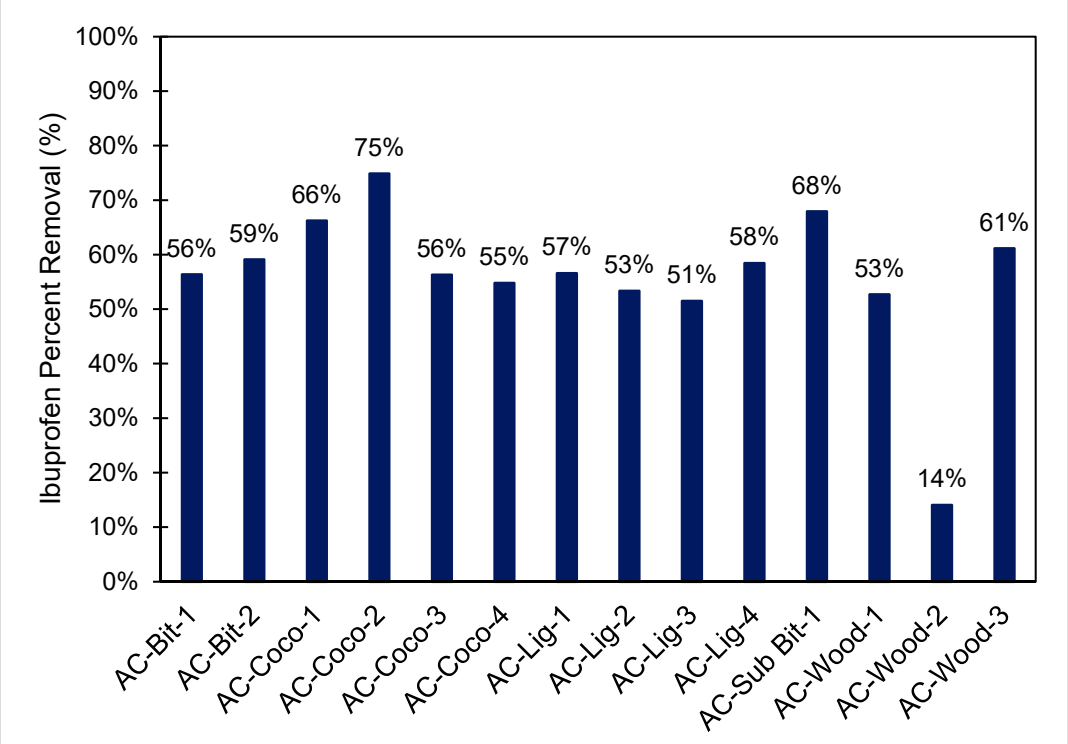


**Figure 1.** Ibuprofen removal by varying activated carbons at equilibrium (48 h) ($C_0$= 1.0 g/L).

Linear regression analysis of ibuprofen adsorption for the various characteristics shown in Table 1 were plotted versus ibuprofen capacity to determine if there is a correlation. Furthermore, the raw materials were separated from each to assess trends within a raw material grouping. Table 2 contains the final ibuprofen concentration (mg/L) and ibuprofen capacity (mg/g) after 48 h contact time.

**Table 2.** Final ibuprofen concentration and carbon capacity at 48 h of varying carbon samples.

| Carbon ID | Final Ibuprofen Concentration (mg/L) | Ibuprofen Capacity (mg ibu/g Carbon) |
|---|---|---|
| **AC-Bit-1** | 440 | 108 |
| **AC-Bit-2** | 402 | 111 |
| **AC-Coco-1** | 340 | 127 |
| **AC-Coco-2** | 247 | 145 |
| **AC-Coco-3** | 429 | 108 |
| **AC-Coco-4** | 444 | 103 |
| **AC-Lig-1** | 438 | 109 |
| **AC-Lig-2** | 470 | 102 |
| **AC-Lig-3** | 477 | 99 |
| **AC-Lig-4** | 409 | 112 |
| **AC-Sub Bit-1** | 315 | 130 |
| **AC-Wood-1** | 465 | 100 |
| **AC-Wood-2** | 845 | 26 |
| **AC-Wood-3** | 382 | 114 |

The total surface area, average pore size, total pore volume, and total micropore volume were plotted versus ibuprofen capacity for all activated carbons (Figures 2 and 3). The dimensions for ibuprofen (0.6 × 1.0 nm) would predict that total micropore volume would correlate to uptake. Total micropore volume had the highest correlation ($R^2$ = 0.26); however, all of the correlations were rather poor (Figure 3). There is an outlier present from AC-Wood-2. The reasoning is unknown for the outlier and requires further experimentation.

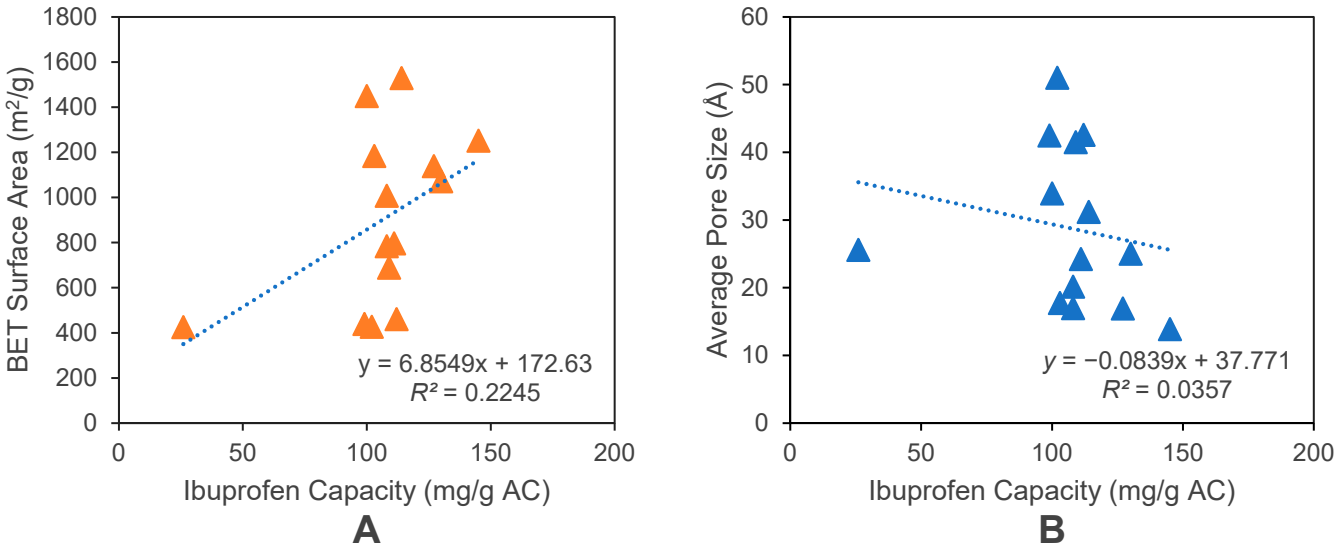


**Figure 2.** Linear regression of BET surface area (**A**) and average pore size (**B**) of the commercial activated carbon samples and the respective ibuprofen capacities at equilibrium.

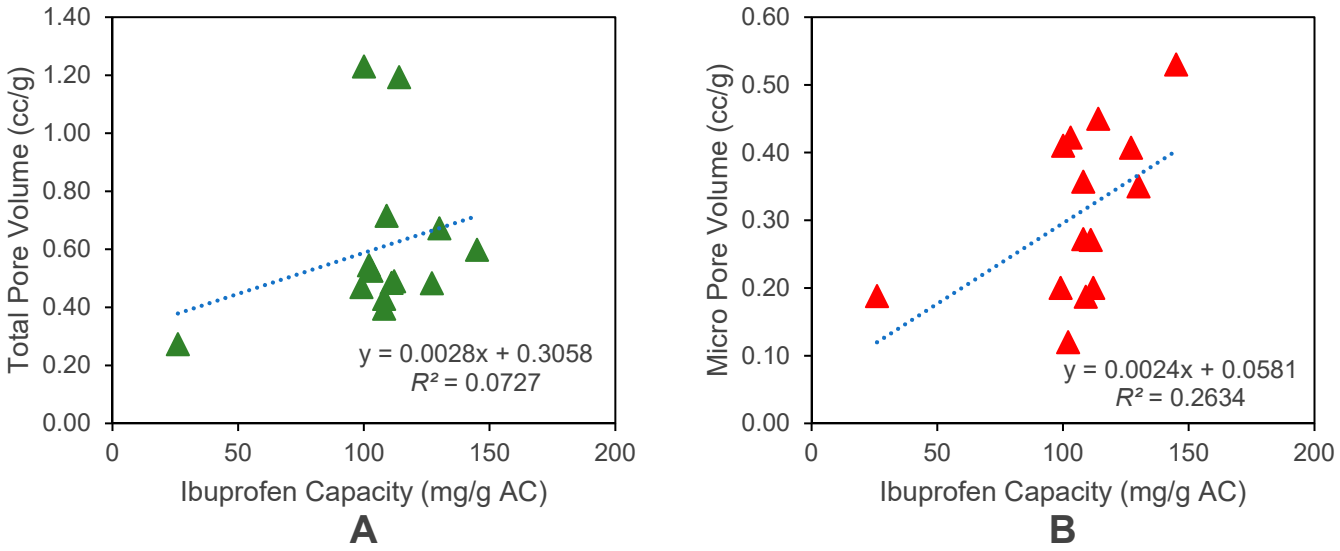


**Figure 3.** Linear regression of total pore volume (**A**) and micropore volume (**B**) of the commercial activated carbon samples and the respective ibuprofen capacities at equilibrium.

Upon further separation of the porosity data based on carbon raw material types, linear regression analysis was performed using micropore volume of the carbons and ibuprofen capacity (Figure 4). The wood-based ACs and coconut-based ACs had a moderate correlation to ibuprofen capacity with an $R^2$ value of 0.7072 and 0.6397, respectively. The lignite-based ACs displayed a lower correlation using micropore volume of $R^2 = 0.1145$. This may be due to the inherently low quantity of micropore.

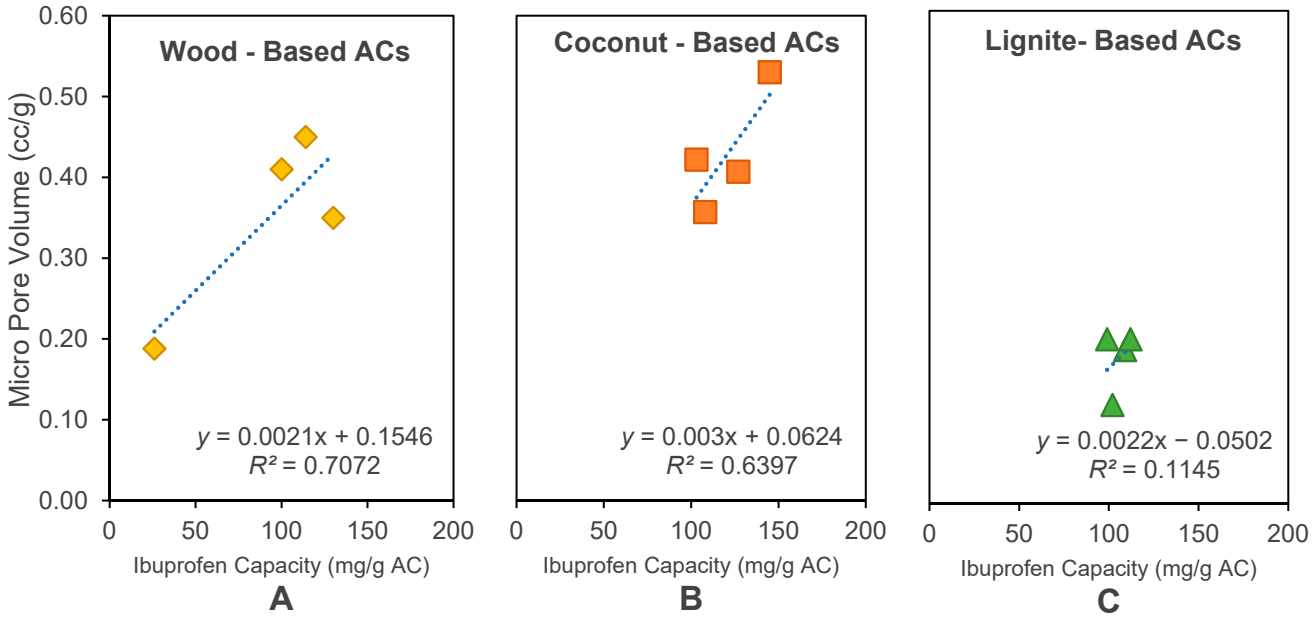


**Figure 4.** Linear regression of micropore volume vs. ibuprofen capacity at equilibrium of wood-based activated carbons (**A**), coconut-based activated carbons (**B**), and lignite-based activated carbons (**C**).

### *3.3. Effect of Particle Size Distribution on Ibuprofen Adsorption*

To further understand the feasibility of using activated carbon as a point-of-entry pharmaceutical removal technology, particle size distribution using a coconut-based AC was evaluated. It was hypothesized that as the particle size decreased, capacity would increase for a 30 min contact time. The coconut-based AC was selected because it demonstrated

the highest average ibuprofen capacity compared to the other raw materials (Figure 1). Removal of ibuprofen ranged from 23% at the largest particle size (1–2 mm) to 89–91% for the carbons milled to less than <212 µm (Figure 5). There was no significant difference in ibuprofen removal for the samples sized to less than 212 µm.

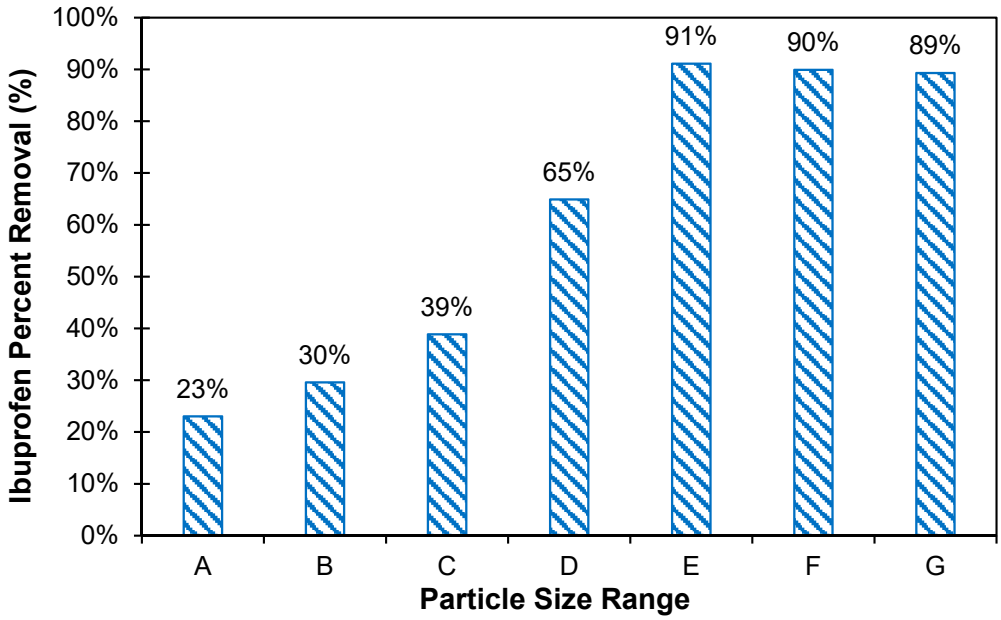


**Figure 5.** Carbon particle size distribution effect on adsorption kinetics using AC-Coco-1 (coconut) at 1 min contact time ($C_0$ = 1.0 g/L).

A contact time of 30 min for the powdered samples resulted in significant removal of ibuprofen, demonstrating the ability for a powdered activated carbon (PAC) to rapidly adsorb pharmaceuticals, specifically ibuprofen, at short contact times. Table 3 contains information on the final ibuprofen concentration (mg/L), ibuprofen capacity (mg/g), and final solution pH. The final concentration ranged from 776 to 90 mg/L depending on the particle size. At the particle sizes of less than 212 µm, the capacity tripled from 7 mg/g to 27 mg/g. Additionally, the final solution pH increased from 9.97 to 10.91.

**Table 3.** Solution concentration, capacity, and final solution pH of ibuprofen solution after treatment with carbon of varying particle sizes.

| Particle Size Distribution of Coconut-Based Activated Carbon | Ibuprofen Final Concentration in Solution (mg/L) | Ibuprofen Capacity (mg ibu/g Carbon) | Final Solution pH |
|---|---|---|---|
| **PSD A:2 mm-1 mm** | 776 | 7.0 | 9.97 |
| **PSD B:1 mm-850 µm** | 710 | 9.0 | 10.44 |
| **PSD C:850 µm-500 µm** | 616 | 12.0 | 10.53 |
| **PSD D:500 µm-212 µm** | 354 | 19.0 | 10.63 |
| **PSD E:212 µm-75 µm** | 90 | 27.0 | 10.83 |
| **PSD F:75 µm-45 µm** | 102 | 27.0 | 10.91 |
| **PSD G:45 µm-20 µm** | 108 | 27.0 | 10.37 |

The impact of granular activated carbon (GAC) vs. PAC for micro-pollutant has been observed by various researchers [39–42]. Adsorption in the liquid phase may be greater for PAC, than GAC, because of the short intra and interparticle path length required for the molecule to be adsorbed. Therefore, a 30 min contact time would not be enough for a larger-sized activated carbon to achieve high adsorption capacities. A similar trend was

observed by Yener et al. [41] and El Qada et al. [42] using commercial activated carbons for methylene blue removal.

All future work will be done using a particle size of less than 212 µm to ensure that particle size is not reducing adsorption. For further applications, this data demonstrates that activated carbon is capable of adsorbing a significant concentration of ibuprofen under a short contact time. We plan to utilize this to develop a user-friendly dissolving activated carbon pellet which releases appropriately sized PAC while ensuring the effluent pH remains neutral.

### *3.4. Rapid Ibuprofen Adsorption*

In reality, the contact time for activated carbon to adsorb a pharmaceutical at a point of entry application would be much shorter than 30 min. Lignite, bituminous coal, and coconut-derived activated carbons were compared for ibuprofen adsorption for contact times less than 15 min (Figure 6). Although the coconut-based carbon performed the best in previous experiments, in some applications, mesopore development is more important when rapid adsorption is required. Therefore, it is expected that the trend will occur as AC-Coco-1 > AC-Bit-1 > AC-Lig-1 for ibuprofen uptake.

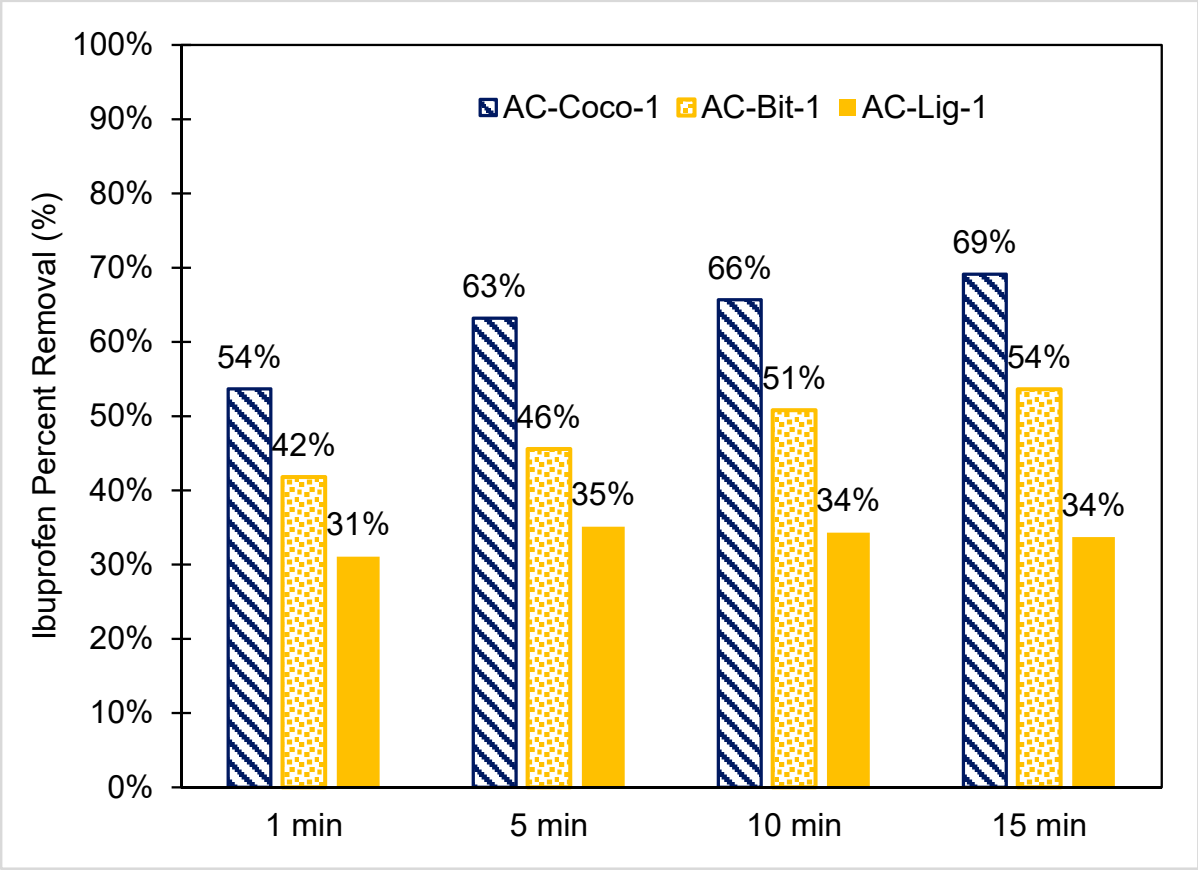


**Figure 6.** Ibuprofen kinetic removal: influence on activated carbon raw material at various contact times ($C_0$ = 1.0 g/L).

AC-Lig-1 did not have increased adsorption with increased contact time. AC-Coco-1 and AC-Bit-1 adsorption increased with increased contact time from 54% to 69% and from 42% to 54%, respectively. Therefore, maximum adsorption capacity had not been achieved by the 15 min contact time. However, a 5 min contact time is sufficient to reduce the ibuprofen concentration by more than half.

### *3.5. Competitive Ibuprofen Adsorption with Methylene Blue and Sodium Hypochlorite*

Competitive adsorption is of concern as adsorbates compete for adsorption sites. Furthermore, typically, the adsorbate of interest is present in much lower concentrations compared to other compounds. However, that may not be the case for the adsorption of pharmaceuticals in a point-of-entry system. Here, the impacts of methylene blue (3 mg/L) and sodium hypochlorite (100 mg/L) on ibuprofen adsorption at a contact time of 1 min were observed (Figure 7).

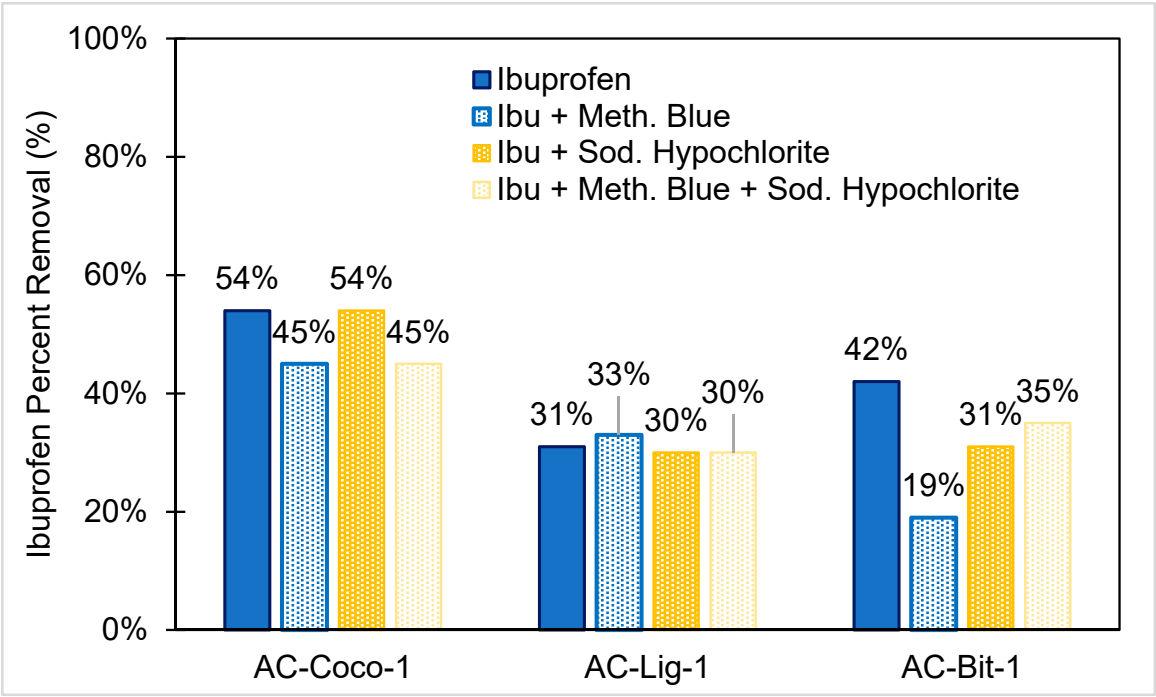


**Figure 7.** Ibuprofen removal at 1 min contact time in the presence of 3 mg/L of methylene blue and 100 mg/L sodium hypochlorite with AC-Coco-1, AC-Lig-1, and AC-Bit-1 ($C_0$ = 1.0 g/L).

Methylene blue, an organic molecule, has a rectangular area of 1.7 × 0.76 × 0.33 nm [43]. The size is very similar to the molecular size of ibuprofen and is expected to compete for similar pore sizes when comparing adsorption of the same carbon type. For all solutions containing methylene blue, removal was 100%. Sodium hypochlorite is not expected to compete with ibuprofen but may change the surface chemistry of the carbon [44,45].

In Figure 7, AC-Coco-1 adsorbed 54% of ibuprofen without additional competition and in the presence of sodium hypochlorite. Therefore, the surface chemistry can be assumed to remain unchanged upon 1 min contact of the sample with sodium hypochlorite. AC-Lig-1 adsorption was not impacted by the introduction of methylene blue and sodium hypochlorite in solution. AC-Bit-1 adsorption decreased from 42% to 35–31% in the presence of competing compounds.

The decrease in adsorption for AC-Bit-1 in the presence of sodium hypochlorite may be caused by the change in surface functional groups. The impact of chlorine on methylisoborneol (MIB) adsorption, which is a small constituent, was investigated by Gillogly et al. [46]. They concluded that adsorption capacity for MIB was greatly reduced by free chlorine because it would oxidize adsorption sites on the activated carbon surface. Consistently with previous work, it appears that the bituminous carbon had the largest decrease with chlorination, and it may contain more active surface sites that can be oxidized. Overall, in the selection of activated carbons for this short contact time adsorption application, one cannot dismiss the activated carbon raw material in the selection of the product.

### *3.6. Impact of Background Water Constituents on Ibuprofen Adsorption*

The impact of background water on ibuprofen adsorption was observed using deionized water and natural water from Lake Alice located in Gainesville, FL, USA. The natural water was initially filtered through a 0.45 µm vacuum filter prior to adding 1000 mg/L of ibuprofen. The natural water characteristics are in Table 4.

**Table 4.** Natural water from Lake Alice (Gainesville, FL, USA) characteristics before and after spiking with 1 g/L ibuprofen.

| Water ID | TOC (ppm) | pH | ORP (mV) |
|---|---|---|---|
| **Natural Water** | 5.2 | 7.1 | 411 |
| **Natural Water + 1 g/L ibu** | 443.1 | 7.7 | 406 |

In Figure 8, the removal of ibuprofen in deionized water was greatest for AC-Coco-1 at 54% removal at 1 min contact time. However, in natural water, the sample removed 30% of ibuprofen at the same contact time. Because AC-Coco-1 porosity consists of 84.3% micropore volume ($V_{micro}$ = 0.407 cc/g), it is hypothesized that the reduction in adsoption is due to micropore blockage by dissolved organic matter (DOM) in the natural waters [47]. Both direct competition and pore blockage of smaller DOM compounds will lower adsorption capacity through either desorption by displacement of compounds or steric hinderance [48].

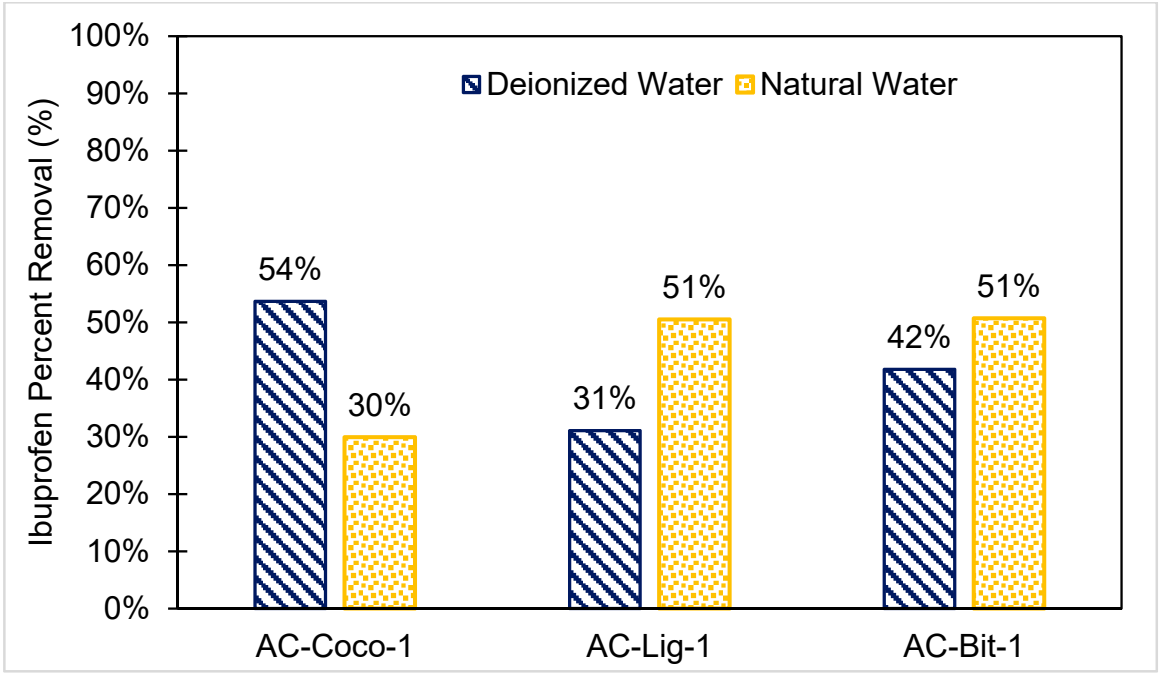


**Figure 8.** Ibuprofen adsorption at 1 min contact time of coconut, lignite, and bituminous activated carbon in deionized and natural waters ($C_{0\text{-deionized}}$ = 1.0 g/L; $C_{0\text{-natural}}$ = 1.1 g/L).

Both AC-Lig-1 and AC-Bit-1 had increased adsorption in natural water compared to deionized water from 31% to 51% and 42% to 51%, respectively (Figure 8). The increase in adsorption may be due to complexation of the ibuprofen with dissolved organic matter. Both samples do not consist entirely of micropores like in AC-Coco-1; therefore, micropore blockage is not expected to hinder adsorption. AC-Lig-1 and AC-Bit-1 total pore volume consists of 26.2% of micropore volume ($V_{micro}$ = 0.18 cc/g) and 68.9% of micropore volume ($V_{micro}$ = 0.27 cc/g), respectively (Table 1).

The decrease in ibuprofen adsorption could be attributed to hydrophobic interactions and hydrogen bonding or pore blockage [49]. The impact of natural organic matter (NOM) will be dependent on the type of pharmaceutical in solution. Bui et al. [50] researched the

impact of NOM on pharmaceutical adsorption to silica. They observed that the hydrophobicity of both the pharmaceutical and NOM will impact adsorption. If the log $K_{ow}$ of ibuprofen and the NOM are similar, interaction between the two compounds are favorable.

## 4. Discussion

Removal of pharmaceuticals using activated carbon have often been discussed based on full-scale treatment plants that frequently use PAC. The plants have a contact time from 15 min up to 4 h depending on the compounds being targeted. Additionally, the initial pharmaceutical concentrations analyzed are in the mg/L to ng/L range. Our proposed approach is to treat wastewater at the point-of-entry, specifically toilet water filtration, to avoid complexation of natural organic matter with the pharmaceuticals, the formation of unknown daughter products, or competitive adsorption of the pharmaceuticals with prevalent organic compounds at higher concentration (i.e., geosmin) in the WWTP.

Implementation and effectiveness of point-of-entry treatment will relate to whether the technology is implemented in households or public spaces like hospitals. The concentration of excreted pharmaceuticals is expected to be in the ng/L range. If introduced as pills, the technology would need to be engineered to slowly dissolve at a rate similar to the disintegration of pharmaceutical pills. Because the pills are engineered to disintegrate either in the gastrointestinal tract, mouth, or liquid solution, more research is required to impart an assumption on a feasible contact time needed for complete dissolution [51]. Additionally, some pharmaceutical compounds will remain as salts if the concentration is above the solubility limit, further complicating the system.

For the sake of identifying ibuprofen capacity of commercially available ACs, 1 g/L concentration was used. It was found that coconut and wood ACs have a good correlation between ibuprofen removal and micropore volume. This is in good accordance with the results found by Guedidi et al. [52].

Competitive adsorption was analyzed from both compounds found in a toilet bowl and natural organic matter. The technology is still feasible with competing species, but there are concerns of possible complexation between natural organic matter and ibuprofen. This is not within the scope of the research but has been well-documented [50,53]. If implemented, the technology may change the raw wastewater characteristics. A change in the pH and solids concentration may occur with activated carbon having a basic pH. The PAC is expected to settle out of solution through the primary settling step, but because of the particle size of the powder, some will stay in solution to the secondary or biological treatment step. Woermann and Sures [54] studied the impact of PAC and PAC dosed with diclofenac (non-steroidal anti-inflammatory drug) on *Daphnia magna* and concluded that PAC may led to immobilization, mortality, and reduction in growth if it adheres to the daphnids' cuticle and antennae or adsorbs nutrients in the media; it was further concluded that if the PAC adsorption sites have been saturated (like PAC exposed to raw wastewater) prior to contact with the daphnids, the PAC would be ingested but would not result in adverse effects. Therefore, more research is required to confidently know the impact of increased PAC to the WWTP technologies, but there is confidence in knowing that the technology will have achieved adsorption capacity prior to entering the plant.

## 5. Conclusions

In this study, various commercially available activated carbons were analyzed for ibuprofen removal from deionized water to simulate point-of-entry removal from the toilet bowl. Since adsorption is preferred to occur in the toilet bowl prior to the waste entering the main drain, rapid adsorption was analyzed with a more than 50% reduction in ibuprofen with the coconut and bituminous AC. The impact of particle size was also investigated using a coconut AC to be preferentially <212 μm.

Competitive adsorption was investigated for implementation using methylene blue and sodium hypochlorite. It was also used to demonstrate the necessity for point-of-entry removal rather than treatment at the WWTP. Methylene blue significantly reduced

ibuprofen adsorption of the mesoporous bituminous AC, while sodium hypochlorite had no apparent effect on the carbon surface functional groups at low contact times. Although the results demonstrate the dosing with PAC is a feasible technology for ibuprofen removal, there is a disadvantage. PAC is not user-friendly and may be dosed improperly. Future experiments should focus on the approach to introducing activated carbon at the point-of-entry, competitive adsorption with urine compounds, and optimal dosage for implementation.

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## References

1. U.S. Food and Drug Administration: Center for Drug Evaluation and Research. Drug Disposal: Drug Take Back Locations. 2020. Available online: https://www.fda.gov/drugs/disposal-unused-medicines-what-you-should-know/drug-disposal-drug-take-back-locations (accessed on 4 April 2021).
2. Lienert, J.; Bürki, T.; Escher, B. Reducing micropollutants with source control: Substance flow analysis of 212 pharmaceuticals in faeces and urine. *Water Sci. Technol.* **2007**, *56*, 87–96. [CrossRef] [PubMed]
3. Sheta, S.M.; Abd-Elzaher, M.M.; El-Sheikh, S.M. A novel nano-lanthanum complex: Synthesis, characterization and application as a macrofuran chemosensor in pharmaceutical, biological and environmental samples. *RSC Adv.* **2021**, *11*, 9675–9681. [CrossRef]
4. Hernando, M.D.; Mezcua, M.; Alba, A.R.F.; Barceló, D. Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. *Talanta* **2006**, *69*, 334–342. [CrossRef]
5. Corcoran, J.; Winter, M.J.; Tyler, C.R. Pharmaceuticals in the aquatic environment: A critical review of the evidence for health effects in fish. *Crit. Rev. Toxicol.* **2010**, *40*, 287–304. [CrossRef]
6. Kümmerer, K. Antibiotics in the aquatic environment—A review—Part I. *Chemosphere* **2009**, *75*, 417–434. [CrossRef] [PubMed]
7. Kümmerer, K. Antibiotics in the aquatic environment—A review—Part II. *Chemosphere* **2009**, *75*, 435–441. [CrossRef]
8. Kümmerer, K. The presence of pharmaceuticals in the environment due to human use—Present knowledge and future challenges. *J. Environ. Manag.* **2009**, *90*, 2354–2366. [CrossRef]
9. Dos Santos, C.; Nardocci, A. Prioritization of pharmaceuticals in drinking water exposure based on toxicity and environmental fate assessment by in silico tools: An integrated and transparent ranking. *Comput. Toxicol.* **2019**, *9*, 12–21. [CrossRef]
10. Webb, S.; Ternes, T.; Gibert, M.; Olejniczak, K. Indirect human exposure to pharmaceuticals via drinking water. *Toxicol. Lett.* **2003**, *142*, 157–167. [CrossRef]
11. Arnold, K.E.; Brown, A.R.; Ankley, G.T.; Sumpter, J.P. Medicating the environment: Assessing risks of pharmaceuticals to wildlife and ecosystems. *Philos. Trans. R. Soc. B Biol. Sci.* **2014**, *369*, 20130569. [CrossRef]
12. Cecconet, D.; Molognoni, D.; Callegari, A.; Capodaglio, A. Biological combination processes for efficient removal of pharmaceutically active compounds from wastewater: A review and future perspectives. *J. Environ. Chem. Eng.* **2017**, *5*, 3590–3603. [CrossRef]
13. 2020 Water Quality Report—Manatee County. Available online: https://www.mymanatee.org/departments/utilities/manatee_county_water_division/water_quality_information/2020_water_quality_report (accessed on 4 June 2021).
14. Olivieri, A.W.; Pecson, B.; Crook, J.; Hultquist, R. California water reuse—Past, present and future perspectives. *Adv. Chem. Pollut. Environ. Manag. Prot.* **2020**, *5*, 65–111. [CrossRef]
15. Schimmoller, L. Fit for Purpose Water: The Cost of Overtreating Reclaimed Water. 2014. Available online: https://watereuse.org/watereuse-research/fit-for-purpose-water/ (accessed on 31 May 2021).
16. Capodaglio, A.G. Fit-for-purpose urban wastewater reuse: Analysis of issues and available technologies for sustainable multiple barrier approaches. *Crit. Rev. Environ. Sci. Technol.* **2020**, 1–48. [CrossRef]
17. Jones, O.A.; Lester, J.N.; Voulvoulis, N. Pharmaceuticals: A threat to drinking water? *Trends Biotechnol.* **2005**, *23*, 163–167. [CrossRef] [PubMed]

18. Gros, M.; Petrović, M.; Ginebreda, A.; Barceló, D. Removal of pharmaceuticals during wastewater treatment and environmental risk assessment using hazard indexes. *Environ. Int.* **2010**, *36*, 15–26. [CrossRef] [PubMed]
19. Faulconer, E.; Mazyck, D.W. Influence of activated carbon surface oxygen functionality on elemental mercury adsorption from aqueous solution. *J. Environ. Chem. Eng.* **2017**, *5*, 2879–2885. [CrossRef]
20. Tennant, M.F.; Mazyck, D.W. The role of surface acidity and pore size distribution in the adsorption of 2-methylisoborneol via powdered activated carbon. *Carbon* **2007**, *45*, 858–864. [CrossRef]
21. Casasús, A.I.; Hagan-Rogers, A.M.; Rodriguez, R.; Mazyck, D.W. Novel photo-activated method for removal of mercury from industrial wastewater. *J. Water Process. Eng.* **2020**, *38*, 101667. [CrossRef]
22. Jaman, S.; Rodriguez, R.; Mazyck, D.W. Evaluation of Common Granular Activated Carbon Parameters for Trace Contaminant Removal. *J. Environ. Eng.* **2019**, *145*, 04019035. [CrossRef]
23. Valcarce, C.O.; Gonzaga, E.W.; Mazyck, D.W. Evaluating the Efficacy of PAC and Water Parameters to Remove Trace Organics. *J. Am. Water Work. Assoc.* **2017**, *109*, E50–E60. [CrossRef]
24. Singh, S.K.; Townsend, T.G.; Mazyck, D.; Boyer, T.H. Equilibrium and intra-particle diffusion of stabilized landfill leachate onto micro- and meso-porous activated carbon. *Water Res.* **2012**, *46*, 491–499. [CrossRef]
25. Rodriguez, R.; Contrino, D.; Mazyck, D.W. Role of Activated Carbon Precursor in Mercury Removal. *Ind. Eng. Chem. Res.* **2020**, *59*, 17740–17747. [CrossRef]
26. Alves, T.C.; Cabrera-Codony, A.; Barceló, D.; Rodriguez-Mozaz, S.; Pinheiro, A.; Gonzalez-Olmos, R. Influencing factors on the removal of pharmaceuticals from water with micro-grain activated carbon. *Water Res.* **2018**, *144*, 402–412. [CrossRef]
27. Mansour, F.; Al-Hindi, M.; Yahfoufi, R.; Ayoub, G.M.; Ahmad, M.N. The use of activated carbon for the removal of pharmaceuticals from aqueous solutions: A review. *Rev. Environ. Sci. Bio/Technol.* **2018**, *17*, 109–145. [CrossRef]
28. Tan, X.; Liu, Y.; Zeng, G.; Wang, X.; Hu, X.; Gu, Y.; Yang, Z. Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere* **2015**, *125*, 70–85. [CrossRef] [PubMed]
29. Solanki, A.; Boyer, T.H. Physical-chemical interactions between pharmaceuticals and biochar in synthetic and real urine. *Chemosphere* **2019**, *218*, 818–826. [CrossRef]
30. Guillossou, R.; Le Roux, J.; Mailler, R.; Vulliet, E.; Morlay, C.; Nauleau, F.; Gasperi, J.; Rocher, V. Organic micropollutants in a large wastewater treatment plant: What are the benefits of an advanced treatment by activated carbon adsorption in comparison to conventional treatment? *Chemosphere* **2019**, *218*, 1050–1060. [CrossRef] [PubMed]
31. Solanki, A.; Boyer, T.H. Pharmaceutical removal in synthetic human urine using biochar. *Environ. Sci. Water Res. Technol.* **2017**, *3*, 553–565. [CrossRef]
32. Kitak, T.; Dumičić, A.; Planinšek, O.; Šibanc, R.; Srčič, S. Determination of Solubility Parameters of Ibuprofen and Ibuprofen Lysinate. *Molecules* **2015**, *20*, 21549–21568. [CrossRef] [PubMed]
33. Khalifeh, I.M. *Thermodynamic Evaluation of Ibuprofen Solubility in Aqueous and Non-Aqueous Cosolvent Systems*; Purdue University: West Lafayette, IN, USA, 2000.
34. Yu, Q.; Li, M.; Ji, X.; Qiu, Y.; Zhu, Y.; Leng, C. Characterization and methanol adsorption of walnut-shell activated carbon prepared by KOH activation. *J. Wuhan Univ. Technol. Sci. Ed.* **2016**, *31*, 260–268. [CrossRef]
35. Zeng, Y.; Prasetyo, L.; Nguyen, V.T.; Horikawa, T.; Do, D.; Nicholson, D. Characterization of oxygen functional groups on carbon surfaces with water and methanol adsorption. *Carbon* **2015**, *81*, 447–457. [CrossRef]
36. Dun, W.; Wu, S.; Tang, W.; Wang, X.; Sun, D.; Du, S.; Gong, J. Solubility of Ibuprofen Sodium Dihydrate in Acetone + Water Mixtures: Experimental Measurement and Thermodynamic Modeling. *J. Chem. Eng. Data* **2014**, *59*, 3415–3421. [CrossRef]
37. Lowell, S.; Shields, J.E.; Thomas, M.A.; Thommes, M. Surface Area Analysis from the Langmuir and BET Theories. In *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density*; Springer: Dordrecht, The Netherlands, 2004; Volume 16, pp. 58–81. [CrossRef]
38. ASTM International. ASTM D6851-20, Standard Test Method for Determination of Contact pH with Activated Carbon. 2020. Available online: https://compass.astm.org/EDIT/html_annot.cgi?D6851+20 (accessed on 1 May 2021).
39. Real, F.J.; Benitez, F.J.; Acero, J.L.; Casas, F. Adsorption of selected emerging contaminants onto PAC and GAC: Equilibrium isotherms, kinetics, and effect of the water matrix. *J. Environ. Sci. Health Part A* **2017**, *52*, 727–734. [CrossRef]
40. Sodeinde, O.A. Preparation of a Locally Produced Activated Carbon from Coconut Shells and Its Use in Reducing Hexamine Cobalt(III). *Int. J. Chem. Eng. Appl.* **2012**, *2012*, 67–71. [CrossRef]
41. Yener, J.; Kopac, T.; Dogu, G.; Dogu, T. Dynamic analysis of sorption of Methylene Blue dye on granular and powdered activated carbon. *Chem. Eng. J.* **2008**, *144*, 400–406. [CrossRef]
42. El Qada, E.N.; Allen, S.J.; Walker, G. Adsorption of Methylene Blue onto activated carbon produced from steam activated bituminous coal: A study of equilibrium adsorption isotherm. *Chem. Eng. J.* **2006**, *124*, 103–110. [CrossRef]
43. Arias, M.; López, E.; Nunez, A.; Rubinos, D.; Soto, B.; Barral, M.T.; Diaz-Fierros, F. Adsorption of Methylene Blue by Red Mud, An Oxide- Rich Byproduct of Bauxite Refining. In *Effect of Mineral-Organic-Microorganism Interactions on Soil and Freshwater Environments*; Berthelin, J., Huang, P.M., Bollag, J.M., Andreux, F., Eds.; Springer: Boston, MA, USA, 1999; pp. 361–365.
44. Liu, W.; Zhang, J.; Cheng, C.; Tian, G.; Zhang, C. Ultrasonic-assisted sodium hypochlorite oxidation of activated carbons for enhanced removal of Co(II) from aqueous solutions. *Chem. Eng. J.* **2011**, *175*, 24–32. [CrossRef]
45. Haydar, S.; Ferro-García, M.; Rivera-Utrilla, J.; Joly, J. Adsorption of p-nitrophenol on an activated carbon with different oxidations. *Carbon* **2003**, *41*, 387–395. [CrossRef]

46. Gillogly, T.E.; Snoeyink, V.L.; Holthouse, A.; Wilson, C.M.; Royal, E.P. Effect of chlorine on PAC's ability to adsorb MIB. *J. Am. Water Work. Assoc.* **1998**, *90*, 107–114. [CrossRef]
47. Pelekani, C.; Snoeyink, V. Competitive adsorption in natural water: Role of activated carbon pore size. *Water Res.* **1999**, *33*, 1209–1219. [CrossRef]
48. Aschermann, G.; Neubert, L.; Zietzschmann, F.; Jekel, M. Impact of different DOM size fractions on the desorption of organic micropollutants from activated carbon. *Water Res.* **2019**, *161*, 161–170. [CrossRef]
49. Newcombe, G.; Drikas, M. Adsorption of NOM onto activated carbon: Electrostatic and non-electrostatic effects. *Carbon* **1997**, *35*, 1239–1250. [CrossRef]
50. Bui, T.X.; Choi, H. Influence of ionic strength, anions, cations, and natural organic matter on the adsorption of pharmaceuticals to silica. *Chemosphere* **2010**, *80*, 681–686. [CrossRef] [PubMed]
51. Desai, P.M.; Liew, C.V.; Heng, P.W.S. Review of Disintegrants and the Disintegration Phenomena. *J. Pharm. Sci.* **2016**, *105*, 2545–2555. [CrossRef] [PubMed]
52. Guedidi, H.; Reinert, L.; Lévêque, J.-M.; Soneda, Y.; Bellakhal, N.; Duclaux, L. The effects of the surface oxidation of activated carbon, the solution pH and the temperature on adsorption of ibuprofen. *Carbon* **2013**, *54*, 432–443. [CrossRef]
53. Oh, S.; Shin, W.S.; Kim, H.T. Effects of pH, dissolved organic matter, and salinity on ibuprofen sorption on sediment. *Environ. Sci. Pollut. Res. Int.* **2016**, *23*, 22882–22889. [CrossRef] [PubMed]
54. Woermann, M.; Sures, B. Ecotoxicological effects of micropollutant-loaded powdered activated carbon emitted from wastewater treatment plants on Daphnia magna. *Sci. Total Environ.* **2020**, *746*, 141104. [CrossRef]