ABSTRACT

DENG, QIANRU. Removal of Biochemically Active Compounds by Powdered Activated Carbon Adsorption Processes. (Under the direction of Dr. Detlef Knappe).

Biochemically active compounds (BACs), such as endocrine disrupting chemicals, antimicrobial compounds, and pharmaceutically active compounds, are ubiquitous in wastewater treatment plant effluents and in drinking water sources that are impacted by wastewater discharges. Powdered activated carbon (PAC) adsorption is one water treatment process that can effectively remove BACs, but little information is available on factors that affect BAC removal by PAC. The principal objective of this study was to identify factors that control the BAC removal effectiveness of PAC adsorption processes. Specific objectives were to determine the effects of the following factors on BAC removal: 1) PAC type (coal-based, wood-based, lignite-based); 2) PAC particle size (as-received and submicrometer-sized PAC, or S-PAC); 3) background water matrix; 4) solution/coagulation pH; 5) presence of metal hydroxide floc; and 6) timing of PAC addition relative to the addition of the coagulant.

Batch kinetic tests and adsorption isotherm tests were conducted with six BACs [bezafibrate (BZF), diclofenac (DCF), ibuprofen (IBP), metoclopramide (MCP), sulfamethoxazole (SMX), and trimethoprim (TMP)]. Among the six tested BACs, MCP and TMP were the most adsorbable, BZF and DCF represented compounds of intermediate adsorbability, and IBP and SMX were the two least adsorbable compounds. Removal of the weak acid SMX increased with decreasing pH and removal of the weak base TMP increased with increasing pH. Also, PAC type and particle size were found to
affect BAC removal. In particular, BAC uptake rates obtained with S-PAC were considerably faster than those obtained with as-received PAC.

Jar tests were conducted with SMX, TMP, and IBP that were spiked into two North Carolina surface waters and one wastewater treatment plant effluent (WWTPE). The timing of PAC addition affected TMP and turbidity removal. TMP removal was lower when PAC was added together with coagulants than when PAC was added either 5 minutes before the coagulant or 9 minutes into the flocculation step. Turbidity removal was lowest when PAC was added 9 minutes into the flocculation step. Sub-micrometer PAC (S-PAC) greatly enhanced BAC removal. To obtain 90% removal of SMX and IBP from the two surface waters, the required S-PAC dose was 15-25 mg/L, while 75 mg/L or more was required for the as-received PACs.
Adsorption Processes

by

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DEDICATION

To my family.
Qianru Deng was born in Guangyuan, China on February 11, 1986. She received her Bachelor of Engineering degree in Environmental Engineering from Sichuan University, Chengdu in July 2008. After graduation, in Fall 2008, she started her Master of Science program in Department of Civil, Construction and Environmental Engineering at North Carolina State University, under the direction of Dr. Detlef Knappe.
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Chapter 1.

INTRODUCTION AND OBJECTIVES

1.1. Problem Statement

The presence of biochemically active compounds (BACs) such as endocrine disrupting chemicals (EDCs), antimicrobial compounds, and other pharmaceutically active compounds (PhACs) in the aquatic environment is an issue of great importance. Many drugs are not fully metabolized by humans and animals and are excreted. Also, unused pharmaceuticals are often flushed down the toilet or poured down the drain. Many BACs are poorly removed during conventional wastewater treatment (Ternes, 1998, Nasu et al., 2001, Paxeus, 2004, Göbel et al., 2007), and WWTP discharges are therefore an important source through which BACs are introduced into the environment and into drinking water sources. Numerous BACs have been detected in surface and ground water (Lindsey et al., 2001, Kolpin et al., 2002, Heberer et al., 2002, Yang et al., 2004, Jones et al., 2005).

Although BACs are typically present at trace levels (ng/L range) in finished drinking water, the public is concerned about potential human health effects associated with chronic BAC exposure (Loos et al., 2007, Vieno et al., 2007, Benotti et al., 2009). While BAC concentrations in drinking water are well below the levels that would expose consumers to therapeutic doses, the effects of chronic exposure to trace concentrations of BACs are not well understood (Snyder et al., 2003, Jones et al., 2005). One study has shown that a mixture of EDCs and PhACs at nanogram per liter levels has the potential to
induce adverse effects in human cell lines (Pomati, et al., 2006). To date, no drinking water standards or guidelines have been issued in the United States, but four estrogen compounds were recently added to the US EPA Contaminant Candidate List (CCL). If risk assessors and epidemiologists are to link any adverse health outcomes with BAC exposure, a better understanding of their occurrence and removal in drinking water is critical.

Ecotoxicological effects of BACs have been demonstrated in a wide range of studies (Fry and Toone, 1981, Guillette et al., 1994, Folmar et al., 1996, Harries et al., 1996, Jobling et al., 1998, Jenkins et al., 2001, Hayes et al., 2002). The presence of EDCs may cause intersexuality in fish (Guillette et al., 1994, Folmar et al., 1996, Harries et al., 1996, Jobling et al., 1998, Jenkins et al., 2001) and demasculinize frogs (Hayes et al., 2002), and the presence of antimicrobial compounds may lead to the evolution of antibiotic-resistant bacteria. A USGS study found that at least 80% of male smallmouth bass caught in Virginia and Maryland tributaries of the Potomac River grew eggs (Farenthold, 2006). In addition, 54% of male largemouth bass caught in the Potomac River near the Blue Plains wastewater treatment plant (WWTP) of Washington D.C. showed signs of feminization and 23% were intersex. While the specific cause of the feminization of male fish in the Potomac watershed has not yet been identified, other studies have linked incidents of intersexuality to the presence of EDCs that enter streams through WWTP discharges (Guillette et al., 1994, Folmar et al., 1996, Harries et al., 1996, Jobling et al., 1998, Jenkins et al., 2001, Hayes et al., 2002).
1.2. Research Objectives

The overall objective of this research was to evaluate the effectiveness of powdered activated carbon (PAC) adsorption processes for BAC removal. Specific objectives were to evaluate the effects of the following factors on BAC removal: 1) PAC type (coal-based, wood-based, lignite-based); 2) PAC particle size (as-received and submicrometer-sized PAC, or S-PAC); 3) background water matrix; 4) solution/coagulation pH; 5) presence of metal hydroxide floc; and 6) timing of PAC addition relative to the addition of the coagulant (simultaneous addition of PAC and coagulant, PAC addition 5 minutes prior to coagulant, PAC addition 9 minutes into the flocculation process).
1.3. References


Chapter 2

REMOVAL OF BIOCHEMICALLY ACTIVE COMPOUNDS BY POWDERED ACTIVATED CARBON ADSORPTION

Abstract

Biochemically active compounds (BACs), such as endocrine disrupting chemicals, antimicrobial compounds, and pharmaceutically active compounds, are ubiquitous in wastewater treatment plant effluents and in drinking water sources that are impacted by wastewater discharges. Powdered activated carbon (PAC) adsorption is one water treatment process that can effectively remove BACs, but little information is available on factors that affect BAC removal by PAC. The objectives of this study were to evaluate 1) the effectiveness of different PAC types (coal based, wood based, lignite based) for BAC removal; 2) the effect of PAC particle size (as-received and submicrometer-sized PAC, or S-PAC) on BAC uptake rates, and 3) the effects of solution pH and background water matrix on BAC removal. Batch kinetic tests and adsorption isotherm tests were conducted with six BACs [bezafibrate (BZF), diclofenac (DCF), ibuprofen (IBP), metoclopramide (MCP), sulfamethoxazole (SMX), and trimethoprim (TMP)]. Among the six tested BACs, MCP and TMP were the most adsorbable, BZF and DCF represented compounds of intermediate adsorbability, and IBP and SMX were the two least adsorbable compounds. Removal of the weak acid SMX increased with decreasing pH and removal of the weak base TMP increased with increasing pH. Also, PAC type and particle size were found to affect BAC removal. In particular, BAC uptake rates obtained with S-PAC were considerably faster than those obtained with as-received PAC. Batch kinetic data were
well described by a pseudo single-solute homogeneous surface diffusion model.

2.1. Introduction

The presence of biochemically active compounds (BACs) such as endocrine disrupting chemicals (EDCs), antimicrobial compounds, and other pharmaceutically active compounds (PhACs) in the aquatic environment is an issue of great importance. Several studies have illustrated that BACs are present in both surface water (Lindsey et al., 2001, Heberer et al., 2002, Kolpin et al., 2002, Yang et al., 2004, Jones et al., 2005) and in finished drinking water (Loos et al., 2007, Vieno et al., 2007, Benotti et al., 2009). These studies showed that BACs typically occur in the range of nanograms per liter to micrograms per liter in surface water, and at concentrations of hundreds of nanograms per liter or less in finished drinking water. While BAC concentrations in drinking water are well below the levels that would expose consumers to therapeutic doses, the effects of chronic exposure to trace concentrations of BACs are not well understood (Snyder et al., 2003, Jones et al., 2005). Ecotoxicological effects of BACs have been demonstrated in a wide range of studies (Fry and Toone, 1981, Guillette et al., 1994, Folmar et al., 1996, Harries et al., 1996, Jobling et al., 1998, Jenkins et al., 2001, Hayes et al., 2002). Also, mixtures of EDCs and PhACs at nanogram per liter levels have the potential to induce adverse effects in human cell lines (Pomati et al., 2006). If risk assessors and epidemiologists are to link any further health outcomes with BACs exposure, a better understanding of their occurrence and removal in drinking water is critical.

Wastewater treatment plant effluents are an important source of BACs in the aquatic
environment. Biological treatment processes have been shown to be ineffective in the removal of many antibiotics and other pharmaceuticals. Ingerslev and Halling-Sorensen (2000) found that 12 different sulfonamides were not readily biodegradable in activated sludge. Kummerer et al. (1997) found that many pharmaceuticals could not be biodegraded during conventional biological treatment, nor could they be adsorbed by sewage sludge.

Conventional drinking water treatment processes such as coagulation, sedimentation and filtration achieve minimal removal of BACs. Aluminum sulfate and ferric chloride coagulants or chemical lime softening removed less than 20% of most 60 EDC/PhACs that were studied (Westerhoff et al., 2005). Drinking water treatment therefore relies primarily on adsorptive and oxidative processes to remove or transform BACs. An ozone dose of 0.5 mg/L was shown to oxidize more than 90% of some BACs (e.g., diclofenac and carbamazepine) while other BACs (e.g., clofibrate acid and dieldrin) were poorly oxidized (<20%) even at an ozone dose of 3 mg/L (Westerhoff et al., 2005, Adams et al., 2002, Ternes et al., 2002).

Among the wide range of BACs, some compounds showed higher adsorbability by PAC than others. Over a 4-hour contact time, addition of 5 mg/L of PAC removed >90% of testosterone and trimethoprim but removed only about 10% of sulfamethoxazole and ibuprofen (Westerhoff et al., 2005). The observed diversity in removal efficiencies is attributed to the diverse physicochemical properties of the BACs (Yu et al., 2009).
Although the adsorbability of many BACs has been measured, little is known about the factors that control the effectiveness of activated carbon adsorption processes. With granular activated carbon (GAC), natural organic matter (NOM) loading was found to reduce the adsorption capacity of BACs (Ternes et al., 2002, Yu et al., 2009). To date, few studies have addressed the characteristics of pharmaceutical adsorption by PAC. Adams et al. (2002) found that background NOM in natural water adversely affected antibiotic adsorption by PAC, especially at lower PAC doses. Westerhoff et al. (2005) related the pharmaceutical adsorption by PAC to octanol-water partition coefficients (log Kow) of the neutral compound. Further details to characterize the adsorption process of pharmaceuticals are necessary. For example, since many BACs are ionizable, the solution pH affects their degree of ionization and hydrophobicity, and thus their adsorbability.

Recent studies found that sub-micrometer powdered activated carbon (S-PAC) greatly enhances the removal of NOM and micropolllutants such as taste and odor compounds (Matsui et al., 2009). To date, no information about the effectiveness of S-PAC for BAC removal is available in the published literature. The work of Matsui et al. (2009) shows that the greater effectiveness of S-PAC for NOM removal is attributed to both a higher equilibrium adsorption capacity for NOM and faster adsorption kinetics. For micropolllutants such as taste and odor compounds, S-PAC exhibits faster adsorption kinetics than a corresponding as-received PAC, but the equilibrium adsorption capacity is similar for both S-PAC and as-received PAC.
The principal objective of this study was to assess the effectiveness of PAC adsorption for the removal of six BACs [bezafibrate (BZF), diclofenac (DCF), ibuprofen (IBP), metoclopramide (MCP), sulfamethoxazole (SMX), and trimethoprim (TMP)], and to identify factors that affect BAC uptake rates. In particular, the following factors were evaluated: 1) PAC type (coal-based, wood-based, lignite-based); 2) PAC particle size (as-received PAC and submicrometer-sized PAC, or S-PAC); 3) solution pH; and 4) background water matrix (mainly NOM concentration). BAC removal rates were measured in batch kinetic tests, and PAC performance was described by the pseudo-single solute homogeneous surface diffusion model (HSDM).

2.2. Materials and Methods

2.2.1. Pharmaceuticals

In this study, the adsorptive removal of six BACs were evaluated in bench-scale tests. The selected BACs included the antimicrobial compounds sulfamethoxazole (SMX) and trimethoprim (TMP); the antiemetic metoclopramide (MCP); the lipid regulator bezafibrate (BZF); the non-steroidal anti-inflammatory diclofenac (DCF) and the analgesic ibuprofen (IBP). Table 1 summarizes the molecular structures of the studied BACs as well as representative concentrations in surface and finished drinking waters. All pharmaceuticals were purchased from Sigma Chemical Corporation (St. Louis, MO, USA). All chemicals were stored at ambient temperature except TMP which was stored at 4 °C.
Table 2 summarizes the physical-chemical characteristics of the selected pharmaceuticals, including the octanol-water partition coefficient of the neutral form of each compound ($\log K_{ow}$) and the octanol-water partition coefficient at pH 7 ($\log D$). The $pK_a$ values illustrate that BZF, DCF, IBP, and SMX are predominantly present in their anionic form at neutral pH. In contrast, the cationic form of MCP dominates at pH 7. For TMP, cationic and neutral forms coexist in almost equal proportions at neutral pH.

SMX, BZF, IBP, and DCF stock solutions were prepared daily in phosphate buffered ultrapure (DI) water (pH 7); TMP stock solutions were prepared in acidified DI water (pH 4) to enhance solubility; and MCP stock solutions were prepared in DI water. All stock solutions were prepared at concentrations of 2.0 mg/L, and stock solutions were filtered through a 0.22-µm PTFE membrane before use. The targeted initial pharmaceutical concentration was ~100 µg/L (<0.5 µM) for adsorption tests. This concentration is sufficiently low that the determined removal percentages are expected to match those obtained at concentrations more commonly encountered in the environment (e.g., Rossner et al., 2009).

### 2.2.2. Water

Two North Carolina drinking water sources and one wastewater treatment plant effluent (WWTPE) were used. The drinking water sources were OWASA water (50/50 University Lake/Cane Creek reservoir blend, Carrboro, NC) and Cape Fear river water (Wilmington, NC). The WWTPE was collected at the North Cary Water Reclamation Facility (Cary, NC) after UV disinfection. Upon collection, water was stored in 55-gal stainless steel drums at
4°C. Water was filtered through 0.45-µm membranes prior to use unless specified otherwise. Dissolved organic carbon (DOC) concentrations, \( \text{UV}_{254} \) absorbance, specific ultraviolet absorption (SUVA\(_{254} \)), pH, alkalinity, and total hardness of the three waters are shown in Table 3.

### 2.2.3. Powdered Activated Carbons

Four PACs prepared from different base materials and with different activation methods were studied (Table 4). Three PACs (NuChar, Hydrodarco B, and WPH) were used in their as-received form. In addition, a superfine version of the WPH PAC was prepared, which was termed S-WPH. The mean diameter of S-WPH was \(~0.3\ \mu\text{m}\) while those of the as-received PACs were in the range of 17-25 \(\mu\text{m}\).

### 2.2.4. Batch kinetic tests

Batch kinetic tests were performed with the four PACs shown in Table 4. Pharmaceuticals were spiked at an initial concentration of \(~100\ \mu\text{g/L}\) into the water of interest. Experiments were conducted in 32-oz. amber glass bottles, and solutions were mixed with a PTFE-coated magnetic stir bar. Experiments were conducted at the ambient pH of each water unless otherwise specified. After taking samples to determine the initial BAC concentration, the desired amount of PAC was added under continuous mixing. PACs were oven-dried (105°C), weighed, and soaked in a small volume of DI water one day prior to use. Samples for pharmaceuticals analysis were taken after PAC contact times of 2, 5, 10, 15, 30, 60 and 120 minutes. Additional samples were taken after a contact time
of 2 weeks. Solution pH was measured at the beginning and end of each kinetic test (Orion pH meter 420 A, Fisher Scientific, Pittsburgh, PA).

2.2.5. Adsorption isotherm tests

Isotherm tests were performed with three PACs (NuChar, WPH, and S-WPH). Pharmaceuticals were spiked at an initial concentration of ~100 µg/L into the water of interest. Subsequently, PAC was added at concentrations ranging from 0.5-70 mg/L. Experiments were conducted in 8-oz. amber glass bottles that were placed on a shaker table operating at 100 rpm (Innova 2300, New Brunswick Scientific, Edison, New Jersey). Experiments were conducted at ambient pH unless otherwise specified. Adsorbent-free blanks containing the tested water spiked with the same BAC concentration as the samples receiving PAC were used to assess pharmaceutical losses during the equilibration time. BAC losses were negligible. Samples for BAC analysis were taken after a PAC contact time of 2 weeks.

2.2.6. Analytical methods

Concentrations of the six pharmaceuticals were determined with a high-performance liquid chromatography system equipped with a dual-wavelength UV detector (HPLC, Breeze, Waters Corporation, Milford, MA). Pharmaceuticals were separated on a C18 column (2.6 µm, 4.6 x 100 mm, Kinetex C18 100A, Phenomenex, Torrance, CA). Prior to analysis, samples were filtered through a 0.22-µm PTFE membrane. Concentrations in bench-scale tests were sufficiently high that samples could be analyzed by direct injection,
and limits of quantitation are listed for each compound in Table 1.

A gradient method was used for the analysis of SMX, TMP and MCP. Eluent A consisted of 50% v/v acetonitrile and 50% v/v 25 mM ammonium acetate buffer (pH 5) and eluent B of 10% v/v acetonitrile and 90% v/v 25 mM ammonium acetate buffer (pH 5). Each analysis started with 100% eluent B. From 1 to 9 minutes, the eluent was ramped linearly from 100% eluent B to 75% eluent B and 25% eluent A. Isocratic methods were used for BZF, DCF, and IBP. For BZF, the mobile phase was 25% v/v acetonitrile and 75% v/v 25 mM ammonium acetate buffer (pH 5). For DCF and IBP, the mobile phase was 37% v/v acetonitrile and 63% v/v 25 mM ammonium acetate buffer (pH 5). The mobile phase flow rate was 1 mL/min for all analyses, and the sample injection volume was 200 µL. The detector wavelength was set at 266 nm for SMX, 238 nm for TMP, 274 nm for MCP, 240 nm for BZF, 282 nm for DCF, and 222 nm for IBP.

TOC and DOC were measured with a total organic carbon analyzer (TOC-5000A, Shimadzu Scientific, Columbia, MD). UV\textsuperscript{254} absorbance was measured with a UV/vis spectrophotometer (UNICAM UV1).

Solution pH was measured with a calibrated pH meter (Orion pH meter 420 A, Fisher Scientific, Pittsburgh, PA).
2.3. Results and Discussion

2.3.1. Adsorbability of pharmaceuticals

Uptake rates of six pharmaceuticals are compared in Figure 1 for PAC doses of 10 and 20 mg/L. Results were obtained with NuChar PAC that was added to OWASA water that was previously filtered through a 0.45-µm membrane. Uptake rates were determined at ambient pH (~ 7.2). The data in Figure 1 show that MCP and TMP are the most adsorbable compounds; BZF and DCF represent compounds of intermediate adsorbability; and IBP and SMX represent the two least adsorbable compounds. Based on the results shown in Figure 1, subsequent adsorption experiments focused primarily on TMP and SMX, which bracket the adsorbabilities of the selected pharmaceuticals. As shown in Appendix 1, uptake rates of TMP and SMX that were spiked separately did not significantly differ from those with TMP and SMX spiked together in one batch. Therefore, some experiments were conducted by spiking TMP and SMX in the same batch.

2.3.2. Effect of pH on SMX and TMP adsorbability

SMX and TMP uptake kinetics at pH 4, 5.5 and 7 are compared in Figure 2. NuChar PAC doses were 20 mg/L for SMX and 5 mg/L for TMP. The lower PAC dose for TMP was chosen to more clearly illustrate pH effects on TMP removal. For SMX, removal increased with decreasing pH, especially as the pH was lowered from 7 to 5.5 (Figure 2a). For TMP, the opposite trend was found; removal decreased with decreasing pH (Figure 2b). The results in Figure 2 can be explained by the acid/base characteristics of SMX and
TMP. The pK\textsubscript{a} of SMX is 5.8, which means that at pH 5.8, 50% of SMX exists in the neutral form and 50% in the anionic form. When the pH increases above pH 5.8, the anionic form begins to dominate, and when the pH decreases below pH 5.8, the neutral form begins to dominate (Figure 3a). The neutral form of SMX is less soluble than the anionic form, and as a result, SMX adsorbability increases as the fraction of the neutral form increases; i.e., with decreasing pH.

For TMP, the cationic form dominates at pH values below its pK\textsubscript{a} of 7.1, and the neutral form dominates at pH values above pH 7.1 (Figure 3b). Again, the neutral form is less soluble than the ionic form, therefore, TMP adsorbability increases as the fraction of the neutral form increases (i.e., with increasing pH).

### 2.3.3. Background water matrix effects

SMX and TMP removals obtained in two NC drinking water sources and one WWTPE are summarized in Figure 4. The waters differed primarily in their DOC concentrations (5.2 mg/L for OWASA, 6.6 mg/L for Cape Fear river, 7.3 mg/L for Cary WWTPE). The results in Figure 4 show that differences in TMP and SMX removal were small between the two drinking water sources (Cape Fear river and OWASA water). This observation illustrates that the concentration of competing background organic matter in Cape Fear river water did not differ substantially from that in OWASA water. In contrast, the background organic matter in the WWTPE exerted a stronger competitive effect. The effect of the WWTPE matrix was especially pronounced for SMX because the WWTPE exhibited both a higher DOC concentration and a higher pH. As discussed in the previous
section, SMX is a weak organic acid that transitions from the neutral to the anionic form as pH increases. As a result, the adsorbability of SMX decreases with increasing solution pH. The effects of the WWTPE matrix on TMP removal were less pronounced. TMP is a weak organic base that transitions from the cationic to the neutral form as pH increases. As a result, its adsorbability increases with increasing pH. Even though the pH of the WWTPE was higher than that of the two drinking water sources, TMP removal was lower in the WWTPE. Thus, the WWTPE contained organic matter that competed more strongly with the trace organic contaminants than the organic matter in the two drinking water sources.

2.3.4. Effect of PAC type and particle size

SMX and TMP removal

The effect of PAC type on SMX removal from OWASA water is shown in Figures 5 and 6. In Figure 5, SMX uptake data are shown for PAC contact times of up to 2 hours. In Figure 6, SMX uptake data are compared at contact times of 15 minutes, 2 hours, and 2 weeks, the latter indicating the maximum uptake capacity that is achieved at adsorption equilibrium. All PACs were tested at a dose of 10 mg/L. As shown in Figure 5, SMX removals among the three as-received PACs (NuChar, Hydrodarco-B, WPH) were similar (~20% removal after a contact time of 60 minutes). There were small differences in the SMX uptake rates among the as-received PACs; e.g., SMX removal during the first 20 minutes was somewhat higher with NuChar PAC than with WPH and Hydrodarco B PACs. At longer contact times, SMX uptake was slightly higher with WPH PAC.
In contrast to the results obtained with the as-received PACs, SMX removal with the superfine version of WPH (S-WPH) was approximately three times larger, ~60% after a contact time of 60 minutes. The better performance of S-WPH may have been the result of faster kinetics and/or a larger equilibrium uptake capacity. To distinguish between the two, SMX uptake results from longer-term experiments were compared for WPH and S-WPH after a contact time of 2 weeks (Figure 6). A comparison of the 2-week data for WPH and S-WPH in Figure 6 shows that the SMX adsorption capacities of the as-received and superfine versions of WPH were similar. Therefore, the grinding process did not change the maximum uptake capacity for SMX, only the SMX uptake kinetics.

More generally, the results shown in Figure 6 permit a comparison between SMX uptake at short contact times, when adsorption kinetics are important, and at long contact times, when adsorption equilibrium is important. At adsorption equilibrium, the following order in SMX uptake was observed: WPH ~ S-WPH > Hydrodarco B > NuChar. In contrast, at very short contact times, the order was S-WPH >> NuChar > WPH ~ Hydrodarco B. Relative to SMX uptake at equilibrium, SMX uptake after a contact time of 15 minutes was ~96% for S-WPH, ~67% for NuChar, ~34% for Hydrodarco B, and ~21% for WPH. These results illustrate that almost the entire adsorption capacity of S-WPH was utilized after 15 minutes of contact. In contrast, less than one quarter of the WPH adsorption capacity was utilized at the same contact time. Thus, the use of S-PAC may allow utilities to almost fully utilize the equilibrium uptake capacity of PAC, even when PAC contact times are short, as is often the case.
The effect of PAC type on TMP removal from OWASA water is compared in Figures 7 and 8. In Figure 7, TMP uptake data are shown for contact times of up to 2 hours. For TMP, distinct differences between the three as-received PAC types (NuChar, WPH, Hydrodarco B) were observed. TMP uptake was in the order of NuChar > WPH >> Hydrodarco B. As was the case with SMX, the superfine version of WPH (S-WPH) produced greater TMP removals than any of the as-received PACs (Figure 7). The better performance of S-WPH was primarily a result of improved adsorption kinetics, because the maximum TMP adsorption capacity that was measured after a contact time of 2 weeks was identical for WPH and S-WPH (Figure 8). Because of the rapid adsorption kinetics that can be achieved with S-WPH, almost the entire TMP adsorption capacity was utilized after a contact time of 15 minutes. In contrast, only ~30-50% of the TMP adsorption capacity was utilized after a contact time of 15 minutes for the as-received PACs (Figure 8).

**NOM removal**

In addition to BAC uptake rates, NOM uptake rates were measured by conducting DOC and UV\(_{254}\) absorbance analyses (Figure 9). NOM removal was measured after contact times of 2 hours (non-equilibrium condition) and 2 weeks (equilibrium condition), and results are shown for a PAC dose of 10 mg/L. After a contact time of 2 hours, DOC removal was ~10% or less for the as-received PACs and ~20% for S-WPH. UV\(_{254}\) removal ranged from ~8-13% for the as-received PACs and was almost 35% for S-WPH. The results for S-WPH suggest that meaningful NOM removal can be achieved with a
reasonable PAC dose of 10 mg/L.

At equilibrium, Figure 9 shows that NOM uptake was in the order S-WPH > NuChar > WPH > Hydrodarco B. Thus, grinding WPH PAC to a finer particle size not only enhanced adsorption kinetics but also increased its maximum adsorption capacity for NOM. One possible explanation for the greater NOM adsorption capacity of S-WPH is that NOM may be able to penetrate only a certain distance into PAC particles (Matsui, personal communication). In that case, a larger percentage of the S-WPH particles is accessible to NOM than is the case for as the as-received WPH.

2.3.5. Modeling of BAC adsorption

To model the rate of BAC adsorption by PAC in natural water, a pseudo single-solute homogeneous surface diffusion model (HSDM) was used (See Appendix 2 for model background). Using this approach, the rate of BAC adsorption by PAC in natural water was modeled as if the target compound was the only solute present. In applying the pseudo single-solute HSDM, the assumption was made that the effect of the background organic matter on the rate of adsorption of the target compound is constant, i.e., the surface diffusion coefficient is not a function of the PAC dose or the initial concentration of the target compound in the natural water (Qi et al., 1994)

One important set of input parameters for the HSDM are the Freundlich isotherm constants K and 1/n. To determine K and 1/n, adsorption isotherm data were described with the Freundlich model (Freundlich, 1906):
\[ q = KC^{1/n} \]  

(2.1)

where \( q \) is the equilibrium solid phase concentration, \( C \) is the equilibrium aqueous phase concentration, and \( K \) and \( 1/n \) are Freundlich isotherm constants. A higher \( K \) value indicates a higher adsorption capacity of the adsorbent for a given target compound. As the \( 1/n \) value decreases from a value of 1, which would be obtained for a homogeneous adsorbent, the heterogeneity of adsorption site energies increases. Figure 10 depicts an example isotherm for bezafibrate and Table 5 provides a summary of all \( K \) and \( 1/n \) values that were obtained in this study. Freundlich isotherms of all six compounds by NuChar, and SMX and TMP by WPH are shown in Appendix 1.

As shown in Table 5, the Freundlich \( K \) values that were obtained with NuChar PAC substantiate that MCP and TMP are the most adsorbable compounds and that SMX and IBP are the least adsorbable. A comparison of Freundlich \( K \) values that were obtained with NuChar and WPH illustrates that WPH exhibited a larger adsorption capacity for both SMX and TMP.

**Determination of \( D_s \)**

Surface diffusion coefficients (\( D_s \)) were determined by a nonlinear least-squares optimization technique that minimizes the error between the experimental data and the model output from the HSDM. The program “SEARCH” (see Appendix 4) written by Traegner and Suidan (1989) was used in this work to determine \( D_s \) values. HSDM fits are shown in Figures 11 and 12 for data sets obtained with NuChar and WPH PACs,
respectively, and the determined $D_s$ values are listed in Table 5. Both Figures 11 and 12 illustrate that the kinetic data were well described by the HSDM. Attempts were also made to describe the S-WPH data with the HSDM, but the model output did not agree well with the experimental data. Most likely, a branched pore diffusion model is required to describe the S-WPH data (Matsui, et al., 2009).

For NuChar PAC, $D_s$ values among the 6 BACs ranged from $6.78 \times 10^{-9}$ to $6.82 \times 10^{-7}$ cm$^2$/s (Table 5), and $D_s$ was inversely correlated with the Freundlich capacity parameter $K$ (Figure 13). A possible explanation for the inverse correlation is that surface diffusion takes place more slowly for BACs that have a higher affinity for the activated carbon surface.

Once the parameters $K$, $1/n$, and $D_s$ were determined for a given initial BAC concentration and PAC dose, the program “HSDM” (see Appendix 4) written by Traegner and Suidan (1989) was used to predict BAC uptake kinetics for a different PAC dose. As shown in Figure 11, HSDM predictions agreed well with the data sets that were collected for model validation. Based on the determined equilibrium and kinetic parameters, the required PAC doses for a desired level of BAC removal were predicted for PAC contact times of 15, 30, and 60 minutes as shown in Appendix 1 (Figures 4 and 5). Table 6 summarizes PAC dosage predictions for 90% BAC removal from OWASA water with NuChar and WPH PACs. To obtain 90% removal for the weakly adsorbing SMX, the HSDM predictions for a 15-minute contact time suggest that NuChar and WPH doses of 70 and 120 mg/L are required, respectively. For a 60-minute contact time, NuChar and
WPH doses of 50 and 60 mg/L were predicted, respectively, for 90% SMX removal. For the more strongly adsorbing TMP, PAC doses of 15 and 8 mg/L are required to achieve 90% removal at contact times of 15 and 60 minutes, respectively. NuChar and WPH PAC dosage predictions for TMP removal were similar (Table 6).

2.4. Conclusions

Batch kinetic and adsorption isotherm tests were conducted to evaluate the effects of PAC type, PAC particle size, and solution pH on BAC adsorption rates and uptake capacities. The following conclusions were derived from the experimental data:

- Among the six BACs that were tested, MCP and TMP were the most adsorbable, BZF and DCF represented compounds of intermediate adsorbability and IBP and SMX represented the two least adsorbable compounds.

- Because of their acid-base characteristics, the removal of BACs is affected by solution pH. Over the tested pH range of 4 to 7, removal of the weak acid SMX increased with decreasing pH (or as the anionic form of SMX became less prevalent). Removal of the weak organic base TMP increased with increasing pH (or as the cationic form of TMP became less prevalent).

- Over the 2-hour duration of batch kinetic tests, TMP removal was strongly affected by PAC type while SMX removal was not. For TMP, wood-based PAC was most effective, followed by coal-based PAC and finally lignite-based PAC. At adsorption
equilibrium, coal based PAC exhibited the largest adsorption capacity for both SMX and TMP. The wood based PAC had the lowest adsorption capacity for SMX and the lignite based PAC had the lowest adsorption capacity for TMP.

- PAC particle size strongly affected BAC and NOM removal. Compared to the as-received PAC, adsorption kinetics of BACs and NOM were faster with S-PAC. In addition, a higher NOM adsorption capacity was obtained with sub-micrometer PAC (S-PAC).

- Batch kinetic data obtained with NuChar and WPH PACs were well described by the pseudo single-solute HSDM. For the wood-based PAC, surface diffusion coefficients for the six BACs ranged from $6.78 \times 10^{-9}$ to $6.82 \times 10^{-7}$ cm$^{2}$/s and were inversely correlated with the Freundlich capacity parameter $K$.

2.5. Acknowledgements

This research was supported by the North Carolina Urban Water Consortium. In addition, Dr. Koichi Ohno (Hokkaido University, Sapporo, Japan) contributed greatly to the experimental work while spending his sabbatical at NC State University.
2.6. References


Lindsey, M. E., M. Meyer, et al. (2001). "Analysis of trace levels of sulfonamide and


Engler-Bunte-Institut, Universität Karlsruhe.


<table>
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<tr>
<th>Name</th>
<th>Compound Class</th>
<th>Molecular Structure</th>
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<th>Surface Water*</th>
<th>Drinking Water*</th>
<th>Limit of quantitation (μg/L)</th>
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+ Benotti, et al., 2009.
Table 2. Properties of selected pharmaceuticals

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<th>pK&lt;sub&gt;a&lt;/sub&gt;</th>
<th>logK&lt;sub&gt;ow&lt;/sub&gt;</th>
<th>logD (pH 7)</th>
<th>Solubility (pH 7) (mg/L)</th>
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<td>Base [+/-]</td>
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<td>4.51*</td>
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* Predicted with Advanced Chemistry Development (ACD/Labs) Software v. 8.14 (as listed in SciFinder Scholar)
+ Experimentally determined values as listed in EPI Suite v. 4.0 database
Table 3. Water quality characteristics of tested waters

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<th>SUVA$_{254}$ (L/mg-m)</th>
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Table 4. PAC characteristics

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<th>Base Material</th>
<th>Activation Method</th>
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<td>American Norit</td>
<td>Lignite Coal</td>
<td>Thermal</td>
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<tr>
<td>WPH</td>
<td>Calgon Carbon Corporation</td>
<td>Bituminous Coal</td>
<td>Thermal</td>
</tr>
<tr>
<td>S-WPH</td>
<td>Custom-made</td>
<td>Bituminous Coal</td>
<td>Thermal</td>
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Table 5. Freundlich isotherm parameters and $D_s$ values describing BAC adsorption from OWASA water on (a) NuChar and (b) WPH PAC.

(a)  
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<tr>
<th></th>
<th>$K$ (mg/g)(L/µg)$^{1/n}$</th>
<th>$1/n$</th>
<th>$D_s$ (cm$^2$/s)</th>
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<td>BZF</td>
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<td>DCF</td>
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<td>MCP</td>
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<td>TMP</td>
<td>15.2</td>
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(b)  
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<th>$K$ (mg/g)(L/µg)$^{1/n}$</th>
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<tr>
<td>SMX</td>
<td>3.50</td>
<td>0.223</td>
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<td>TMP</td>
<td>27.9</td>
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Table 6. HSDM predictions for (a) NuChar and (b) WPH PAC dosages required to obtain 90% BAC removal from OWASA water at the indicated PAC contact times.

(a)

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<td></td>
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<tr>
<td>BZF</td>
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<td>DCF</td>
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<td>SMX</td>
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(b)

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<th>PAC dose (mg/L)</th>
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<td>TMP</td>
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Figure 1. Adsorption uptake kinetics for six pharmaceuticals with NuChar at doses of (a) 10 mg/L and (b) 20 mg/L. Water: OWASA, pH: 7, PAC type: NuChar.
Figure 2. Effect of pH on (a) SMX and (b) TMP adsorption uptake. Water: OWASA, PAC: NuChar, PAC dose: 20 mg/L for SMX and 5 mg/L for TMP.
Figure 3. Speciation of (a) SMX and (b) TMP as a function of pH
Figure 4. SMX and TMP adsorption uptake kinetics from OWASA, Cape Fear river, and Cary WWTP waters. PAC: NuChar, PAC dose: 10 mg/L.
Figure 5. Effect of PAC type on SMX removal kinetics. Water: OWASA, PAC dose: 10 mg/L.
Figure 6. SMX removal at non-equilibrium (15 min, 120 min) and at equilibrium (2 weeks). Water: OWASA, PAC dose: 10 mg/L.
Figure 7. Effect of PAC type on TMP removal kinetics. Water: OWASA, PAC dose: 5 mg/L.
Figure 8. TMP removal at non-equilibrium (15 min, 120 min) and at equilibrium (2 weeks). Water: OWASA, PAC dose: 5 mg/L.
Figure 9. Effect of PAC type on (a) UV\textsubscript{254} and (b) DOC removal. Water: OWASA, PAC dose: 10 mg/L.
Figure 10. BZF isotherm on NuChar in OWASA water.
Figure 11. HSDM fits and predictions of (a) SMX; (b) TMP; (c) MCP; (d) BZF; (e) IBP and (f) DCF by NuChar in OWASA water.
Figure 12. HSDM fits of (a) SMX and (b) TMP by WPH in OWASA water.
Figure 13. Correlation of surface diffusion coefficient $D_s$ and Freundlich isotherm constant $K$ for NuChar in OWASA water.
Chapter 3

REMOVAL OF BIOCHEMICALLY ACTIVE COMPOUNDS BY POWDERED ACTIVATED CARBON ADSORPTION IN THE PRESENCE OF COAGULANTS

Abstract

The presence of biochemically active compounds (BACs) in drinking water sources is of concern to many drinking water utilities and their customers. Activated carbon adsorption processes are one option utilities are employing to control BAC concentrations in drinking water. The principal objective of this study was to identify factors that control the BAC removal effectiveness of PAC adsorption processes at conditions typically encountered during the coagulation/flocculation/sedimentation stages of treatment. Specific objectives were to determine the effects of the following factors on BAC removal: 1) PAC type (wood-based, lignite-based, coal-based); 2) PAC particle size (as-received PAC and submicrometer-sized PAC, or S-PAC); 3) coagulant type and coagulation pH; and 4) timing of PAC addition relative to the addition of the coagulant. Jar tests were conducted with two North Carolina drinking water sources and a wastewater treatment plant effluent, into which the BACs sulfamethoxazole (SMX), trimethoprim (TMP), and ibuprofen (IBP) were spiked. The timing of PAC addition affected TMP and turbidity removal. TMP removal was lower when PAC was added together with coagulants than when PAC was added either 5 minutes before the coagulant or 9 minutes into the flocculation step. Turbidity removal was lowest when PAC was added 9 minutes into the flocculation step. Sub-micrometer PAC (S-PAC) greatly enhanced BAC removal. To obtain 90% removal of SMX and IBP from the two surface
waters, the required S-PAC dose was 15-25 mg/L, while 75 mg/L or more was required for as-received PACs.

**Keywords:** Biochemically active compounds, pharmaceuticals, PAC adsorption, sub-micrometer PAC, coagulation

### 3.1. Introduction

Biochemically active compounds (BACs) such as endocrine disrupting chemicals (EDCs), antimicrobial compounds, and other pharmaceutically active compounds (PhACs) have received widespread attention due to their presence and persistence in the aquatic environment. Numerous pharmaceutical compounds have been shown to pass through sewage treatment plants and are present in surface and ground water (Lindsey et al., 2001, Heberer et al., 2002, Kolpin et al., 2002, Yang et al., 2004, Jones et al., 2005).

Conventional drinking water treatment processes such as coagulation, sedimentation and filtration achieve minimal removal of BACs (Westerhoff et al., 2005). For diclofenac, 30% removal was reported with 50 mg/L ferric sulfate (Vieno et al., 2006). Both powdered and granular activated carbon adsorption processes effectively remove many BACs (Westerhoff et al., 2005, Adams et al., 2002, Ternes et al., 2002). When utilities use powdered activated carbon (PAC), they typically add PAC before, together with, or just after the coagulant (Graham et al., 2000). Adding PAC early in the treatment train lengthens the PAC contact time and facilitates the removal of PAC by sedimentation and filtration. However, incorporation of PAC into the floc has been suspected of hindering
contaminant transport from the bulk solution to the surface of the PAC.

In the presence of coagulant, Gauntlett and Packham (1973) found a large reduction in the rate of dichlorophenol removal by PAC in jar tests. Kramer et al. (1992) observed a reduction in atrazine removal by PAC when coagulating Ohio River water, but no such reduction was observed when PAC and coagulant were added to distilled deionized water. Some researchers have not seen the hindering effect of coagulants on PAC performance. Najm et al. (1991), reported only a slight effect on the removal rate of TCP when PAC was incorporated into coagulant floc. Cook et al. (2001) conducted MIB adsorption experiments in four waters under coagulation conditions. They determined that the coagulation process had no effect on the PAC adsorption of MIB in three waters. But MIB adsorption was adversely affected in one water that had a higher turbidity than the other three waters. The authors attributed this to the tighter binding of PAC in the denser floc structure that formed at high turbidity, reducing the effective contact time and/or active concentration of PAC. Ho et al. (2005) further pointed out that the floc size affects MIB removal. With the incorporation of PACs into larger flocs that formed in water with higher turbidity or with more alum present, the efficiency of mixing and the bulk diffusion kinetics of MIB were reduced, and thus PAC became less accessible because MIB molecules needed to penetrate the floc to reach the PAC.

To date, no studies have investigated the performance of PAC adsorption processes for BAC removal under coagulation conditions. The objective of this study was to identify factors that affect the BAC removal effectiveness of PAC adsorption processes at
conditions typically encountered during the coagulation/flocculation/sedimentation stages of treatment. Specific objectives were to determine the effects of the following factors on BAC removal: 1) PAC type (wood-based, lignite-based, coal-based); 2) PAC particle size (as-received PAC and submicrometer-sized PAC, or S-PAC); 3) coagulant type and coagulation pH; and 4) timing of PAC addition relative to the addition of the coagulant (PAC addition 5 minutes before coagulation, simultaneously with coagulant, and 9 minutes into the flocculation process).

3.2. Materials and Methods

3.2.1. Pharmaceuticals

The pharmaceuticals ibuprofen, sulfamethoxazole, and trimethoprim were selected for bench-scale treatability tests. Table 1 summarizes the physical-chemical characteristics of the selected pharmaceuticals, including the octanol-water partition coefficient of the neutral form of each compound (logK_{ow}) and the octanol-water partition coefficient at pH 6 (logD). The pK_{a} values illustrate that SMX and IBP are predominantly present in their anionic forms at neutral pH. In contrast, the cationic and neutral forms of TMP coexist in almost equal proportions at neutral pH.

Pharmaceuticals were purchased from Sigma Chemical Corporation (St. Louis, MO, USA). Sulfamethoxazole (SMX) and ibuprofen (IBP) were stored at ambient temperature; trimethoprim (TMP) was stored at 4°C. SMX and IBP stock solutions were prepared daily in phosphate buffered ultrapure (DI) water (pH 7); TMP stock solutions were prepared in
acidified DI water (pH 4) to enhance solubility. Stock solutions were prepared at concentrations of 2.0 mg/L, and stock solutions were filtered through a 0.22-µm PTFE membrane before use. The targeted initial pharmaceutical concentration was ~100 µg/L (<0.5 µM) for jar tests. This concentration is sufficiently low that the determined removal percentages are expected to match those obtained at concentrations more commonly encountered in drinking water sources and WWTPEs.

3.2.2. Water

Two North Carolina drinking water sources and one wastewater treatment plant effluent (WWTPE) were used. The drinking water sources were OWASA water (50/50 University Lake/Cane Creek reservoir blend, Carrboro, NC) and Cape Fear river water (Wilmington, NC). The WWTPE was collected at the North Cary Water Reclamation Facility (Cary, NC) after UV disinfection. Upon collection, water was stored in 55-gal stainless steel drums at 4°C. Water was filtered through 0.45-µm membranes prior to use unless specified otherwise. Dissolved organic carbon (DOC) concentrations, UV$_{254}$ absorbance, specific ultraviolet absorption (SUVA$_{254}$), pH, alkalinity and hardness of the three waters are shown in Table 2.

3.2.3. Powdered Activated Carbons

PACs prepared from different base materials and with different activation methods were studied (Table 3). Three PACs (NuChar, Hydrodarco B, and WPH) were used in their as-received form. In addition, a superfine version of the WPH PAC was prepared, which
was termed S-WPH. The mean diameter of S-WPH was ~0.3 µm while those of the as-received PACs were in the range of 17-25 µm.

3.2.4. Jar Tests

Jar tests were conducted with a programmable jar testing apparatus (Phipps & Bird, Richmond, VA). Coagulant stock solutions were prepared daily by dissolving aluminum sulfate (technical grade, Fisher Scientific) or ferric sulfate pentahydrate (technical grade, Fisher Scientific) into DI water. BAC stock solutions were spiked into well mixed water to obtain initial pharmaceutical concentrations of ~100 µg/L. Initial concentration samples were taken after 20 minutes of mixing at 100 rpm. Acid or base was then added as needed for pH adjustment and mixing was paused. The OWASA jar testing protocol was used as follows: (1) coagulant addition, (2) rapid mix at 100 rpm for 30 seconds, (3) flocculate at 25 rpm for 36 minutes, and (4) settle for 3.5 minutes without mixing. When PAC was added before the coagulant, PAC was mixed at 100 rpm for 5 min, after which time the OWASA jar testing protocol was followed. Additional samples were also taken after 10 minutes of settling. The following water quality parameters were measured in the settled water: DOC, UV$_{254}$, turbidity, pH, and pharmaceutical concentrations.

3.2.5. Analytical Methods

BAC concentrations were determined by a high-performance liquid chromatography system equipped with a dual-wavelength UV detector (HPLC, Breeze, Waters Corporation, Milford, MA). Pharmaceuticals were separated on a C18 column (2.6 µm,
4.6 × 100 mm, Kinetex C18 100A, Phenomenex, Torrance, CA). Prior to analysis, samples were filtered through a 0.22-µm PTFE membrane. Concentrations in bench-scale tests were sufficiently high that samples could be analyzed by direct injection, i.e. without sample preconcentration.

A gradient method was used for the analysis of SMX and TMP. Eluent A consisted of 50% v/v acetonitrile and 50% v/v 25 mM ammonium acetate buffer (pH 5) and eluent B of 10% v/v acetonitrile and 90% v/v 25 mM ammonium acetate buffer (pH 5). Each analysis started with 100% eluent B. From 1 to 9 minutes, the eluent was ramped linearly from 100% eluent B to 75% eluent B and 25% eluent A. An isocratic method was used for IBP. For IBP, the mobile phase was 37% v/v acetonitrile and 63% v/v 25 mM ammonium acetate buffer (pH 5). The mobile phase flow rate was 1 mL/min for all analyses, and the sample injection volume was 200 µL. The detector wavelength was set at 266 nm for SMX, 238 nm for TMP, and 222 nm for IBP.

TOC and DOC were measured with a total organic carbon analyzer (Model TOC-5000A and TOC-VCSN, Shimadzu Scientific, Columbia, MD). UV_{254} absorbance was measured with a UV/vis spectrophotometer (UNICAM UV1).

Solution pH was measured with a calibrated pH meter (Orion pH meter 420 A, Fisher Scientific, Pittsburgh, PA).
3.3. Results and Discussion

3.3.1. Coagulation/Flocculation/Sedimentation

Table 4 summarizes results of jar tests, in which the removal of SMX and TMP by alum and ferric sulfate coagulation was evaluated. The selected alum (Al₂(SO₄)₃ • 14.3H₂O) and ferric sulfate (Fe₂(SO₄)₃ • 5H₂O) doses (55 and 70 mg/L, respectively) are typical for utilities operating in the Piedmont region of North Carolina. As shown in Table 4, SMX and TMP removal by alum and ferric sulfate coagulation was minimal (<5%) as expected (e.g., Westerhoff et al. 2005). Coagulation pH did not have a measurable effect on SMX and TMP removal, but it did affect natural organic matter removal and floc settleability. As shown in Table 4, NOM removal, as measured by UV₂₅₄ absorbance and DOC, was higher at pH 5.8 than at pH 6.2 for alum coagulation, and it was higher at pH 5.4 than at pH 5.8 for ferric sulfate coagulation. In contrast, turbidity removal was greater at pH 6.2 than at pH 5.8 for alum coagulation, but it was about the same at both pH values for ferric sulfate coagulation.

3.3.2. Timing of PAC addition

Alum. Figure 1a summarizes SMX removal results obtained in jar tests evaluating (1) alum coagulation alone, (2) PAC treatment alone, and (3) alum coagulation in combination with PAC addition. PAC was added either 5 minutes prior to alum, together with alum, or 9 minutes after alum. Coagulation pH values of 6.2 and 5.8 were tested. Results in Figure 1a show that (1) aluminum hydroxide floc did not interfere with SMX
removal, (2) the timing of PAC addition relative to alum was not important for SMX removal, and (3) SMX removal was slightly higher at pH 5.8 than at pH 6.2 (as expected based on batch kinetic data shown in Chapter 2).

TMP removal results (Figure 1b) are quite different from those obtained with SMX. The data in Figure 1b suggest that (1) aluminum hydroxide floc interfered with TMP adsorption, (2) timing of PAC addition relative to alum addition was important, and (3) TMP removal was slightly higher at pH 6.2 than at pH 5.8 (as expected based on batch kinetic data shown in Chapter 2). The interference of the aluminum hydroxide floc may be related to electrostatic repulsion between TMP, which is predominantly present in cationic form at pH 6.2 and 5.8, and positively charged aluminum hydroxide floc. The interference of the aluminum hydroxide floc was largest when PAC was added together with alum.

Figure 2 summarizes NOM removal data as measured by UV$_{254}$ absorbance and DOC for the same jar tests. Results show that the addition of 5 mg/L NuChar PAC yielded only a small increment in NOM removal (~5%) over that achieved with alum coagulation alone. Both DOC and UV$_{254}$ data showed that NOM removal was greater at the lower coagulation pH, as expected (Pontius, 1990). UV$_{254}$ removal by alum with a dose of 55 mg/L was approximately 60 and 65% at pH 6.2 and 5.8, respectively.

Figure 3 summarizes turbidity removal data. The addition of 5 mg/L NuChar PAC had little effect on turbidity removal that was measured after a settling time of 10 minutes
(Figure 3b). Settled water turbidity data that were obtained after a settling time of 3.5 minutes were too variable to elucidate effects of PAC addition on turbidity removal.

**Ferric Sulfate.** Jar test results obtained with ferric sulfate were generally similar to those obtained with alum. Ferric hydroxide floc and timing of PAC addition did not affect SMX removal (Figure 4a). Also, SMX removal was slightly higher at pH 5.4 than at pH 5.8 (as expected based on batch kinetic data shown in Chapter 2). As was the case with aluminum hydroxide floc, ferric hydroxide floc adversely affected TMP removal, and the interference of the ferric hydroxide floc was largest when PAC was added together with the coagulant (Figure 4b).

Figure 5 summarizes NOM removal data as measured by UV$_{254}$ absorbance and DOC for the jar tests conducted with ferric sulfate. The addition of 5 mg/L NuChar PAC contributed only minimally to NOM removal, while a ferric sulfate dose of 70 mg/L removed about 65 and 70% of the UV$_{254}$ absorbing compounds at pH 5.8 and 5.4, respectively.

Figure 6 summarizes turbidity removal data. Figure 6 suggests that turbidity removal was slightly better at pH 5.4 than at pH 5.8. With PAC added before or together with ferric sulfate, turbidity removal was greater than that obtained when PAC was added during flocculation (either after 3.5 min or 10 min settling). This result suggests that PAC was better incorporated into ferric hydroxide floc when added before or together with the coagulant. Compared to the alum results, ferric sulfate yielded greater turbidity removal.
after 3.5 minute settling.

3.3.3. Effect of PAC type and timing of PAC addition

Figure 7a compares SMX removal data obtained in jar tests conducted with NuChar, WPH and S-WPH. The tested PAC dose was in each case 5 mg/L, and the coagulation pH was 6.2. As before, aluminum hydroxide floc and timing of PAC addition relative to alum addition did not affect SMX removal. However, SMX removals obtained with S-WPH was 2.1-2.8 times those obtained with NuChar and WPH. For TMP, removals with S-WPH were 1.7-2.7 times those obtained with NuChar and WPH (Figure 7b). The presence of aluminum hydroxide floc had an adverse effect on TMP removal by all three PACs, and TMP removal was lowest when PAC was added together with alum.

Figure 8 compares NOM removal obtained with alum only, PAC only, and the combination of alum and PAC treatment. UV$_{254}$ removal was ~60% with alum only and was enhanced by less than 5% with 5 mg/L NuChar and WPH, and by 10% with 5 mg/L S-WPH. Treatment with S-WPH alone lowered the UV$_{254}$ absorbance by 17%, which was larger than the 10% increment obtained beyond what was obtained with alum only. Therefore, the presence of aluminum hydroxide floc may have had a negative effect on the adsorptive removal of NOM by S-WPH. It is also possible, however, that alum coagulation removed a NOM fraction that was adsorbed when S-WPH was added alone.

The turbidity removal data in Figure 9 suggest that the addition of S-WPH adversely affected floc settleability. Poorer turbidity removal in the presence of S-WPH was more
pronounced after the shorter settling time (3.5 minutes, Figure 9a) than after the longer settling time (10 minutes, Figure 9b). The results in Figure 9 further suggest that poorer turbidity removal was a greater issue when PAC was added after alum, i.e., when PAC was added 9 minutes into the flocculation process.

3.3.4. Effect of PAC type and PAC dose

One goal of this study was to determine the effect of PAC dose on BAC removal in jar tests in which PAC was added together with alum. The alum dose of 55 mg/L and the coagulation pH of 6.2 are typical for the OWASA water treatment plant. Jar tests were conducted with SMX and IBP, the two least adsorbable BACs tested in this study. Wood-based NuChar, lignite-based Hydrodarco B, and coal-based WPH PACs were evaluated, and the coal-based PAC was tested in both the as-received and the S-PAC forms. As shown in Figure 10a, SMX removal was most effectively accomplished with S-WPH, and a dose of 20 mg/L produced 90% SMX removal. Among the as-received PACs, SMX removal was in the order NuChar>WPH>Hydrodarco B. To obtain 90% SMX removal, the required dosage for NuChar was about 90 mg/L while that for WPH and Hydrodarco B was >100 mg/L. Results for IBP were similar to those obtained with SMX (Figure 10b). IBP removal was most effectively accomplished with S-WPH, and a dose of about 25 mg/L produced 90% IBP removal. To obtain 90% IBP removal, the required dosage for NuChar was about 100 mg/L while that for WPH and Hydrodarco B was >100 mg/L. Thus, 90% SMX and IBP removal is not achievable with as-received PACs at doses typically employed in drinking water treatment.
Another drinking water source, Cape Fear river water, and Cary WWTPE were also tested with NuChar, WPH and S-WPH. Both waters had higher background NOM concentrations than the OWASA water as measured by UV$_{254}$ absorbance and DOC concentration. Again, S-WPH greatly enhanced SMX and IBP removal relative to the removals that could be achieved with the as-received PACs. In Cape Fear water, to obtain 90% SMX removal, the required dose for S-WPH was about 15 mg/L while that for NuChar and WPH was 75 and 100 mg/L, respectively (Figure 10c). For 90% IBP removal, the required dosage of S-WPH was 30 mg/L, while that for NuChar and WPH was $\geq$100 mg/L. The higher background NOM concentration in Cary WWTPE adversely affected BAC adsorption by PACs, and thus the required (S-)PAC doses for 90% BAC removal were higher. To obtain 90% SMX and IBP removal in the WWTPE, a dosage of 30 mg/L was required for S-WPH, while those for NuChar and WPH were much larger than 100 mg/L.

Figure 11 shows that alum coagulation alone yielded about 60% NOM removal, as measured by UV$_{254}$ absorbance. The addition of 30 mg/L S-WPH PAC produced approximately 25% NOM removal beyond that achieved with alum coagulation. In contrast, the addition of 100 mg/L as-received PAC produced only ~15-20% NOM removal beyond that achieved with alum coagulation. NOM removal was negligible with PAC doses of 5 and 20 mg/L, and increased slowly as the PAC dose was increased to 100 mg/L (Figure 11). Among the three tested as-received PACs, DOC removal did not differ substantially, but removal of UV$_{254}$-absorbing compounds was somewhat greater with WPH PAC at higher doses.
The settled water turbidity data in Figure 12 suggests that as the PAC dose increased, floc settleability improved. As the particle concentration in the water increased with increasing PAC dose, the collision frequency may have increased. As a result, the rate of particle aggregation could have been faster, which may have yielded larger floc particles. In addition, incorporation of more PAC particles into floc likely increased floc density and thus floc settleability. The higher settled water turbidity results for S-WPH suggest that S-WPH was less effectively incorporated into settleable floc than as-received WPH, which was likely a result of its smaller size (Pontius, 1990).

3.4. Conclusions

Jar tests were conducted to evaluate the effectiveness of PAC adsorption processes for BAC removal using coagulation conditions typically encountered in North Carolina drinking water treatment plants. The experimental results showed the following:

- Coagulation with alum and ferric sulfate did not effectively remove SMX and TMP.

- The presence of aluminum and ferric hydroxide floc did not significantly affect SMX removal, but it adversely affected TMP removal. Most likely, electrostatic repulsion between cationic TMP and positively charged metal hydroxide floc, in which the (S-)PAC was embedded, contributed to this result.
• The timing of PAC addition relative to the addition of the coagulant was important for TMP removal, but not for SMX removal. TMP removal was lower when PAC was added together with coagulants than when PAC was added either 5 minutes before the coagulant or 9 minutes into the flocculation step. The timing of PAC addition also affected turbidity removal. When PAC was added before or together with coagulants, turbidity removal was generally greater than that obtained in tests in which PAC was added 9 minutes into the flocculation process. To obtain the best settled water quality in terms of BAC and turbidity removal would, PAC should therefore be added before the coagulant (e.g. at the intake).

• Removal of the weak organic acid SMX increased with decreasing coagulation pH while removal of the weak organic base TMP increased with increasing coagulation pH.

• The application of sub-micrometer diameter PAC (S-WPH) achieved a given BAC removal percentage at lower doses than as-received PACs. To obtain 90% removal of SMX and IBP, S-WPH doses in the 15-25 mg/L range would be required in the tested NC drinking water sources. For the as-received PACs, 90% removal of SMX and IBP required PAC doses of 75 mg/L or greater. The addition of S-WPH also enhanced NOM removal relative to that obtained with as-received PACs. Settled water turbidity in samples that received S-WPH were higher than those that received as-received PAC. Flocculant aids may therefore be required to effectively incorporate S-PAC into settleable floc. The application of S-PAC is
promising because both meaningful BAC and NOM removal can be obtained at reasonable S-PAC doses.

3.5. Acknowledgements

This research was supported by the North Carolina Urban Water Consortium.
3.6. References


Table 1. Properties of selected pharmaceuticals

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<th>Name</th>
<th>Abbreviation</th>
<th>Compound Class</th>
<th>Molecular Structure</th>
<th>Molecular Weight (g/mol)</th>
<th>pK&lt;sub&gt;a&lt;/sub&gt;</th>
<th>logK&lt;sub&gt;ow&lt;/sub&gt;</th>
<th>logD (pH 6)</th>
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<td>IBP</td>
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<td>Sulfamethoxazole</td>
<td>SMX</td>
<td>antibiotic</td>
<td><img src="image2" alt="Molecular Structure" /></td>
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<td>Trimethoprim</td>
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<td>antibiotic</td>
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<td>7.1&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.91</td>
<td>-0.42</td>
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* Predicted with Advanced Chemistry Development (ACD/Labs) Software v. 8.14 (as listed in SciFinder Scholar)

* Experimentally determined values as listed in EPI Suite v. 4.0 database
Table 2. PAC characteristics

<table>
<thead>
<tr>
<th>PAC Name</th>
<th>Manufacturer</th>
<th>Base Material</th>
<th>Activation Method</th>
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<tr>
<td>NuChar</td>
<td>MeadWestvaco</td>
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<td>Hydrodarco B</td>
<td>American Norit</td>
<td>Lignite Coal</td>
<td>Thermal</td>
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<td>WPH</td>
<td>Calgon Carbon Corporation</td>
<td>Bituminous Coal</td>
<td>Thermal</td>
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<tr>
<td>S-WPH</td>
<td>Custom-made</td>
<td>Bituminous Coal</td>
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Table 3. Water quality characteristics of tested waters

<table>
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<tr>
<th>Water Source</th>
<th>DOC (mg/L)</th>
<th>UV$_{254}$ (cm$^{-1}$)</th>
<th>SUVA$_{254}$ (L/mg-m)</th>
<th>pH</th>
<th>Alkalinity (mg/L as CaCO$_3$)</th>
<th>Hardness (mg/L as CaCO$_3$)</th>
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<td>Cape Fear</td>
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<td>Cary WWTPE</td>
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<td>8.0</td>
<td>70.3</td>
<td>60.0</td>
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Table 4. Pharmaceutical, NOM, and turbidity removal by coagulation/flocculation/sedimentation. Water: OWASA.

(a) Coagulant: alum; coagulant dose: 55 mg/L.

<table>
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<tr>
<th>Parameter</th>
<th>pH 6.2</th>
<th>pH 5.8</th>
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<tr>
<td>SMX</td>
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<td>TMP</td>
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<td>UV$_{254}$ absorbance</td>
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<td>DOC</td>
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<td>Turbidity (3.5 min settling)</td>
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<td>Turbidity (10 min settling)</td>
<td>89.13</td>
<td>80.26</td>
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(b) Coagulant: ferric sulfate pentahydrate; coagulant dose: 70 mg/L.

<table>
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<th>Parameter</th>
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<th>pH 5.8</th>
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<td>TMP</td>
<td>3.42</td>
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<td>UV$_{254}$ absorbance</td>
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<tr>
<td>DOC</td>
<td>62.85</td>
<td>56.18</td>
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<tr>
<td>Turbidity (3.5 min settling)</td>
<td>72.64</td>
<td>72.48</td>
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<td>Turbidity (10 min settling)</td>
<td>84.25</td>
<td>86.01</td>
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Figure 1. Effect of coagulation pH on (a) SMX and (b) TMP removal in jar tests evaluating timing of PAC addition. Removals with alum alone and PAC alone are shown for reference. Water: OWASA, coagulant: alum, coagulant dose: 55 mg/L, PAC: NuChar, PAC dose: 5 mg/L.
Figure 2. Effect of coagulation pH on NOM removal as measured by (a) UV$_{254}$ and (b) DOC in jar tests evaluating timing of PAC addition. Removals with alum alone and PAC alone are shown for reference. Water: OWASA, coagulant: alum, coagulant dose: 55 mg/L, PAC: NuChar, PAC dose: 5 mg/L.
Figure 3. Effect of coagulation pH on turbidity removal after (a) 3.5 and (b) 10 minutes of settling. Coagulant: alum, coagulant dose: 55 mg/L, PAC: NuChar, PAC dose: 5 mg/L.
Figure 4. Effect of coagulation pH on (a) SMX and (b) TMP removal in jar tests evaluating timing of PAC addition. Removals with alum alone and PAC alone are shown for reference. Water: OWASA, coagulant: ferric sulfate pentahydrate, coagulant dose: 70 mg/L, PAC: NuChar, PAC dose: 5 mg/L.
Figure 5. Effect of coagulation pH on NOM removal as measured by (a) UV$_{254}$ and (b) DOC in jar tests evaluating timing of PAC addition. Removals with coagulant alone and PAC alone are shown for reference. Water: OWASA, coagulant: ferric sulfate pentahydrate, coagulant dose: 70 mg/L, PAC: NuChar, PAC dose: 5 mg/L.
Figure 6. Effect of coagulation pH on turbidity removal after (a) 3.5 and (b) 10 minutes of settling. Coagulant: ferric sulfate pentahydrate, coagulant dose: 70 mg/L, PAC: NuChar, PAC dose: 5 mg/L.
Figure 7. Effect of PAC type on (a) SMX and (b) TMP removal in jar tests evaluating timing of PAC addition. Removals with coagulant alone and PAC alone are shown for reference. Water: OWASA, coagulant: alum, coagulant dose: 55 mg/L, PAC dose: 5 mg/L, pH: 6.2.
Figure 8. Effect of PAC type on NOM removal as measured by (a) UV$_{254}$ and (b) DOC in jar tests evaluating timing of PAC addition. Removals with alum alone and PAC alone are shown for reference. Water: OWASA, coagulant: alum, coagulant dose: 55 mg/L, PAC dose: 5 mg/L, pH: 6.2.
Figure 9. Effect of PAC type on turbidity removal after (a) 3.5 and (b) 10 minutes of settling. Water: OWASA, coagulant: alum, coagulant dose: 55 mg/L, PAC dose: 5 mg/L, pH: 6.2.
Figure 10. Effect of PAC dose on SMX (a, c, e) and IBP (b, d, f) removal with PAC added together with coagulant. Water: OWASA (a, b), Cape Fear (c, d), Cary WWTP (e, f), coagulant: alum, coagulant dose: 55 mg/L, pH: 6.2.
Figure 11. Effect of PAC dose on NOM removal as measured by (a) UV\textsubscript{254} and (b) DOC with PAC added together with coagulant. Water: OWASA, coagulant: alum, coagulant dose: 55 mg/L, pH: 6.2.
Figure 12. Effect of PAC dose on turbidity after (a) 3.5 and (b) 10 minutes of settling. Water: OWASA, coagulant: alum, coagulant dose: 55 mg/L, pH: 6.2.
APPENDICES
Figure 1. Comparison of SMX and TMP adsorption uptake kinetics from OWASA water when SMX and TMP were spiked separately and together as a mixture. PAC: NuChar; (a) PAC dose: 10 mg/L; (b) PAC dose: 20 mg/L.
Figure 2. Freundlich isotherms for (a) SMX; (b) TMP; (c) MCP; (d) BZF; (e) IBP and (f) DCF. PAC: NuChar; water: OWASA.
Figure 3. Freundlich isotherms for (a) SMX and (b) TMP. PAC: WPH; water: OWASA.
Figure 4. BAC removal from OWASA water as a function of NuChar PAC dosage for (a) SMX; (b) TMP; (c) MCP; (d) BZF; (e) IBP and (f) DCF. Lines and symbols for PAC contact times of 15 min, 30 min, and 1 hour are HSDM predictions. Symbols for a PAC contact time of 2 weeks represent experimental data from adsorption isotherm tests.
Figure 5. BAC removal from OWASA water as a function of NuChar PAC dosage for (a) SMX and (b) TMP. Lines and symbols for PAC contact times of 15 min, 30 min, and 1 hour are HSDM predictions. Symbols for a PAC contact time of 2 weeks represent experimental data from adsorption isotherm tests.
Appendix 2
Background of HSDM Model

To model the rate of adsorption of a target BAC by PAC from natural water, a pseudo-single-solute homogeneous surface diffusion model (HSDM) was used. The model has its roots in the work of Rosen (1952) who mathematically described the rate of adsorption in a fixed bed of homogeneous spherical particles of uniform radius. In the HSDM, PAC particles are assumed to be spherical and of homogeneous structure as well. As pointed out by Sontheimer et al. (1988), the assumption of homogeneity is valid if structural heterogeneity occurs on a scale that is much smaller than the size of the adsorbent particle.

For surface diffusion into a porous sphere, Fick’s first law of diffusion can be expressed as follows (Sontheimer et al., 1988):

\[ J_r = -\rho_p D_s \frac{dq}{dr} \]  

(2.1)

where \( \rho_p \) = particle density,

\( D_s \) = surface diffusion coefficient,

\( q \) = solid phase concentration, and

\( r \) = radial coordinate.

Incorporating equation 2.1 into the shell mass balance equation for a spherical adsorbent particle, the following partial differential equation is obtained that describes the solid phase concentration profile inside of an adsorbent particle as a function of radial position.
Equation 2.2 requires one initial condition and two boundary conditions for its solution as follows:

Initial condition: \[ q(r,0) = 0 \quad \text{for} \quad 0 \leq r \leq d_p / 2 \quad (2.3) \]

First boundary condition: \[ \frac{\partial q(0,t)}{\partial r} = 0 \quad (2.4) \]

Second boundary condition: \[ q(d_p / 2,t) = KC(t)^{1/n} \quad (2.6) \]

The initial condition (equation 2.3) states that originally no adsorbate is present in the adsorbent. The first boundary condition (equation 2.4) expresses symmetry at the center of the adsorbent particle, and the second boundary condition (equation 2.5) relates the bulk liquid phase concentration of the adsorbate to the solid phase concentration of the adsorbate at the external surface of the adsorbent via the Freundlich isotherm equation. The latter boundary condition assumes that instantaneous equilibrium is achieved at the external surface of the adsorbent particle and that the rate of film mass transfer is very high and thus not rate limiting.

To calculate the change in bulk liquid phase concentration of the adsorbate as a function of time in adsorption treatment processes, the above solid-phase mass balance (equation
2.2) needs to be solved in conjunction with an overall mass balance in the reactor configuration in use, which is batch reactor in this case. The following mass balance equation needs to be satisfied:

$$C_0 - C(t) - C_c q_{avg}(t) = 0$$  \hspace{1cm} (2.6)$$

where

- \(C_0\) = initial liquid phase concentration,
- \(C(t)\) = bulk liquid phase concentration at time \(t\),
- \(C_c\) = carbon dose, and
- \(q_{avg}(t)\) = average solid phase concentration at time \(t\).

The average solid phase concentration \(q_{avg}\) can be calculated as follows (Sontheimer et al., 1988):

$$q_{avg}(t) = \frac{24}{d_p^3} \int_0^{d_p/2} g(r,t)r^2\,dr$$  \hspace{1cm} (2.7)$$

To calculate the change in bulk liquid phase concentration as a function of time, equation 2.2 and 2.6 need to be solved simultaneously, which requires the use of numerical methods because one boundary condition is the nonlinear Freundlich isotherm equation. Typically, the technique of orthogonal collocation has been employed to numerically solve the HSDM equations for batch reactors (Thacker et al., 1981, Traegner and Suidan, 1989).
References


Appendix 3
SEARCH PROGRAM

C ************************************************* ***********************
C * This FORTRAN program is used to simultaneously search for the optimum*
C * set of kinetic parameters and/or equilibrium parameters that would *
C * best fit the HSDM to the experimental batch adsorption data. The IMSL*
C * optimization subroutine DUNLSF coupled with the subroutine HSDM *
C * (same as <HSDM.FOR> program) will be used to determine the optimum *
C * parameter values. *
C ** *
C * The control input file <SEARCH.IN> will identify the name of the *
C * experimental data input file, the name of the output file, and the *
C * parameters to be searched. *
C ** *
C * The experimental data input file <SEARCH.DAT> needs to be filled with*
C * the appropriate data, including an initial guess for Ds and kf. Then,*
C * the program is run to evaluate the Ds and kf values that result in *
C * the best fit for the experimental data. If the error for the obtained* *
C * result is high, a different initial guess should be used. The output *
C * of the search program is contained in the file <SEARCH.OUT>. All *
C * other files are intermediate files containing control parameters that* *
C * do not need to be changed. *
C ** *
C * Department of Civil Engineering *
C * UNIVERSITY OF ILLINOIS, URBANA-CHAMPAIGN *
C ** *
C ************************************************* ***********************
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C COMMON /PAR1/ C0V(10),CCONCV(10),RADPV(10),RHOPV(10),
& PARV(4,10),NDPV(10),NDSET,IPS(4),ISCALE(4),
& TM(50,10),YM(50,5,10),IDREP(10),NDPSV(10),
& YF(50,10)
C CHARACTER*80 IFNAME(10)
C DIMENSION X(4),F(500),XGUESS(4),XSCALE(4),FSCALE(500),
& IPARAM(6),RPARAM(7),FVEC(500),FJAC(500,4)
C EXTERNAL FIND
C OPEN(1,FILE='SEARCH.IN',STATUS='OLD')
C K=1
123 CONTINUE
READ(1,1000) IFNAME(K)
IF(IFNAME(K) .NE. 'null') THEN
C *************************************************************
C Read in the name(s) of the data file(s)
C *************************************************************
NDSET=K
K=K+1
GO TO 123
ELSE
C ******************************************************
C Name of output file
C ******************************************************
READ(1,1000) IFNAME(K)
END IF
C READ(1,*) (IPS(I),I=1,4)
C WRITE(*,*) ' YOUR INPUT ',NDSET, ' DATA FILE(S):'
DO 1 K=1,NDSET
WRITE(*,*) IFNAME(K)
1 CONTINUE

94
WRITE(*,*) ' YOUR OUTPUT DATA FILE IS:'
WRITE(*,*) IFNAME(NDSET+1)
C
IPSSUM=0
DO 2 K=1,4
IF(IPS(K) .EQ. 1) THEN
   IPSSUM=IPSSUM+1
END IF
2 CONTINUE
C
DO 11 K=1,NDSET
OPEN(K,FILE=IFNAME(K),STATUS='OLD')
REWIND(K)
READ(K,*) NDPV(K), COV(K), IDREP(K)
DO 22 IP=1,NDPV(K)
   READ(K,*), TM(IP,K), (YM(IP,I,K),I=1,IDREP(K))
22 CONTINUE
READ(K,*), CCONCV(K)
READ(K,*), PARV(3,K)
READ(K,*), PARV(4,K)
PARV(3,K)=PARV(3,K)*1000.0D0**PARV(4,K)
READ(K,*), PARV(1,K)
READ(K,*), PARV(2,K)
11 CONTINUE
C *****************************************************************
C Count total number of data points
C ***************************************************************
DO 95 II=1,NDSET
   NDPSV(II)=0
   DO 94 IJ=1,NDPV(II)
      DO 93 JJ=1,IDREP(II)
         IF(YM(IJ,JJ,II) .LE. 1.1D0) THEN
            NDPSV(II)=NDPSV(II)+1
         END IF
      93 CONTINUE
   94 CONTINUE
95 CONTINUE
C
M1=0
DO 211 KK=1,NDSET
   M1=M1+NDPV(KK)
211 CONTINUE
C
M=0
DO 21 KK=1,NDSET
   M=M+NDPSV(KK)
21 CONTINUE
C
WRITE(*,*) ' TOTAL OBSERVATION TIMES :',M1
WRITE(*,*) ' TOTAL DATA POINTS :',M
WRITE(*,*) ' YOU ARE SEARCHING FOR ',IPSSUM, ' PARAMETERS'
C
K=1
IF(IPS(1) .EQ. 1) THEN
   SCALE=DLOG10(PARV(1,1))
   IF(SCALE .GT. 0.0D0) THEN
      ISCALE(K)=DINT(SCALE)+1
   ELSE
      ISCALE(K)=DINT(SCALE)
   END IF
   XGUESS(K)=PARV(1,1)/(10.0D0**ISCALE(K))
   XXX=XGUESS(K)*10.0D0**ISCALE(K)
   WRITE(*,*) ' PARAMETER # ',K,' == kf', ' ; IG: ', XXX
   K=K+1
END IF
C
IF(IPS(2) .EQ. 1) THEN
   SCALE=DLOG10(PARV(2,1))
   XXX=XGUESS(K)*10.0D0**ISCALE(K)
   WRITE(*,*) ' PARAMETER # ',K,' == kf', ' ; IG: ', XXX
   K=K+1
END IF
C
IF(SCALE .GT. 0.0D0) THEN
    ISCALE(K)=DINT(SCALE)+1
ELSE
    ISCALE(K)=DINT(SCALE)
END IF

XGUESS(K)=PARV(2,1)/(10.0D0**ISCALE(K))
XXX=XGUESS(K)*10.0D0**ISCALE(K)
WRITE(*,*) ' PARAMETER # ',K,' == Ds',' ; IG: ',XXX
K=K+1
END IF

C
IF(IPS(3) .EQ. 1) THEN
    SCALE=DLOG10(PARV(3,1))
    IF(SCALE .GT. 0) THEN
        ISCALE(K)=DINT(SCALE)+1
    ELSE
        ISCALE(K)=DINT(SCALE)
    END IF
    XGUESS(K)=PARV(3,1)/(10.0D0**ISCALE(K))
    XXX=XGUESS(K)*10.0D0**ISCALE(K)
    WRITE(*,*) ' PARAMETER # ',K,' == K',' ; IG: ',XXX
    K=K+1
END IF

C
IF(IPS(4) .EQ. 1) THEN
    SCALE=DLOG10(PARV(4,1))
    IF(SCALE .GT. 0) THEN
        ISCALE(K)=DINT(SCALE)+1
    ELSE
        ISCALE(K)=DINT(SCALE)
    END IF
    XGUESS(K)=PARV(4,1)/(10.0D0**ISCALE(K))
    XXX=XGUESS(K)*10.0D0**ISCALE(K)
    WRITE(*,*) ' PARAMETER # ',K,' == n',' ; IG: ',XXX
END IF

C *****************************************************************
C Call to the search routine
C ************************************************* ****************
OPEN(NDSET+1,FILE=IFNAME(NDSET+1),STATUS='OLD')

N=IPSSUM
DO 150 I=1,N
    XSCALE(I)=1.0D0
150 CONTINUE
DO 160 J=1,M
    FSCALE(J)=1.0D0
160 CONTINUE
IPARAM(1)=0
LDFJAC=M

CALL DUNLSF(FIND,M,N,XGUESS,XSCALE,FSCALE,IPARAM,RPARAM, &
           X,FVEC,FJAC,LDFJAC)

C Send results to output file
C ************************************************* ****************
DO 111 K=1,NDSET
    DO 222 IP=1,NDPV(K)
        WRITE(NDSET+1,1001) TM(IP,K),(YM(IP,II,K),II=1,IDREP(K)), &
        YF(IP,K)
222 CONTINUE
111 CONTINUE

C
1000 FORMAT(A)
1001 FORMAT(2X,6E16.6)

STOP ' all done'
END
C***************************************************************
C This subroutine evaluates the function that defines the least
C squares problem
C ****************************************
SUBROUTINE FIND(M,N,X,F)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /PAR1/ C0V(10),CCONCV(10),RADPV(10),RHOPV(10),
& PARV(4,10),NDPV(10),NDSET,IPS(4),ISCALE(4),
& TM(50,10),YM(50,5,10),IDREP(10),NDPSV(10),
& YF(50,10)
C
DIMENSION X(4),F(500)
DIMENSION TT(50),YY(50)
DIMENSION SSQV(10),XXV(4),YMM(50,5)
C
DATA ICALL /0/
C
ICALL=ICALL+1
C
C If trouble, limit the parameters to the smallest value of 10D-30
C ****************************************
DO 1 KK=1,N
X(KK)=DMAX1(X(KK),1.0D-30)
1 CONTINUE
C
WRITE(*,1000) ICALL,(X(KK)*10.0D0**ISCALE(KK),KK=1,N)
WRITE(NDSET+1,1000) ICALL,(X(KK)*10.0D0**ISCALE(KK),KK=1,N)
C
LL=1
DO 111 K=1,NDSET
C
C LOAD TIME VECTOR FOR THE K'S DATA SET
C ****************************************
DO 2 L=1,NDPV(K)
TT(L)=TM(L,K)
DO 229 KI=1,IDREP(K)
YYM(L,KI) = YM(L,KI,K)
229 CONTINUE
2 CONTINUE
C
LLL=0
DO 9 II=1,4
IF(IPS(II) .EQ. 1) THEN
LLL=LLL+1
XXV(II)=X(LLL)*10.0D0**ISCALE(LLL)
ELSE
XXV(II)=PARV(II,K)
END IF
9 CONTINUE
C
CALL HSDM(C0V(K),CCONCV(K),RADPV(K),RHOPV(K),XXV(1),XXV(2),
& XXV(3),XXV(4),TT,YY,NDPV(K),YYM,IDREP(K))
C
C Set up the residual vector F
C ****************************************
SSQV(K)=0.0D0
DO 3 L=1,NDPV(K)
F(L)=YY(L)
DO 4 ID=1,IDREP(K)
IF(YM(L,ID,K) .LE. 1.1D0) THEN
F(LL)=(YM(L,ID,K)-YY(L)/YM(L,ID,K)
WRITE(*,*) LL,F(LL)
SSQV(K)=SSQV(K)+F(LL)**2
LL=LL+1
END IF
4 CONTINUE
3 CONTINUE
111 CONTINUE
C
WRITE(*,1000) ICALL,(SSQV(I),I=1,NDSET)
WRITE(NDSET+1,1000) ICALL, (SSQV(I),I=1,NDSET)
1000 FORMAT(1X,I5,6E16.6)
C
RETURN
END
C-------------------------------------------------- ------------------
C ************************************************* ****************
C This subroutine numerically solves the HSDM
C ************************************************* ****************
SUBROUTINE HSDM(C01,CCONC1,RADP1,RHOP1,XKF1,DS1,XK1,XN1,
& TT,YY,NDP,YYM,IDREP1)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
DIMENSION TT(1),YY(1),YYM(1,1)
C
DATA ICALL /0/
C
OPEN(31,FILE='PART.C',STATUS='OLD')
OPEN(32,FILE='HSDM.RAW',STATUS='OLD')
C
IF(ICALL .EQ. 0) THEN
C
CALL INPUT
C
CALL INCOL
C
ICALL=1
END IF
C
C0=C01
CCONC=CCONC1
RADP=RADP1
RHOP=RHOP1
XK=XK1
XN=XN1
XKF=XKF1
DS=DS1
C
CALL INIT
C
CALL CALCC(TT,YY,NDP,YYM,IDREP1)
C
RETURN
C
END
C------------------------------------------------------------
SUBROUTINE INPUT
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
OPEN(30,FILE='HSDM.C',STATUS='OLD')
REWIND (30)
READ(30,*) IPRC,IPRI,IPRO
C ************************************************* ****************
C Control Parameters

98
C **************************************************
READ(30,*) NCP
READ(30,*) TOL,METH,MITER
READ(30,*) DTINIT
C
CLOSE (30)
C
RETURN
END
C--------------------------------------------------
SUBROUTINE INCOL
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
DIMENSION DUMMY(14)
C
IFL1=0
IFL2=0
C
10 CONTINUE
C
READ(31,*) ID
IF(ID .EQ. 999) THEN
C **************************************************
C SOMETHING IS WRONG
C **************************************************
WRITE(*,*) ' REQUESTED COLLOCATION MATRIX IS NOT AVAILABLE'
STOP ' ERROR - all done '
END IF
C
IF(ID .EQ. NCP) THEN
IFL1=1
END IF
C **************************************************
C READ IN AND DISTRIBUTE
C **************************************************
IF(IFL1 .NE. 0) THEN
READ(31,1001) (WP(I),I=1,ID)
DO 2 I=1,ID
READ(31,1001) (BP(I,J),J=1,ID)
2 CONTINUE
C
IF(IFL1 .EQ. 0) GO TO 10
IF(IFL1 .EQ. 1) GO TO 11
C
END IF
C
IFL1=1
ENDIF
C
C READ IN AND DISTRIBUTE
C **************************************************
IF(ID .EQ. NCP) THEN
IFL1=1
ENDIF
C
READ(31,1001) (DUMMY(I),I=1,ID)
DO 6 I=1,ID
READ(31,1001) (DUMMY(J),J=1,ID)
6 CONTINUE
GO TO 10
C
END IF
C
I1 CONTINUE
C **************************************************
C WRITE THE MATRICES
C **************************************************
IF(IPRC .EQ. 1) THEN
WRITE(*,*) ' WEIGHTS '
WRITE(*,1001) (WP(I),I=1,NCP)
WRITE(*,*) ' COLLOCATION MATRIX (B)'
C
C **************************************************
C END INCOL
C --------------------------------------------------

READ(30,*) NCP
READ(30,*) TOL,METH,MITER
READ(30,*) DTINIT
C
CLOSE (30)
C
RETURN
END
C--------------------------------------------------
SUBROUTINE INCOL
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
DIMENSION DUMMY(14)
C
IFL1=0
IFL2=0
C
10 CONTINUE
C
READ(31,*) ID
IF(ID .EQ. 999) THEN
C **************************************************
C SOMETHING IS WRONG
C **************************************************
WRITE(*,*) ' REQUESTED COLLOCATION MATRIX IS NOT AVAILABLE'
STOP ' ERROR - all done '
END IF
C
IF(ID .EQ. NCP) THEN
IFL1=1
END IF
C **************************************************
C READ IN AND DISTRIBUTE
C **************************************************
IF(IFL1 .NE. 0) THEN
READ(31,1001) (WP(I),I=1,ID)
DO 2 I=1,ID
READ(31,1001) (BP(I,J),J=1,ID)
2 CONTINUE
C
IF(IFL1 .EQ. 0) GO TO 10
IF(IFL1 .EQ. 1) GO TO 11
C
END IF
C
IFL1=1
ENDIF
C
C READ IN AND DISTRIBUTE
C **************************************************
IF(ID .EQ. NCP) THEN
IFL1=1
ENDIF
C
READ(31,1001) (DUMMY(I),I=1,ID)
DO 6 I=1,ID
READ(31,1001) (DUMMY(J),J=1,ID)
6 CONTINUE
GO TO 10
C
END IF
C
I1 CONTINUE
C **************************************************
C WRITE THE MATRICES
C **************************************************
IF(IPRC .EQ. 1) THEN
WRITE(*,*) ' WEIGHTS '
WRITE(*,1001) (WP(I),I=1,NCP)
WRITE(*,*) ' COLLOCATION MATRIX (B)'

99
DO 13 I=1,NCP
WRITE(*,1001) (BP(I,J),J=1,NCP)
13 CONTINUE
END IF
C
1001 FORMAT(4D20.12)
C
RETURN
END
C--------------------------------------------------------------------
SUBROUTINE INIT
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
NTOT=NCP+1
C ************************************************* ****************
DO 11 I=1,NTOT-1
Y(I)=0.0D0
11 CONTINUE
C ************************************************* ****************
C LIQUID PHASE
C ************************************************* ****************
Y(NTOT)=1.0D0
C ************************************************* ****************
C COMPUTE DEPENDENT PARAMETERS
C ************************************************* ****************
Q0=XK*C0**XN
C
CD=CCONC*Q0/C0
C
B1=XKF*RADP*C0
B2=DS*RHOP*Q0*1000.0D0
BIOT=B1/B2
C
TFAC=DS/(RADP*RADP)
C
IF(IPRI .EQ. 1) THEN
WRITE(32,1001) C0,CCONC,CD
WRITE(32,1004) DS
WRITE(32,1005) XKF
WRITE(32,1006) BIOT
WRITE(32,1007) RADP
WRITE(32,1008) RHOP
WRITE(32,1009) XK
WRITE(32,1010) XN
WRITE(32,1011) TFAC
C *****************************************************************
C CONTROL PARAMETER
C ************************************************* ****************
WRITE(32,1013) NTOT,TOL,METH,MITER,DTINIT,DTOUT,TFINAL
END IF
C ************************************************* ****************
C FORMAT STATEMENTS
C *****************************************************************
1001 FORMAT(2X,'C0 = ',E12.6,/,2X,'CCONC = ',E12.6,/,2X,'CD = ',E12.6)
1004 FORMAT(1X,'DS = ',E12.5)
1005 FORMAT(1X,'XKF = ',E12.5)
1006 FORMAT(1X,'BIOT = ',E12.5)
1007 FORMAT(1X,'RADP = ',E12.5)
1008 FORMAT(1X,'RHOP = ',E12.5)
1009 FORMAT(1X,'XK = ',E12.5)
1010 FORMAT(1X,'XN = ',E12.5)
1011 FORMAT(1X,'TFAC = ',E12.5)
C
1013 FORMAT(1X,'NTOT =',I4,/,&
   1X,'TOL =',E16.6,/,&
   1X,'METH =',I4,/,&
   1X,'MITER =',I4,/,&
   1X,'DTINIT =',E16.6,/,&
   1X,'DTOUT =',E16.6,/,&
   1X,'TFINAL =',E16.6,/,&
   1X,'NULL')
C
RETURN
END
C--------------------------------------------------------------------
SUBROUTINE CALCC(TT,YY,NDP,YYM,IDREP1)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
   & XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /VAR/ Y(15),NTOT
C
DIMENSION TT(1),YY(1),YYM(1,1)
C
DIMENSION A(1,1),PARAM(50)
C
EXTERNAL FCN,FCNJ
C
N=NTOT
IDO=1
DO 50 I=1,50
PARAM(I)=0.0D0
50 CONTINUE
PARAM(1)=DTINIT
PARAM(12)=METH
PARAM(13)=MITER
C
T=0.0D0
C
ITRY=0
ITRYT=0
TPHYS=0.0D0
ITER=0
C
DO 100 IP=1,NDP
C
ITER=ITER+1
TEND=TT(IP)*TFAC
C
IF(TT(IP) .LE. 0.01) THEN
YY(IP)=1.0D0
GO TO 100
END IF
C
ITRY=0
C
CALL DIVPAG(IDO,N,FCN,FCNJ,A,T,TEND,TOL,PARAM,Y)
C
ITRY=ITRY+ITRY
T=TEND
TPHYS=T/TFAC
C
WRITE(*,1000) TPHYS,(YYM(IP,KKI),KKI=1,IDREP1),Y(NTOT)
1000 FORMAT(1X,5E16.6)
C
YY(IP)=Y(NTOT)
C
100 CONTINUE
C
IDO=3
CALL DIVPAG(IDO,N,FCN,FCNJ,A,T,TEND,TOL,PARAM,Y)
C
RETURN
END
C--------------------------------------------------------------------
SUBROUTINE FCNJ(N,T,Y,PD)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
DIMENSION Y(N),PD(N,N)
C
RETURN
END
C--------------------------------------------------------------------
SUBROUTINE FCN(N,T,Y,YPRIME)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,DTFINAL,ITMAX,ITRY
C
DIMENSION Y(N),YPRIME(N)
DIMENSION BB(14)
C
ITRY=ITRY+1
C
NTOT=N
II=0
C
NICP=NCP-1
C
DO 30 J=1,NICP
BB(J)=0.0D0
30 CONTINUE
C
WW=0.0D0
C
DO 50 I=1,NICP
II=II+1
LL=0
C
DO 40 J=1,NCP
BB(I)=BB(I)+BP(I,J)*Y(LL)
40 CONTINUE
C ************************************************* ****************
C MASS BALANCE INSIDE PARTICLE (EXCEPT BOUNDARY)
C ************************************************* ****************
YPRIME(II)=BB(I)
WW=WW+WP(I)*YPRIME(II)
50 CONTINUE
C ************************************************* ****************
C SOLID-LIQUID INTERFACE (HEAT EQ. AT INTERFACE
C ************************************************* ****************
II=II+1
BSUM=0.0D0
C
DO 11 KKK=1,NCP
BSUM=BSUM+BP(NCP,KKK)*Y(KKK)
11 CONTINUE
II CONTINUE
C
IF(Y(II) .LT. 0.0D0) THEN
YPRIME(II) = (((BIOT*(Y(NTOT)-0.0D0)-WW)/WP(NCP))+BSUM)*0.5D0
ELSE
YPRIME(II) = (((BIOT*(Y(NTOT)-(Y(II)**(1.0D0/XN)))-WW)/
& WP(NCP))+BSUM)*0.5D0
END IF
C ************************************************* ****************
C LIQUID PHASE MASS BALANCE
C ************************************************* ****************
YPRIME(NTOT)=-3.0D0*CD*(WW+(YPRIME(II)*WP(NCP)))
C
RETURN
END
APPENDIX 4
HSDM PROGRAM

This FORTRAN program <HSDM.FOR> solves the HSDM system of partial differential equations for a closed batch reactor or a plug flow reactor using the orthogonal collocation technique. The IMSL subroutine DIVPAG is used to solve for the bulk concentration profile versus time. The input file <HSDM.IN> requires the user to enter the parameters Co, Ds, kf, K, 1/n, apparent density, and final time. The other control terms do not need to be changed. After running the program, the output file <HSDM.OUT> will contain the bulk concentration profile as a function of time.

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********************************************************************
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP (14),BP (14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
 & XN,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
C
OPEN(30,FILE='HSDM.IN',STATUS='OLD')
OPEN(31,FILE='PART.C',STATUS='OLD')
OPEN(32,FILE='HSDM.OUT',STATUS='OLD')
C
CALL INPUT
C
CALL INCOL
C
CALL INIT
C
CALL CALCC
C
STOP ' all done'
C
END
C--------------------------------------------------------------------
C This subroutine reads the data from the input file HSDM.IN
C ********************************************************************
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP (14),BP (14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
 & XN,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C
READ(30,*) IPRC,IPRI,IPRO
C
READ(30,*) C0
READ(30,*) CCONC
READ(30,*) DS
READ(30,*) XKF
READ(30,*) XK
READ(30,*) XN
XK = XK*1000.0D0**XN
READ(30,*) RADP
READ(30,*) RHOP
C ************************************************* ****************
C Control parameters
C ************************************************* ****************
READ(30,*) NCP
READ(30,*) TOL,METH,MITER
READ(30,*) DTINIT
READ(30,*) DTOUT
READ(30,*) TFINAL
READ(30,*) ITMAX
C RETURN
END
C--------------------------------------------------------------------
C ************************************************* ****************
C This subroutine determines the weights and collocation matrix
C ************************************************* ****************
SUBROUTINE INCOL
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
COMMON /VAR/ Y(15),NTOT
C DIMENSION DUMMY(14)
C IFL1=0
IFL2=0
C 10 CONTINUE
C READ(31,*) ID
IF(ID .EQ. 999) THEN
C SOMETHING IS WRONG
WRITE(*,*) ' REQUESTED COLLOCATION MATRIX IS NOT AVAILABLE'
STOP ' ERROR - all done '
END IF
C IF(ID .EQ. NCP) THEN
IFL1=1
END IF
C ************************************************* ****************
C Read weights into array WP and collocation matrix into array BP
C ************************************************* ****************
IF(IFL1 .NE. 0) THEN
READ(31,1001) (WP(I),I=1,ID)
DO 2 I=1,ID
READ(31,1001) (BP(I,J),J=1,ID)
2 CONTINUE
IF(IFL1 .EQ. 0) GO TO 10
IF(IFL1 .EQ. 1) GO TO 11
END IF
C IF(IFL1 .EQ. 0) THEN
READ(31,1001) (DUMMY(I),I=1,ID)
DO 6 I=1,ID
READ(31,1001) (DUMMY(J),J=1,ID)
6 CONTINUE
GO TO 10
END IF
C 11 CONTINUE
C Write the arrays to the screen if desired
C ************************************************* ****************
IF(IPRC .EQ. 1) THEN
  WRITE(*,*) ' WEIGHTS '
  WRITE(*,1001) (WP(I),I=1,NCP)
  WRITE(*,*) ' COLLOCATION MATRIX (B)' 
  DO 13 I=1,NCP
    WRITE(*,1001) (BP(I,J),J=1,NCP)
  13 CONTINUE
END IF
C
1001 FORMAT(4D20.12)
RETURN
END
C--------------------------------------------------------------------
C ************************************************* ****************
C This subroutine writes initial data to the output file HSDM.OUT
C ************************************************* ****************
SUBROUTINE INIT
C
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
C COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
C COMMON /COL/ NCP,WP(14),BP(14,14)
C COMMON /PARM/ C0,Q0,CCONC,DS,XKF, 
  & XK,XN,RADP,RHOP,BIOT,CD,TFAC
C COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
C COMMON /VAR/ Y(15),NTOT
C
NTOT=NCP+1
C *****************************************************************
C Initial conditions for the solid phase
C ************************************************* ****************
DO 11 I=1,NTOT-1
  Y(I)=0.0D0
11 CONTINUE
C ************************************************* ****************
C Initial condition for the liquid phase
C ************************************************* ****************
Y(NTOT)=1.0D0
C ************************************************* ****************
C Compute dependent parameters
C ************************************************* ****************
Q0=XK*C0**XN
CD=CCONC*Q0/C0
B1=XKF*RADP*C0
B2=DS*RHOP*Q0*1000.0D0
BIOT=B1/B2
C
TFAC=DS/(RADP*RADP)
C
IF(IPRI .EQ. 1) THEN
  WRITE(32,1001) C0,CCONC,CD
  WRITE(32,1004) DS
  WRITE(32,1005) XKF
  WRITE(32,1006) BIOT
  WRITE(32,1007) RADP
  WRITE(32,1008) RHOP
  WRITE(32,1009) XK
  WRITE(32,1010) XN
  WRITE(32,1011) TFAC
  WRITE(32,1013) NTOT,TOL,METH,MITER,DTINIT,DTOUT,TFINAL
END IF
C ************************************************* ****************
C FORMAT STATEMENTS
C ************************************************* ****************
1001 FORMAT(2X,'C0 = ',',E12.6,/)
& 2X,'CCONC = ',E12.6,/, 
& 2X,'CD = ',E12.6,/) 
C 1004 FORMAT(1X,'DS = ',E12.5) 
1005 FORMAT(1X,'XKF = ',E12.5) 
1006 FORMAT(1X,'BIOT = ',E12.5) 
1007 FORMAT(1X,'RADP = ',E12.5) 
1008 FORMAT(1X,'RHOP = ',E12.5) 
1009 FORMAT(1X,'XK = ',E12.5) 
1010 FORMAT(1X,'XN = ',E12.5) 
1011 FORMAT(1X,'TFAC = ',E12.5) 
C 1013 FORMAT(1X,'NTOT =',I4,/, 
& 1X,'TOL =',E16.6,/, 
& 1X,'METH =',I4,/, 
& 1X,'MITER =',I4,/, 
& 1X,'DTINIT =',E16.6,/, 
& 1X,'DTOUT =',E16.6,/, 
& 1X,'TFINAL =',E16.6,/, 
& 1X,'NULL') 
C RETURN 
END 
C-------------------------------------------------------------------- 
C ************************************************* **************** 
C This subroutine solves the differential equation 
C ************************************************* **************** 
SUBROUTINE CALCC 
C IMPLICIT DOUBLE PRECISION (A-H,O-Z) 
C COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER 
COMMON /COL/ NCP,WP(14),BP(14,14) 
COMMON /PARM/ C0,Q0,CCONC,DS,XKF, 
& XK,XN,RADP,RHOP,BIOT,CD,TFAC 
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY 
COMMON /VAR/ Y(15),NTOT 
C DIMENSION A(1,1),PARAM(50) 
C EXTERNAL FCN,FCNJ 
C persecuted subroutine DIVPAG 
C ***************************************************************** 
C Set parameters for IMSL subroutine DIVPAG 
C ***************************************************************** 
N=NTOT 
IDO=1 
DO 50 I=1,50 
PARAM(I)=0 
50 CONTINUE 
PARAM(1)=DTINIT 
PARAM(12)=METH 
PARAM(13)=MITER 
C T=0.00D0 
C ITRY=0 
ITRYT=0 
TPHYS=0.00D0 
ITER=0 
C WRITE(*,*) TPHYS,Y(NTOT) 
WRITE(32,1500) TPHYS,Y(NTOT) 
C 100 CONTINUE 
C ITER=ITER+1 
TEND=T+DTOUT*TFAC 
C ITRY=0 
CALL DIVPAG(IDO,N,FCN,FCNJ,A,T,TEND,TOL,PARAM,Y)
C
ITRY=ITRY+ITRY
T=TEND
TPHY=1/TFAC
C
WRITE(*,*) TPHY,Y(NTOT)
WRITE(32,1500) TPHY,Y(NTOT)
C
1500 FORMAT(1X,F8.2,T10,F10.6)
C
IF (T/TFAC .LT. TFINAL) GO TO 100
C
WRITE(*,*) 'ITRY = ',ITRY
WRITE(32,*) ' 999 999 999 999 999 999 999'
RETURN
END
C--------------------------------------------------------------------
C ************************************************* ****************
C This is a dummy subroutine that is required by DIVPAG
C ************************************************* ****************
SUBROUTINE FCNJ(N,T,Y,PD)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMON /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
C
DIMENSION Y(N),PD(N,N)
C
RETURN
END
C--------------------------------------------------------------------
C ************************************************* ****************
C This subroutine calculates the Jacobian required by DIVPAG
C ************************************************* ****************
SUBROUTINE FCN(N,T,Y,YPRIME)
C
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C
COMMDCOM /CTRL/ IPRC,IPRI,IPRO,TOL,METH,MITER
COMMON /COL/ NCP,WP(14),BP(14,14)
COMMON /PARM/ C0,Q0,CCONC,DS,XKF,
& XK,XN,RADP,RHOP,BIOT,CD,TFAC
COMMON /WORK/ DTINIT,DTOUT,TFINAL,ITMAX,ITRY
C
DIMENSION Y(N),YPRIME(N)
DIMENSION BB(14)
C
ITRY=ITRY+1
C
NTOT=N
KX=0
II=0
C
NICP=NCP-1
C
DO 30 J=1,NICP
BB(J)=0.0D0
30 CONTINUE
C
WW=0.0D0
C
DO 50 I=1,NICP
II=II+1
LL=0
C
DO 40 J=1,NCP
LL=LL+1
BB(I)=BB(I)+BP(I,J)*Y(LL)
40 CONTINUE
C Mass balance inside particle (except boundary)
C *************************************************************************
YPRIME(II)=BB(I)
C
WW=WW+WP(I)*YPRIME(II)
50 CONTINUE
C ************************************************* ****************
C Solid-liquid interface (heat eq. at interface)
C ************************************************* ****************
II=II+1
BSUM=0.0D0
C
DO 11 LLL=1,NCP
  BSUM=BSUM+BP(NCP,LLL)*Y(LLL)
11 CONTINUE
C
IF(Y(II) .LT. 0.0D0) THEN
  YPRIME(II) = (((BIOT*(Y(NTOT)-0.0D0)-WW)/WP(NCP))+BSUM)*0.5D0
ELSE
  YPRIME(II) = (((BIOT*(Y(NTOT)-(Y(II)**(1.0D0/XN)))-WW)/WP(NCP))+BSUM)*0.5D0
END IF
C ************************************************* ****************
C Liquid phase mass balance
C ************************************************* ****************
YPRIME(NTOT)=-3.0D0*CD*(WW+(YPRIME(II)*WP(NCP)))
RETURN
END