

MECHANISMS OF COMPETITIVE ADSORPTION BETWEEN
TRACE ORGANIC CONTAMINANTS AND NATURAL ORGANIC MATTER ON
ACTIVATED CARBON

BY

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DISSERTATION

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ABSTRACT

Activated carbon adsorption is widely used in water treatment for removal of various organic micropollutants; nonetheless, the presence of natural organic matter (NOM) in source water can reduce its efficiency for micropollutant removal. NOM has been shown to compete with target contaminant via different mechanisms: direct competition for available adsorption sites which reduces equilibrium capacity for target compounds, blocking of pore entrance which reduces diffusion rate of the target compounds, and covering of surface sites which may actually enhances diffusion rate of the target compounds. The objective of this dissertation study was to further elucidate the individual competitive effects, to investigate how pore sizes of adsorbents and molecular structure of competing compounds affect competition and to gain a comprehensive understanding of the competitive adsorption.

Atrazine, a widely used herbicide in the United States, was used as the trace-level target contaminant and NOM from different source waters as well as NOM surrogates were used as the competing compounds. Powdered activated carbons (PACs) with different pore size distribution (PSD) were used.

The PSD was found to have great influence on the pore blockage (PB) effect caused by NOM. The equilibrium capacity of the NOM used in this study was best correlated to the amount of pores of diameter 15-50 Å, which was also inversely related to the magnitude of the pore blockage effect. Activated carbon that has more surface area in this pore size range had a smaller PB effect on atrazine adsorption kinetics at the same NOM loading. This finding indicated that mesopores are important in realizing adsorption capacity for trace compounds by alleviating the adverse PB effect.

The site covering effect was confirmed with additional types of PACs and various competing compounds. More important, the correlation equation that describes the enhanced surface diffusion coefficient for atrazine as a function of the loading of the site-covering compounds was found to be independent of either the PAC type or the competing compound type. The key component was to quantify the competing compound as the equivalent background compound (EBC), which reflected the extent of active sites being covered.

The site competing effect, the site covering effect and the pore blocking effect were evaluated for five NOM surrogates with different sizes. The smaller molecules were generally more effective in reducing the equilibrium capacity of the target compound. However, for molecules of similar molecular weight, elongated molecules tended to have more equilibrium effect than round molecules. From a kinetic perspective, the enhancement in diffusivity was within one order of magnitude for all five surrogates, while the extent of the PB effect was greatly relying on molecular size that large-sized surrogates caused a much stronger PB effect. Therefore, the overall kinetic effect was dependent on molecular size and the PB effect was usually dominant except for very small molecules.

Consistent with the enhanced kinetics associated with pre-adsorbed site-covering competing compounds, atrazine preloading was found to also increase the diffusion coefficient of atrazine, and the extent of enhancement caused by atrazine was greater than that caused by competing compounds. Several explanations were proposed for the difference, which include the micropore filling hypothesis and the artifact associated with the EBC method that was used for site-covering loading quantification.

To Father and Mother

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CHAPTER 1

INTRODUCTION

The use of activated carbon for adsorption in water treatment can be traced back to 2000 B. C., when people found that charcoal put in water can make it clear (1). However, the use of activated carbon in modern water treatment didn't start until the 1920s when preliminary studies sprouted in both North American and Europe (2). It started as technology for dechlorination after chlorine disinfection and for taste and odor control (2-4). Its excellent adsorption properties and abundant availability make it still the most popular choice for adsorbents with versatile utilization in current water treatment systems. Now it is used to remove synthetic organic chemicals (SOCs) such as pesticides, dyes and pharmaceutical compounds, in addition to taste and odor control. It is also used for disinfection by-product (DBP) control.

Natural organic matter (NOM), which is mixture of organics including humic substances, is ubiquitously present in natural water, and it has been shown to be DBP precursors and membrane foulants (5-8). Although activated carbon adsorption is able to take care of a portion of NOM, it is usually not used for NOM removal because there are other more cost-effective ways such as coagulation and flocculation. If removals larger than those that can be achieved by coagulation and flocculation are needed, the application of granular activated carbon is an important alternative to be considered. Moreover, the presence of NOM is often undesirable in adsorption process because NOM competes with target contaminants, resulting in increased carbon usage and related cost (9-12). Adsorption of NOM causes reduction in adsorption capacity for target contaminants via direct site competition (9, 12), and reduction in internal diffusivity of adsorbates via pore blockage (9, 13). Recent studies further discovered other competitive effects including surface blockage effect in which adsorbed molecules decreased external film diffusion rate in GAC systems and the enhancement effect in which adsorbed molecules increased adsorption diffusion rate (14, 15).

Of the competitive effects introduced above, all except one concern kinetics of adsorption. The difference in kinetic effects was thought to be caused by the size of a competing compound and whether it was pre-adsorbed (preload). Competing compounds with

comparable size of the target compound occupy active sites and therefore reduce surface resistance for target compound diffusion, while competing compounds with larger sizes accumulate in bigger pores and therefore reduce the size of or block pores, resulting in a strong counter-effect of slowing down diffusion rate for the target compound. However, pore blocking compounds, if not preloaded, did not cause pore blockage. Consequently, NOM, the mixture of differently sized compounds, can exert both effects at the same time.

The current competitive adsorption study still lack of connection between individual competitive effects and a good approach for competitive adsorption modeling. In reality a target compound can under influence of various competing effects and the transient nature of kinetics makes it an even complex problem to model. Moreover, we are looking for ways to control adverse effects from competition and improve adsorption efficiency.

The study described herein on competitive adsorption was designed to have two long-term benefits: to provide better model prediction of adsorption in the presence of competing components and to provide information that can be used to manufacture activated carbon with fewer detrimental competitive effects. The objectives of this study were to gain better understanding of the mechanism of competitive adsorption between trace compounds and NOM, to investigate effects of adsorbent and adsorbate properties on competitive adsorption and to improve our ability to mathematically model competitive adsorption of trace organic compounds. Atrazine was selected to represent trace-level organic contaminants, and NOM was obtained from local water sources. Surrogate compounds were also used in some experiments to represent NOM of a particular size range. The specific tasks were:

- To characterize the pore size distribution (PSD) of a group of powdered activated carbons (PAC);
- To quantify capacity loss for the target compound in competitive isotherms and to investigate how that is related to PSD of the activated carbon;
- To quantify kinetic loss for the target compound caused by preloading activated carbons with pore blocking compounds and to investigate how the amount of loss is related to the PSD of the activated carbons;

- To expand our knowledge of the newly-discovered internal diffusion coefficient enhancement effect by studying more adsorbent-adsorbate combinations; and
- To better understand the changes of surface diffusion coefficient of atrazine as a function of previous loading history, and to model adsorption kinetics with a non-constant diffusion coefficient.

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CHAPTER 2

LITERATURE REVIEW

SYNTHETIC ORGANIC CONTAMINANTS IN DRINKING WATER

Synthetic organic chemicals (SOCs) are organics that originate from domestic and commercial activities, and many of those that have been identified in water supplies have adverse health effects. The majority of SOCs includes pesticides, organic solvents, chemical dyes, metal degreasers, and polychlorinated biphenyls, which is a family of compounds that was formerly widely used (1). Removal of SOCs is an important part of water treatment.

Pesticides (insecticides, herbicides and fungicides) are an important group of SOCs, not only because of their abundance, but also because of their toxicity to aquatic life and to humans. The routes that pesticides follow to enter a water body include rainfall runoff, snowmelt runoff and atmospheric processes of wet and dry atmospheric deposition (2). The widespread use of organic herbicides/pesticides in agricultural and non-agricultural areas over the past several decades has led to their frequent detection in surface water, ground water and aquatic sediment. In the National Water Quality Assessment (NAWQA) program, one of the efforts carried out by the U.S. Geological Survey (USGS), water samples were taken from 2227 ground water sites (wells and springs) during the year 1993 to 1995. Kolpin and Barbash *et al.* (3, 4) examined the data for pesticides and pesticide transformation products, and looked more closely at six compounds, atrazine, cyanazine, simazine, alachlor, acetochlor, which are high-use agricultural herbicides, and prometon, which is a nonagricultural herbicide detected frequently in the study. Concentrations were mostly below the Maximum Contaminant Level (MCL) or Lifetime Health Advisory Level (HAL), with exceptions for atrazine at two sites. Agricultural usage data also showed that atrazine has the highest use among the six compounds, and for most sites, there is a positive correlation between detection and usage.

The NAWQA program was and is being carried out on surface water as well as groundwater. USGS reports (5 and 6) show that at least one herbicide would be detected for most surface water bodies that were monitored, and that atrazine was again the

herbicide that is most likely to exceed its Maximum Contaminant Level (MCL). This also was found in other studies (7). Therefore atrazine was often used to represent a wide range of pesticides, and it has been extensively used in scientific studies. Information on its removal will benefit the overall understanding of the behavior of other contaminants in water treatment processes.

Atrazine, a triazine-class herbicide and the most extensively applied herbicide (8), has been used as an effective pre- and post-emergent herbicide in the production of corn and grain sorghum since the 1960s, and crop yields have increased ever since because it reduces weed growth, which competes for moisture and nutrients. Meanwhile there is concern that its widespread use poses a threat to public-water supplies as well as aquatic ecosystems because of its ability to easily dissolve in water. In 1992, the U.S. Environmental Protection Agency established the MCL for atrazine in finished public-water supplies of 3.0 $\mu\text{g/L}$ (9). In Pope's report (10) on atrazine detection in Delaware River Basin in northeast Kansas region during the year 1992-1994, researchers found that atrazine concentrations in streams and lakes tend to peak from about mid-May to mid-July, and the concentrations at some sites can be as high as 20 $\mu\text{g/L}$. However, during other periods concentrations higher than the MCL were rare.

To control the seasonal fluctuation in herbicides and pesticides occurrence, water treatment plants often use powdered activated carbon (PAC) because the following advantages: it can be added whenever needed, its dosage can be adjusted easily in response to influent concentration changes, it does not require an additional reactor, and exhausted carbon can be removed by following sedimentation or filtration processes. In contrast to PAC, there is granular activated carbon (GAC) that is usually used in a packed column/bed. Its advantages include a long contact time to ensure a small carbon usage rate, and ease of separation and regeneration.

NATURAL ORGANIC MATTER AND ITS COMPETITIVE EFFECTS ON TRACE ORGANIC COMPOUND ADSORPTION

Natural organic matter (NOM) is present in all ground and surface waters, with typical concentrations ranging from 0.5 mg/L to 12 mg/L as total organic carbon (TOC) (11). It

is a complex mixture of thousands of organic compounds, which can be roughly classified into six groups: humic substance, hydrophilic acids, carbohydrates, carboxylic acids, amino acids and hydrocarbons. The molecular weight (MW) of NOM compounds can vary widely, ranging from less than a hundred to over ten thousand; and the molecular size of NOM molecules ranges from about 0.5 to 5 nm (12, 13). As will be explained later in this section, the size of NOM molecules leads to different competition mechanisms.

NOM, by itself usually benign, has been found to have adverse effects in water treatment. It is one of the causes of color, taste and odor of water; it supports growth of microbes in finished water and thus impairs the bio-stability in distribution systems (14); it can foul membranes; and it reacts with disinfectants like chlorine and ozone to form undesirable disinfection byproducts (DBPs) such as trihalomethanes, haloacetic acids and haloaldehydes (15), which are potential carcinogens and mutagens. In studies on activated carbon adsorption, NOM competes with target contaminants, which are usually small synthetic organic compounds with molecular weights of a hundred to several hundred Dalton and at trace-level concentrations of micrograms to nanograms per liter (1). The NOM competition therefore reduces activated carbon capacity for the target contaminants and increases the amount of activated carbon used for a certain treatment goal. For these reasons, a high concentration of NOM is undesirable in meeting increasingly stringent water quality requirements.

Depending on the size of NOM molecules relative to that of a target adsorbate, NOM competes with target trace contaminants via different mechanisms. Small NOM molecules with comparable size to the trace compounds tend to adsorb on the same sites as trace compounds, thereby reducing the number of sites available to trace compounds. This is termed site competition and the direct consequence is reduced equilibrium capacity for the trace compound (16). If the Freundlich equation is used to describe adsorption equilibrium, a reduced K value will be obtained in the presence of NOM with slight changes in $1/n$. The extent of direct competition is determined by the characteristics of NOM (17 and 18), the physical/chemical properties of PAC (19), and the initial concentration of the trace compounds relative to that of NOM (20 and 21).

In contrast, large NOM molecules, which may not adsorb strongly or adsorb on the same sites as the trace compounds due to size exclusion, are capable of constricting or blocking pores, thereby reducing adsorption kinetics of the trace compounds (16, 22, 24, 25). In reactors where contact time does not allow equilibrium to be reached, the reduced kinetics may have a detrimental effect on removal performance. The reduction in diffusivity is more pronounced on “preloaded carbon”, where carbon has been in contact with competing NOM and loaded with large NOM molecules (24, 25), as what is encountered in GAC adsorbers. The reduction in diffusion coefficient was found to be dependent on the loading of pore-blocking compounds/NOM. They also found that for the particular PAC tested in their study NOM that blocks pores is mostly in the MW range of 200 to 700 Dalton (25), so water with a high NOM concentration in this size range is likely to block pores to a high extent. Another factor that affects pore blockage is its pore size distribution (PSD), which is discussed in the next section.

Another effect caused by competitive adsorption was discovered in a recent study (26), in which site-competing compounds enhanced the adsorption diffusion coefficient of the target compound. By occupying active sites, the competing compound was thought to reduce the surface resistance for target compound diffusion and thereby increase its diffusion coefficient. The enhancement effect will be discussed in details in a later section in this chapter.

PORE SIZE DISTRIBUTION AND ITS EFFECT ON ADSORPTION

Pore size of a pore material is divided into four categories according to the International Union of Pure and Applied Chemistry (IUPAC) classification of pore diameter: macropores ($> 500 \text{ \AA}$), mesopores ($20\text{-}500 \text{ \AA}$), secondary micropores ($8\text{-}20 \text{ \AA}$) and primary micropores ($<8 \text{ \AA}$) (27).

Analysis of Pore Properties of Activated Carbon

There are various theories developed for analysis of surface area and pore size distribution of porous materials. The general approach is to perform a full pressure range gas adsorption/desorption cycle on the material to be analyzed, and to analyze the gas adsorption/desorption data using adsorption models to calculate pore surface area and

volume distribution. Nitrogen adsorption at 77 K is the most common method and is suitable for most porous solids; other gases like methane and carbon dioxide are sometimes used for certain purposes (28).

Total surface area analysis. The most widely accepted procedure for the determination of total surface area of activated carbon is the BET method using the nitrogen adsorption isotherm at 77K. The linear part of isotherm in a relative pressure P/P_0 range of 0.05~0.35 is used to fit the BET equation, and the linear region will shift to lower relative pressure for microporous materials. Standard BET (Brunauer, Emmett and Teller) procedure requires a minimum of three points in the appropriate pressure range, but for nitrogen as the adsorbate, the model can be simplified to the one-point BET method. In the absence of mesopores and/or macropores, the Langmuir equation, which is the limiting case of the BET equation applicable to monolayer adsorption, can also provide a good insight into the surface area of an adsorbent.

Pore size distribution analysis. Analysis of pore size distribution (PSD) poses a more formidable task to researchers. The review paper by Groen et al. 2003 (29) as well as the operation manual for the Quantachrome analyzer (QUANTACHROME INSTRUMENTS, Boynton Beach, Florida, USA) gives a good summary of the different models.

The Barret, Joyner and Halenda (BJH) method, which is based on the Kelvin equation, is the classical pore size model. Together with theories on multilayer adsorption, it is often used for calculation of the PSD over the mesopore and part of the macropore range. The Dubinin-Radushkevich (DR) method is based on the Polanyi potential theory of adsorption which says that the adsorption volume occupied by liquid adsorbate at various adsorption potentials can be expressed as a Gaussian function. This method works well for a large number of microporous materials. The Henderson-Kisliuk (HK) method assumes the micropores are slit-shaped rather than cylindrical and calculates the distribution of these pores from the low relative pressure region of the adsorption isotherm. It assumes that the adsorption potential is a function of the effective pore width. The density functional theory (DFT) method is based on the assumption that molecules adsorbed within pores tend to pack according to the strength of both surface forces and interactions with other molecules, i.e., molecules adsorbed within small pores cannot

pack as efficiently as those found within large pores, and as a result, their molar density varies as a function of pore size. The DFT method has been largely applied to characterize microporous carbons via nitrogen adsorption at 77K. For nitrogen, a standard material, the Vulcan kernel, is used to calibrate the model. Research shows that the result using the DFT method was close to expectation, displaying a gradual increase of large micropores and development of small mesopores (30).

Based on the above discussion on the methods, nitrogen gas adsorption was selected for our activated carbon analysis, in conjunction with BET total surface area method and DFT porosity analysis method for micropores and mesopores.

PSD and Non-competitive Adsorption

A good number of studies have confirmed the selective adsorption of molecules on pores of certain size range. Kasaoka et al. (31) used a series of dyes as probes and tested their adsorption on microporous carbons. They found that size exclusion of adsorbate molecules occurred when the average micropore diameter was smaller than 1.7 times the molecule's second widest dimension. Ebie et al. (32) conducted single solute adsorption experiments with small halogenated organic compounds and found that they primarily adsorbed in pores smaller than 15 Å. In the same study they found that one type of NOM, composed of many macromolecules, adsorbed in larger pores with a size range of 30-100 Å. Preferential adsorption of low MW fractions of humic acid solutions has been reported (33, 34). It became obvious that pore size has a great influence on adsorption capacity, in addition to the surface chemistry effect discussed in other studies (35-37). Tamat et al. (38) examined dye adsorption on two carbons which have similar BET surface areas but very different mesopore surface areas. Different adsorption patterns were found for the 9 dyes of different sizes that were used, which led to the conclusion that surface area with respect to different pore sizes, rather than the total surface area, is the important factor in determining adsorption capacity. Hsien et al. 2000 (39) did a similar study of carbons with different mesopore volumes but similar BET surface areas and micropore structure. By comparing adsorption of small adsorbates, phenol and iodine, and a large adsorbate, tannic acid, he concluded that mesopores may enhance adsorption in the inner and narrow micropores by accelerating the diffusion into small

pores and by opening up throats that prevent adsorbate entrance.

The selective adsorption of NOM compounds with different sizes altered the PSD of the activated carbon (40), which would consequently affect its adsorption of other compounds.

PSD and Competitive Adsorption

The above studies established a good base for the study on competitive adsorption, and more specifically, how adsorbent pore size affects the competition between micropollutants and competing compounds.

Activated carbon fibers (ACFs) were often used for study, mainly because their pores are uniform in size and are oriented along the fiber axis. Therefore the complication of connected pores with different diameters can be eliminated in order to better target the effect of a particular pore size.

Hopman et al. (41) studied the effect of NOM loading on pesticides removal using two differently-sized ACF. The ACF with only small pores adsorbed little NOM due to size exclusion, and the NOM preloading showed little effect compared to the virgin carbon. On the other hand, the ACF with larger pores adsorbed a large amount of NOM, and the preloaded carbon showed faster atrazine breakthrough than the virgin carbon. These results suggest that competition can be minimized by manufacturing molecular sieve carbons with pores whose size is large enough to admit the micropollutants of interest but small enough to exclude NOM.

In a later study by Pelekani et al. (42), two microporous ACFs with narrow and broad pore sizes were used in the adsorption of atrazine from natural water. They found that for the ACF with pores small enough to exert a size exclusion effect on NOM molecules, the competition did not cause capacity loss for the target compound, which was consistent with Hopman's finding. However, pore blockage by NOM accumulated on the outer surface reduced adsorption kinetics of the trace compound. Yet for the other ACF with larger pores, preloading the carbon with NOM had much stronger effect on both capacity and kinetics, compared to its virgin counterpart.

Pelekani and co-workers later did more detailed research on the effect of PSD and

competitive adsorption (43, 44). Three additional ACFs were used to expand the pore size range and dyes with different molecular weights, Methylene Blue (MB), Malachite Green (MG) and Congo Red (CR), were used to represent NOM fractions with different molecular weights. They made several important findings. When the competing compound, either a dye with low molecular weight or low molecular weight fraction of NOM, was of similar size to the target contaminant, direct site competition was the dominating mechanism because adsorption sites were equally assessable to both compounds. Increasing pore volume or shifting pore size distribution helped little to minimize this type of competition. However, an increase in molecular size of the competing compound, which made the competing molecule larger than the target, shifted the competition mechanism from direct competition to pore mouth blockage, and finally to outer surface blockage, all of which result in reduction in adsorption capacity of the target compound. On the other hand, in the presence of large competing molecules, broadening the PSD to include secondary micropores and mesopores reduced the degree of pore blockage, but increased the amount of direct competition, because some of the target compounds now adsorbed on the sites in larger pores that were accessible to the competing compound. Use of surrogates to represent NOM in adsorption studies had been presented in several other studies because it made it possible to study NOM components of different size ranges and to better understand competition. The knowledge gained with NOM surrogates needs to be transferred back to real NOM.

The research discussed above focused primarily on the capacity loss of trace compounds due to competition, and research on the reduction in adsorption kinetics is relatively limited and needs further investigation. A qualitative study shows that a PAC with higher surface area in mesopores had less reduction in diffusivity of the trace compound under the same loading of the competing compound, poly-styrene sulfonate (PSS), which was used as a surrogate for pore blocking NOM (24). However to better understand what size range in mesopores is responsible for alleviation of the PB effect and to generalize the finding to other competing compounds, further studies are needed.

THE COMPSORB MODEL

Model Introduction

COMPSORB, sometimes called “the three-component model”, was developed by Li et al. (46) to simulate trace compound removal in the presence of competing compounds in PAC adsorption/membrane filtration systems. The three components are a target trace compound, site-competing (SC) compounds and pore-blocking (PB) compounds. This is the first adsorption model that has incorporated both SC and PB effects.

Major model assumptions are:

- (1) The competitive effects of NOM can be represented by two fictive compounds, one for the SC fraction that competes directly with the trace compound for adsorption sites, and the other for the PB fraction that reduces adsorption kinetics of the trace compound.
- (2) The SC affected only the equilibrium capacity of the trace compound atrazine, but not its surface diffusion coefficient, D_s .
- (3) The PB affected only the adsorption kinetics of both atrazine and SC by reducing their surface diffusion coefficients but not their equilibrium capacities. The relationship between D_s and the PB loading was quantified using an exponential equation with two parameters. It was assumed that PB affected the D_s values of SC and the trace compound in an identical manner.
- (4) Neither the trace compound nor SC affects the adsorption equilibrium capacity or kinetics of PB.

These assumptions and the reactor adsorption/filtration configuration of were incorporated into the development of the mathematical model, COMPSORB. The model was tested using atrazine as the trace compound, *p*-dichlorobenzene (*p*-DCB) of molecular weight of 158 Dalton to represent the SC compound and poly (styrene sulfonate) (PSS) of molecular weight 1.8K Dalton to represent the PB compound. The model output is the predicted concentration profiles of all three surrogate compounds, atrazine, *p*-DCB and PSS in one filtration cycle. The model was successfully verified by comparing experiment data with model predictions (47).

Parameterization for the COMPSORB Model

The COMPSORB model was developed using surrogate compounds (*p*-DCB and PSS), which have definite molecular structure and adsorption parameters. However, to apply this model to competitive adsorption between a trace compound and NOM, the latter being an unknown mixture of numerous organic chemicals, an extra step of parameterization of NOM is necessary. For modeling purposes, NOM needs to be represented as one SC fraction and one PB fraction, each of which has its adsorption parameters determined. Physical separation of NOM fractions is not feasible. Instead, a parameterization procedure was established through a series of independent experiments in order to describe NOM as fictive SC and PB compounds (48). The SC fraction of the NOM was modeled as one equivalent background compound (EBC), (20), whose adsorption parameters were assigned the same numbers as atrazine. The concentration of the SC fraction was then obtained by fitting the competitive isotherms with the IAST (ideal adsorbed solution theory) model (49). The concentration of the remaining PB fraction was calculated by subtracting the SC fraction from the total NOM concentration expressed as TOC. This approach was verified by comparing predicted and experimental atrazine adsorption results for two natural waters in the adsorption/membrane filtration reactor (48).

ENHANCEMENT OF ADSORPTION DIFFUSION RATE

Increased diffusivity for a trace compound in the presence of competing compounds/NOM has been observed in other research; however, the slight increase, compared to the substantial decrease caused by pore blockage compounds, was sometimes overlooked, or taken as model fitting error in parameterization (24). In a recent study by To et al. the enhancement of diffusion coefficients was closely studied via a series of carefully-designed experiments where the pore blockage effect was minimal (26). They found that site-competing compounds could actually increase the surface diffusion rate of the target compound by occupying adsorption sites and reducing the surface resistance for the trace compound diffusion. They also found that the enhancement of the diffusion coefficient was linearly dependent on the loading of the site-competing compound, when it was quantified as the EBC following the procedure

developed in another study (48). Knowing the enhancement effect they were able to separate it from the PB effect following the procedure they developed in a later study (50). Several soil adsorption studies have also observed faster kinetics of a target contaminant in the presence of competing solutes and attempted to explain the phenomenon by proposing the dual-mode model: a hole (pore)-filling domain and a diffusion domain (51, 52). They explained that filling of pores by a competing compound increased the rate of diffusion of the other compound. Although soil and activated carbon differ in composition and porous structure, results from soil studies can enlighten research on activated carbons. Some other studies suggested that in a bi-solute system a compound with lower affinity for an adsorbent tended to become more mobile and had faster kinetics because surface sites are preferentially occupied by the other compound with strong affinity (53, 54). Pore-filling and site-coverage, although termed differently, have some similarity. They both refer to situations where molecules fill up space that may have strong affinity for the trace compound, and therefore increase its diffusivity.

The increased diffusivity may have important effects on water treatment. For example, fast desorption of adsorbed contaminants from GAC adsorbers due to competition is undesirable; or how a loaded GAC adsorber handles a sudden spike of a contaminant. Therefore, it is important to carefully look at the mechanisms and how pore-filling and surface coverage can be related or unified to quantitatively describe the enhanced diffusivity.

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CHAPTER 3

MATERIALS AND METHODS

Laboratory work and computer mathematical modeling were performed to achieve the research objectives discussed before. This Chapter provides an overall presentation of materials and methods that were used in the dissertation research and details in experimental conditions and fine modification pertinent to specific objectives will be discussed in respective chapters following.

Laboratory work was focused on two types of experiments, the adsorption isotherms and the adsorption kinetics. For both of them, we varied the constituents in test solution to simulate non-competitive and competitive adsorption scenarios, so to investigate competitive effects under various circumstances. Tests on activated carbon property and reactor performance had also been performed. Modeling-wise, the key part is to model adsorption kinetics in the presence of competition as we have discovered several competitive effects that may have counter effects on surface diffusion coefficient of the target compound.

Water

Distilled de-ionized (DDI) water was used as organic free water (OFW), which was considered to have no competitive species. It was collected from the glass carboy of the distillation machine in Newmark Civil Engineering Laboratory on the test day.

The groundwater from Clinton Water Works (CWW), Clinton, IL was used as the source for natural organic matter (NOM). CWW water was collected at the plant pump station before any treatment and stored at 4°C in a stainless steel barrel. Prior to an experiment, the water was warmed to ambient temperature and passed through a nylon membrane filter with a nominal pore size of 0.45 µm (OSMONICS, Minnetonka, MN) to remove suspended solids. The dissolved organic carbon (DOC) concentration of CWW water, measured with a Phoenix 8000 TOC analyzer (Tekmar-Dohrmann, Cincinnati, OH), varied between 7.0-7.5 mg/L $\pm$ 0.2 mg/L as the water got aged.

Adsorbents

Five powdered activated carbons (PACs) were used in this study. Four of them (SA UF, SA Super, W20, W35) are commercial products from NORIT Netherlands, B.V., Amersfoort, Netherlands, made from the same raw material, but with different levels of activation. One old batch of SA UF (NORIT France, S.a.r.l., Le Blanc Mesnil Cedex, France) was also used in some early experiments, and it behaved similarly to the new batch of SA UF.

The fifth PAC is called Pellet II, which was produced by activating an agglomerated carbon black impregnated with a cellulose-ZnCl₂ solution in a nitrogen atmosphere in the Department of Materials Science and Engineering laboratory, University of Illinois at Urbana-Champaign. It features a high surface area in the mesoporous region. It was machine-ground and sieved through US Mesh Sieve size No. 400 (37 µm diameter opening) prior to use.

All carbons were stored in glass bottles inside a desiccator. Prior to use, the carbon was taken out of the desiccator, oven-dried overnight at 105°C, and placed back in the desiccator for cooling.

Some literature data were also used, which covered an extra powdered activated carbon, WPH by Calgon Carbon Corp., Pittsburgh, PA.

Trace Organic Contaminant

Carbon 14 radio-labeled atrazine (217 Da) was used as the target trace compound. Atrazine is a widely used herbicide in the US and has also been used in a good number of adsorption studies. Batches from two manufactories were used (Syngenta Crop Protection, Inc., Greensboro, NC; American Radiolabeled Chemicals, Inc., 101 ARC Drive St. Louis, MO). For each of a new batch put into use, atrazine isotherm in DDI water was performed for quality control. Stock solutions of atrazine were prepared for each batch by dissolving solid atrazine in DDI water to make a concentration around 10-15 mg/L. The stock solution was mixed on a stir plate for a day until all solid had been dissolved. They were stored in a fridge at 4°C and were later used to prepare all test solutions.

Aqueous concentration of atrazine was determined by mixing 2.5 mL of sample with 18 mL of scintillation cocktail solution (Ecoscint, National Diagnostics, Inc. Atlanta, Georgia, USA) in a 20-mL glass vial and analyzed by a liquid scintillation counter (Tri-carb Model 1600A, Packard Instrument Co., Downers Grove, IL).

Competing Compounds

NOM in the CWW water was the competing compounds and the competitive effects were realized by conducting atrazine adsorption experiments in CWW water. Concentration of NOM was quantified by DOC (dissolved organic carbon) analyzer.

Competing compounds in literature data includes one more type of NOM, which was the Suwannee River NOM (SR NOM, International Humic Substances Society, St. Paul, Minnesota, USA). Also included were NOM surrogates of different molecular weights: *p*-dichlorobenzene (*p*-DCB), poly-styrene sulfonate of nominal size of 1800 Dalton (PSS-1.8k) and five dyes, Methyl Orange (MO), Brilliant Yellow (BY), Congo Red (CR), Xylenol Orange (XO), and Evans Blue (EB). Details on chemical handling and analysis can be found in reference 21, 7 and 15.

Adsorption Isotherms Experiments

Atrazine isotherm tests were conducted using the conventional bottle-point technique (1). The following types of isotherms were performed.

Single-solute adsorption isotherms. Single solute isotherms were established for the target compound and each of the competing compounds/NOM. A test solution was prepared by spiking stock solution of the test compound to DDI and mixing it on a stir plate. The test solution was dispensed into amber isotherm bottles, each of which has pre-weighed PAC inside. Bottles were then sealed with Teflon tape and caps and put in a shaker for 7 days. Preliminary tests had proved duration of 7 days is enough to reach equilibrium. Atrazine samples were taken by drawing 5 mL of solution from a bottle using a gas tight syringe and pushing it through a 13 mm 0.45 μ m nylon filter. The first 2.5 mL was discarded and the next exact 2.5 mL was collected in a 20-mL vials.

Competitive isotherms. Competitive isotherm tests were performed in a similar way as

single solute isotherms, except that the test solutions were made by adding atrazine stock solution into filtered CWW water. The different initial concentrations of atrazine were realized by varying the volume of the stock solution added. Equilibrium samples at 7 days for atrazine and for NOM were taken and analyzed. The sampling process for atrazine can be found in the previous paragraph and the DOC samples were taken by filtering 60 mL of solution through 25 mm 0.45 μ m nylon filters with 40 mL being collected. Please also refer to the previous sections for analysis processes for individual compounds.

Adsorption Kinetic Experiments

Two types of adsorption kinetic tests were performed, the adsorption kinetics on virgin (fresh) PAC and the adsorption kinetics on partially loaded (preloaded) PAC.

Adsorption kinetics on fresh PAC. Like isotherm tests, adsorption kinetics on Fresh PAC was conducted for single solute adsorption and for competitive adsorption. Test solution was made by adding stock solutions of individual compounds to DDI water or to CWW water to reach target initial concentrations of each species.

The test solution was dispensed into containers that were furnished with mixing apparatus, which were either a Jar tester or stir plates with stir bars. For details in mixing equipment, please refer to individual chapters 4-7. At time zero, suspensions of pre-weighed carbon were dosed into each container to reach a target carbon dose, and the aqueous samples were taken over the next 4 hours. For sampling and analysis procedure, please refer to previous sections.

Adsorption kinetics on preloaded PAC. A preload step was added before the regular kinetic test in order to produce PAC that had been partially loaded. The preloadings were either by the competing compound NOM, by the target compound atrazine itself, or by both. Pre-weighed PAC was in contact with solution that contains NOM or atrazine, depending on what compound we were going to test, for 4 days. Concentrations of preload species were measured at the end of 4 days to determine the loading. A spike of atrazine was then dosed into each bottles and its concentration was monitored over the following 4 to 6 hours. For sampling and analysis procedure, please refer to previous

sections.

Pore Size Distribution Analysis

PSD analyses were performed using N₂ gas adsorption at 77 K with an Autosorb-1 Volumetric Sorption Analyzer controlled by Autosorb-1 software (Quantachrome Corp., Boynton Beach, Florida). All samples were degassed at 150°C until the outgas pressure rise was below 5 Hg/min prior to analysis. The Brunnauer Emmett Teller (BET) surface areas were determined from the N₂ adsorption isotherm. The total pore volume was estimated from the amount of nitrogen adsorbed at the relative partial pressure $P/P_0 = 0.95$. The non-local density functional theory (DFT) model was applied to the N₂ adsorption data at 77 K to get pore size distributions and micropore volumes (2). The pores were divided into four groups according to the International Union of Pure and Applied Chemistry classification: macropores ($> 500 \text{ \AA}$), mesopores ($20\text{-}500 \text{ \AA}$), secondary micropores ($8\text{-}20 \text{ \AA}$) and primary micropores ($<8 \text{ \AA}$) (3).

Hybrid Adsorption/Filtration System Experiments

Experiments were performed with a flow-through hybrid adsorption/membrane reactor. The membrane reactor was a 350 mL stirred cell (Millipore, Bedford, MA) with a Etch-Track membrane (Whatman, Clifton, NJ) having a nominal pore size of $1 \text{ }\mu\text{m}$ installed on the bottom. The cell was filled with influent water, which is made of pretreated natural water spiked with atrazine. A pulse input of pre-weighed PAC in the form of slurry made with OFW was added through the pressure relief port located in the top plate of the cell. A peristaltic pump (Masterflex, Cole Parmer, Barrington, IL) was used to maintain a constant flow rate of 10 mL/min throughout the experiment for an overall operating time of 360 min, which corresponds to the interval between two consecutive membrane backwashes. Effluent samples were collected for atrazine and DOC analyses.

Adsorption Kinetics Modeling

Homogeneous surface diffusion model (4, 5) was used to model adsorption kinetics on PAC. The model assumes activated carbon is spherical particles with homogeneous structure and adsorbate molecules diffuse along internal surface in pores to adsorption

sites with a uniform surface diffusion coefficient D_s .

HSDM can be solved numerically and its solution had been formulated using FORTRAN program by other researchers. The model was used in this research to fit experimental data for D_s . In competitive adsorption, pseudo-single-solute was assumed and the equilibrium parameters of the adsorbate were modified to reflect the capacity loss due to competition.

HSDM can also have analytical solution (6) for which we developed a solution using MATLAB. Please refer to Chapter 7 and Appendix for details on the new approach to solve HSDM.

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CHAPTER 4

EFFECTS OF ACTIVATED CARBON PORE SIZE DISTRIBUTION ON THE COMPETITIVE ADSORPTION OF AQUEOUS ATRAZINE AND NATURAL ORGANIC MATTER*

INTRODUCTION

Activated carbon is used in water treatment to remove a wide range of organic contaminants such as taste & odor compounds and synthetic organic chemicals. However, natural organic matter (NOM) that is present in all natural water bodies competes with target contaminants and significantly increases the required dose of activated carbon and related treatment cost. NOM is a ubiquitous, heterogeneous mixture of organic compounds present in both ground and surface waters at concentrations in the range of 0.1 and 20 mg/L as total organic carbon (1). The molecular weight of NOM constituents varies from a few hundred to over 10,000 (2). NOM competes via two major mechanisms, direct site competition and pore blockage (3-5). Small, strongly adsorbing molecules of NOM with size comparable to that of the target compound are mainly responsible for direct site competition, thereby reducing the adsorption capacity for the target compound. Larger NOM molecules adsorb in large pores and reduce the effective pore diameter, thus, decreasing the rate of adsorption of smaller molecules that must pass through these pores to reach smaller pores.

The extent to which NOM competes with target compounds depends on the characteristics of the NOM (6, 7), the physical/chemical properties of PAC (8), and the initial concentration of the trace compounds relative to that of NOM (9, 10). Single-solutes have been shown to preferentially adsorb in pores with diameter similar to their molecular size (11), and to undergo size exclusion in pores with average diameter smaller than 1.7 times the molecule's second widest dimension (12). One type of NOM has been reported to adsorb in pores with a size range of 30-100 Å (13).

Hopman et al. (14) studied the effect of NOM preloading on the removal of atrazine and found that a carbon with only relatively small micropores adsorbed little NOM due to

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size exclusion, and NOM preloading resulted in little reduction of atrazine adsorption capacity. In contrast, a carbon with larger micropores adsorbed higher levels of NOM, which in turn resulted in a reduction in the adsorption capacity for atrazine. Pelekani et al. (15-17) found that NOM could cause a large reduction in the atrazine adsorption capacity of carbon containing only small micropores. Pelekani and co-workers (15) also found that direct site competition was the dominant mechanism responsible for capacity reduction when the competing compound was of similar size to the target contaminant, and an increase in molecular size of the competing compound shifted the competition mechanism from direct competition to blockage of the pore mouth of a predominantly microporous carbon.

Li et al. (2) showed that constriction of internal carbon pores caused a reduction in the rate of diffusion of target compounds. By comparing two carbons (4, 18), the extent of reduction in diffusion coefficient caused by adsorption of the same concentration of pore-blocking compound (in mg/g of PAC), was found to be less pronounced for the carbon with larger volume of mesopores.

The objective of this study was to quantify the effect of PSD on the competitive adsorption effects of NOM. A series of powdered activated carbons (PACs) made from one raw material by similar manufacturing process, and a new PAC developed from another raw material activated by a different method were used to study the removal of atrazine from natural water. The major difference in these PACs is the pore size distribution (PSD). The effect of PSD on contaminant removal was also investigated in a flow-through adsorption/filtration system, using the COMPSORB kinetic model (4).

MATERIALS AND METHODS

Water

Experiments were performed with distilled de-ionized (DDI) water as organic free water (OFW) and groundwater from Clinton Water Works (CWW), Clinton, IL. Please refer to Chapter 3 for details in collecting and handling. Experiments in DDI water were considered as single-solute adsorption without competition, and experiments in CWW water were considered to undergo competitive effects caused by NOM from CWW water.

The dissolved organic carbon (DOC) concentration of CWW water was 7.0 ± 0.2 mg/L.

Adsorbents

Five powdered activated carbons (PACs) were used in this study. Four of them (SA UF, SA Super, W20, W35) are commercial products from NORIT Netherlands and the fifth carbon (Pellet II) was produced in the Department of Materials Science and Engineering laboratory, University of Illinois at Urbana-Champaign. Details can be found in Chapter 3.

Adsorbates

Atrazine radio-labeled with Carbon 14 was used as the target trace compound, and NOM in CWW water was treated as the competing compound.

Isotherm Experiments

Atrazine isotherm tests were conducted in OFW and in CWW water using the conventional bottle-point technique (19). Details on how to conduct the isotherm tests can be found in Chapter 3.

For single-solute atrazine isotherms in DDI water, an initial concentration of around 100 $\mu\text{g/L}$ was used for SA Super, W35 and W20 and an initial concentration of around 200 $\mu\text{g/L}$ was used for SA UF and Pellet II. Such high initial concentrations were used to assure detectable equilibrium concentrations after adsorption.

Lower initial concentrations were used for atrazine adsorption in CWW water because NOM competition greatly reduced adsorption capacity for atrazine. For each PAC, two initial concentrations of atrazine, 10 $\mu\text{g/L}$ and 50 $\mu\text{g/L}$, were used in the presence of NOM, which produced different levels of competition and provided higher reliability in later model fitting.

Adsorption Kinetic Experiments

Two types of adsorption kinetic tests were carried out for atrazine: (a) adsorption on virgin carbon in OFW, which established the baseline surface diffusion coefficient, $D_{s,0}$, and (b) adsorption on carbon preloaded with CWW NOM. For the test in OFW, atrazine

was dosed into each of the square beakers (B-KER, Phipps and Bird, Richmond, VA) that contained 2 L of OFW to reach a target initial atrazine concentration. At time zero, a suspension of pre-weighed carbon was dosed into the jar to reach a carbon concentration in the range of 1-4 mg/L. The test solution was mixed by mechanical stirring at 170 rpm in a Phipps and Bird (Richmond, VA) jar tester, and samples were taken over the next 4 hours. For the preloading tests, a 4-day preloading step was performed before the kinetic runs, and carbon doses were varied between 2-16 mg/L in order to achieve different carbon surface loadings of NOM. The suspension was continuously mixed for 4 days, at approximately 100 rpm. The kinetic test was started at the end of the 4 day preloading period by dosing atrazine into each jar to achieve the same initial atrazine concentration. At the same time the stirring speed was increased to 170 rpm. Atrazine samples were taken at predetermined times and analyzed following procedures described in Chapter 3.

Hybrid Adsorption-filtration System Experiments

Details on the adsorption/filtration experiment have been discussed in Chapter 3. The purpose of this experiment was to study the PSD effects in a more practical setting to see it affects adsorption efficiency. The COMPSORB model (4) was used to simulate the adsorption performance as well.

Pore Size Distribution (PSD) Analyses

Details on PSD analysis can also be found in Chapter 3.

RESULTS AND DISCUSSION

PSD Results

The PSD of the five PACs used in this study are shown in Figure 4.1. Pellet II has the highest total surface area as well as the highest surface area in the lower mesopore range of 20-50 Å, followed by SA UF and SA Super, W35, and W20 in decreasing order for both of these surface area categories. In contrast, this sequence in cumulative area changes within the lower micropore range, resulting in SA Super and SA UF having the highest surface area in micropores smaller than 12 Å followed by W35, Pellet II and W20 in decreasing order.

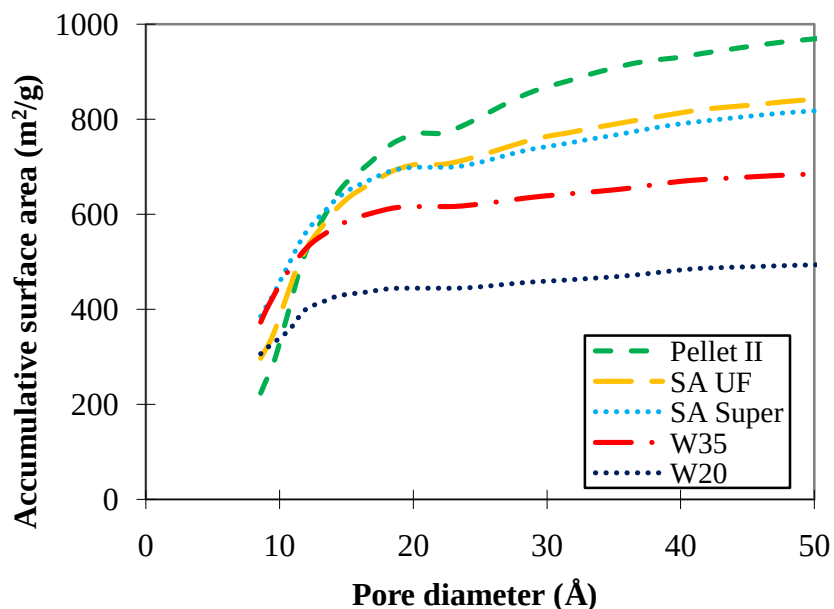


Figure 4.1 Pore size distribution of the five PACs

Adsorption Capacities of Atrazine and NOM

Single-solute atrazine isotherms obtained with the five carbons are shown in Figure 4.2(a). The adsorption capacity for atrazine is similar for SA UF, SA Super and W35. Pellet II has an intermediate capacity and W20 the lowest capacity for atrazine, in a similar sequence with cumulative surface area in lower micropore range. Therefore it was not the total surface area that determines that adsorption capacity for atrazine, which has the relatively low molecular weight of 216 Dalton; rather, pores within the micropore region mainly contribute to atrazine adsorption. NOM adsorption isotherms

NOM isotherms obtained with the five carbons equilibrated with CWW water are shown in Figure 4.2 (b). A comparison of these isotherms to those for single solute atrazine in Figure 4.2 (a) reveals some interesting differences. For example, Pellet II has a lower capacity than W35 for atrazine, but a much larger capacity for NOM. Atrazine has a molecular weight of 216 Dalton, while high performance size exclusion chromatography shows that NOM from CWW water has a molecule weight distribution that ranges from one hundred to higher than one thousand with an weight-averaged molecular weight of 328 Dalton (20). Because most NOM molecules are larger than atrazine, they would adsorb in larger pores which are most abundant in Pellet II compared to the other carbons (Figure 4.1).

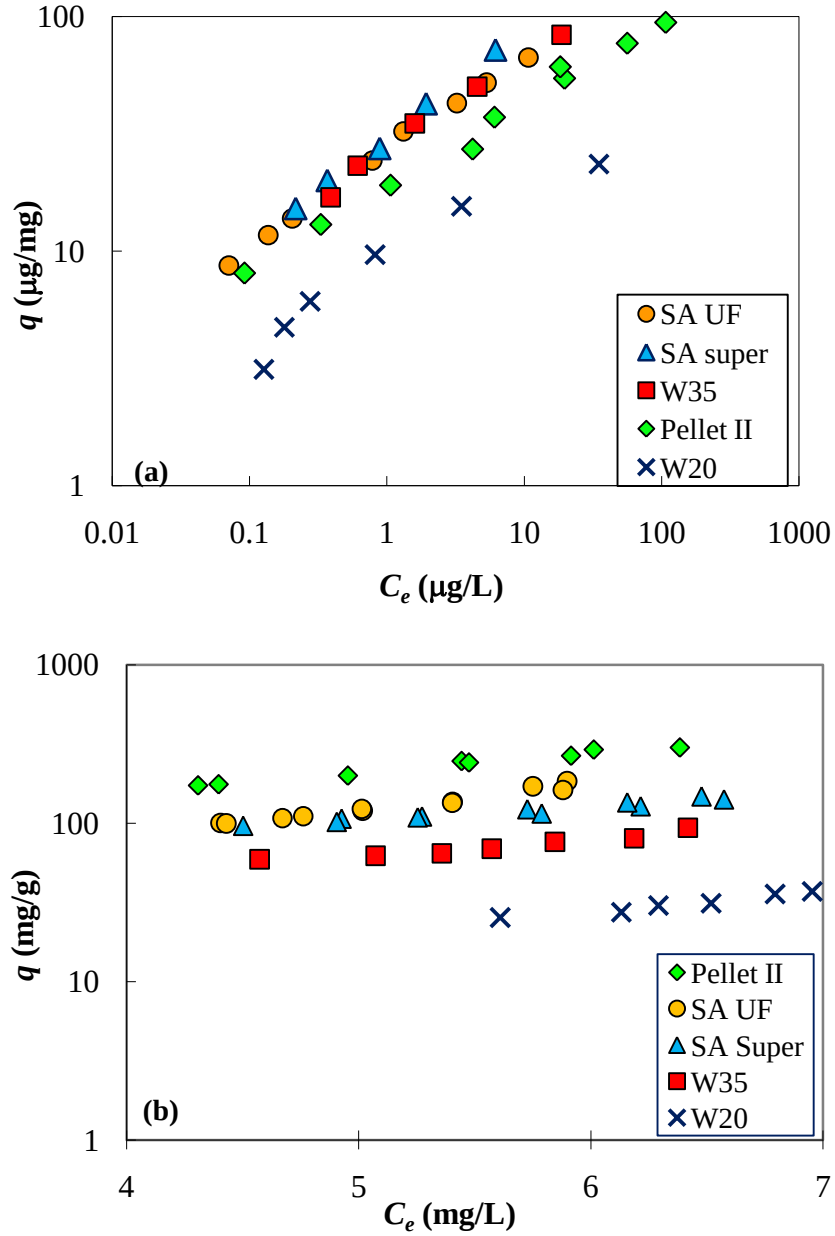


Figure 4.2 Atrazine and NOM adsorption isotherms
(a) Atrazine adsorption isotherms in DDI
(b) CWW-NOM adsorption isotherms

The pore size range within which most of the NOM adsorption takes place could be identified by correlating NOM adsorption capacity with surface area for selected pore size ranges. The solid phase concentration at 20% NOM removal (aqueous concentration reduction from $C_0 = 7.0$ mg/L to $C_e = 5.6$ mg/L), $q_{0.2}$, was used instead of the Freundlich constant K to represent the adsorption capacity for NOM because Instead, that

equilibrium concentration falls in the middle of the concentration range covered by the isotherms. The alternative of using the Freundlich K value, which is the capacity at an aqueous phase concentration of 1 mg/L, was not used because it was significantly outside the range of the measured data. To lower the NOM concentration to 1 mg/L will require use of enormous amount of activated carbon and therefore does not represent a realistic scenario.

The pore surface area was calculated for four groups corresponding to pore size ranges of 0-15 Å, 15-50 Å, 50-100 Å, and 100-300 Å for each carbon. The NOM capacity (i.e., $q_{0.2}$) was then plotted versus the surface area in each group, with the linear fit forced through the origin. The 15-50 Å range gave the best fit ($r^2 = 0.923$), shown in Figure 4.3, which supports the importance of these pores for CWW NOM adsorption, while the other three pore size ranges gave poorer fits with r^2 of 0.393 (0-15 Å), 0.840 (50-100 Å), and 0.523 (100-300 Å). Other pore size ranges were also tested, whose correlation quality did not superb the one with 15-50 Å. It is also recognized that this approach gives a general indication of the most important pore size range rather than an absolute measure of the pores that are responsible for NOM adsorption. Some NOM adsorption in pores outside this range is highly probable, especially because of the wide range of molecular sizes that make up NOM. The NOM adsorbing size range is expected to be NOM specific that NOM of different water source is expected to correlate with pores of different size range due to molecular weight difference in the NOM components. The other NOM that we have worked with is Suwannee River NOM (SR NOM), which had been analyzed to have a number-averaged and weight-averaged molecular weight of $MW_n = 3701$ Da and $MW_w = 9602$ Da. That SR NOM was expected to mainly adsorb in pores with larger diameters.

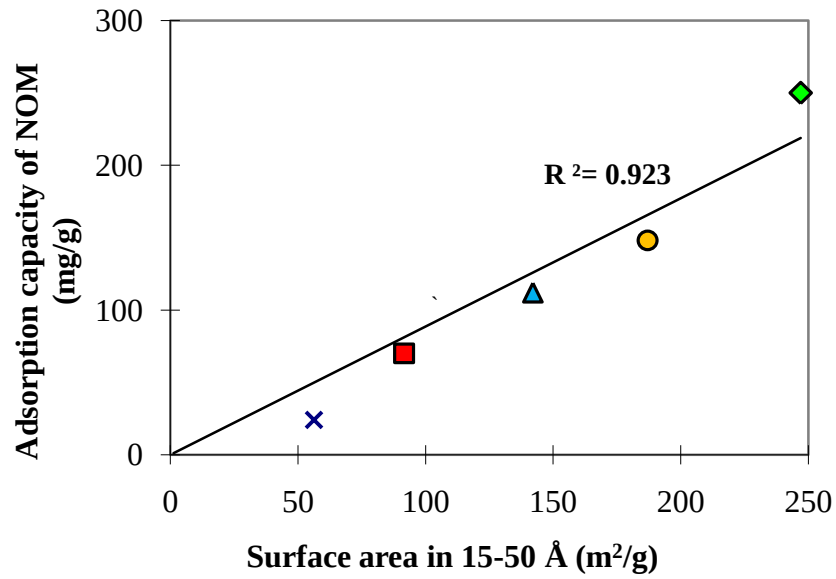


Figure 4.3 Adsorption capacities for CWW NOM as a function of surface area for pores with diameter in the range of 15-50 Å

The atrazine adsorption isotherms in the presence of this NOM are presented below.

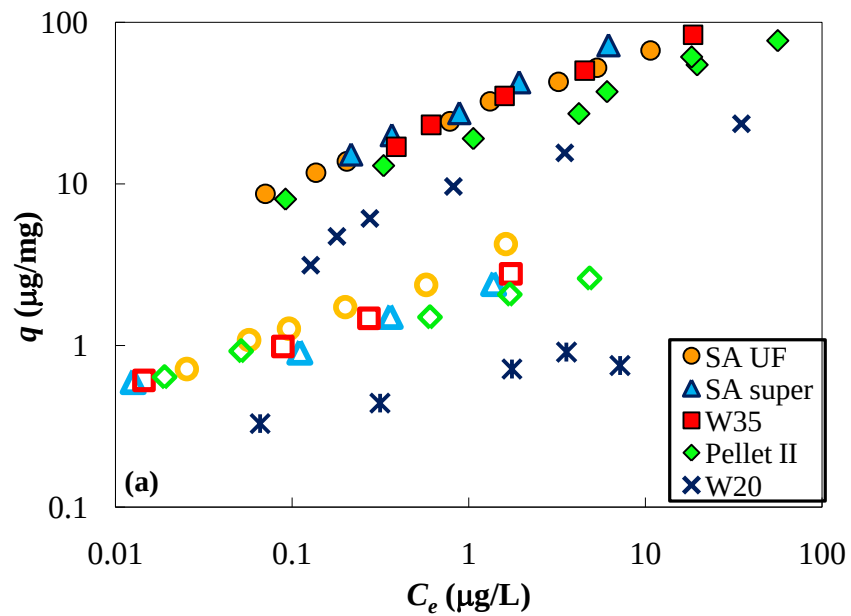


Figure 4.4 continued on next page

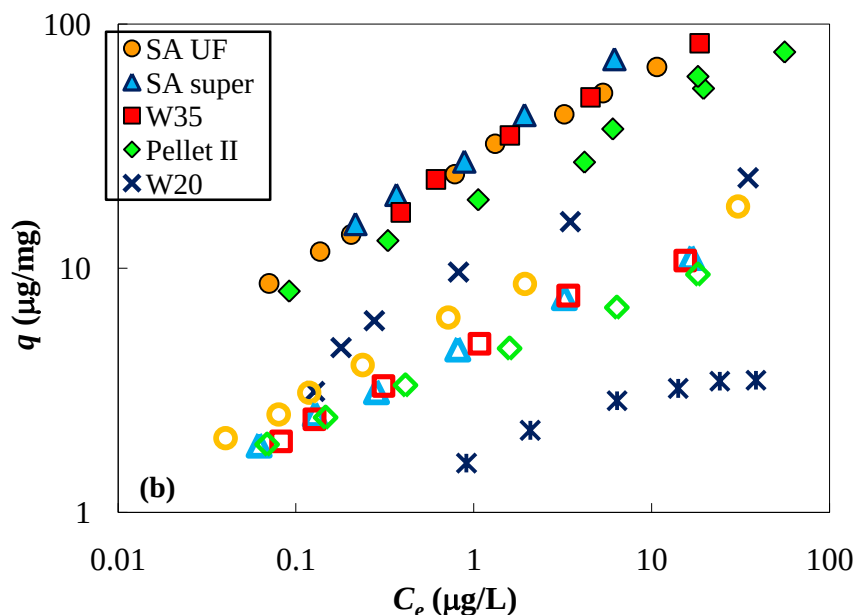


Figure 4.4 Adsorption isotherms of atrazine in the presence of NOM on PACs (open marks) at (a) $C_{0,\text{atrazine}} = 10 \mu\text{g/L}$, and (b) $C_{0,\text{atrazine}} = 50 \mu\text{g/L}$, in comparison to non-competitive isotherms (solid marks)

The first information that can be derived from Figures 4.4 (a) and (b) is that a lower initial concentration of atrazine resulted in lower isotherms in figure (a) than those in figure (b). This is consistent with the observation that strength of competition is dependent on the relative concentration of the two competing components (11). However, in this study we were more interested in how PSD affected competitive adsorption; therefore, the reduction in Freundlich K for each carbon and each initial condition were summarized in Table 4.1 to see whether it was related to PSD. What we found was that the percentage reduction in K was similar for all PACs as shown in columns 4 and 6, despite of different in carbon type and PSD.

Table 4.1 Freundlich K for atrazine in non-competitive adsorption and in competitive adsorption in CWW water at (a) $C_{0,\text{atrazine}} = 10 \mu\text{g/L}$, and (b) $C_{0,\text{atrazine}} = 50 \mu\text{g/L}$

PAC	Non-competitive K	K_1	Reduction for K_1	K_2	Reduction for K_2
SA Super	30	2.2	93%	4.8	84%
W35	28	2.3	92%	4.7	83%
W20	10	0.62	94%	1.4	86%
Pellet II	20	1.6	92%	4.5	78%

Atrazine Adsorption Kinetics

Atrazine adsorption kinetics were studied as a function of the amount of NOM pre-adsorbed on the carbons. The difference in NOM loading was achieved by dosing different amounts of each PAC into the same volume of CWW water. The adsorption kinetic data were analyzed by the Homogeneous Surface Diffusion Model (HSDM) (21-23) to determine the surface diffusion coefficient D_s , for each of the preloaded carbons.

Kinetic data with HSDM fits are presented in Figure 4.5 (a) - (e) for each of the 5 PACs.

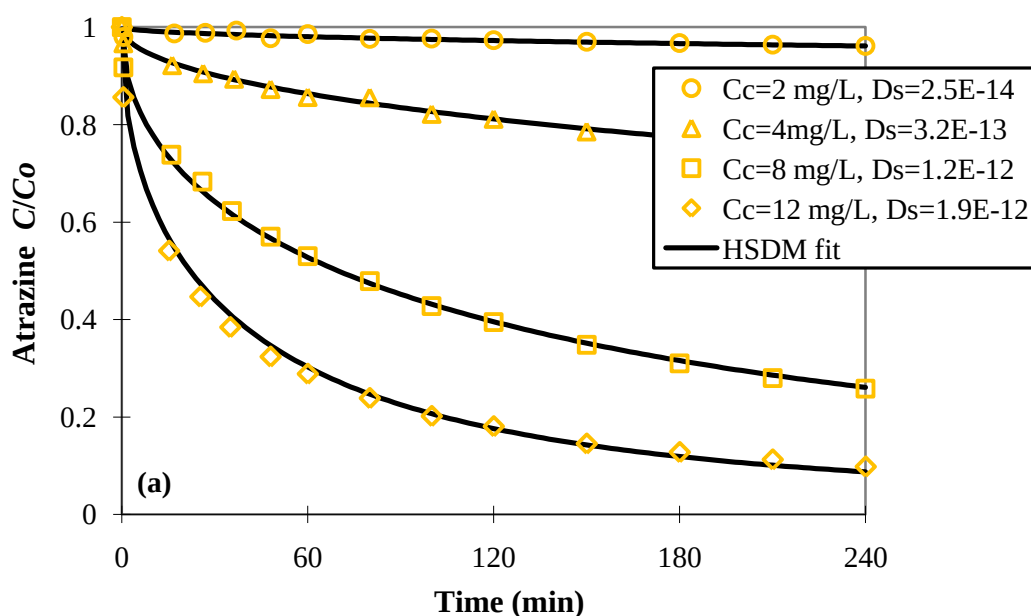


Figure 4.5 continued on next page

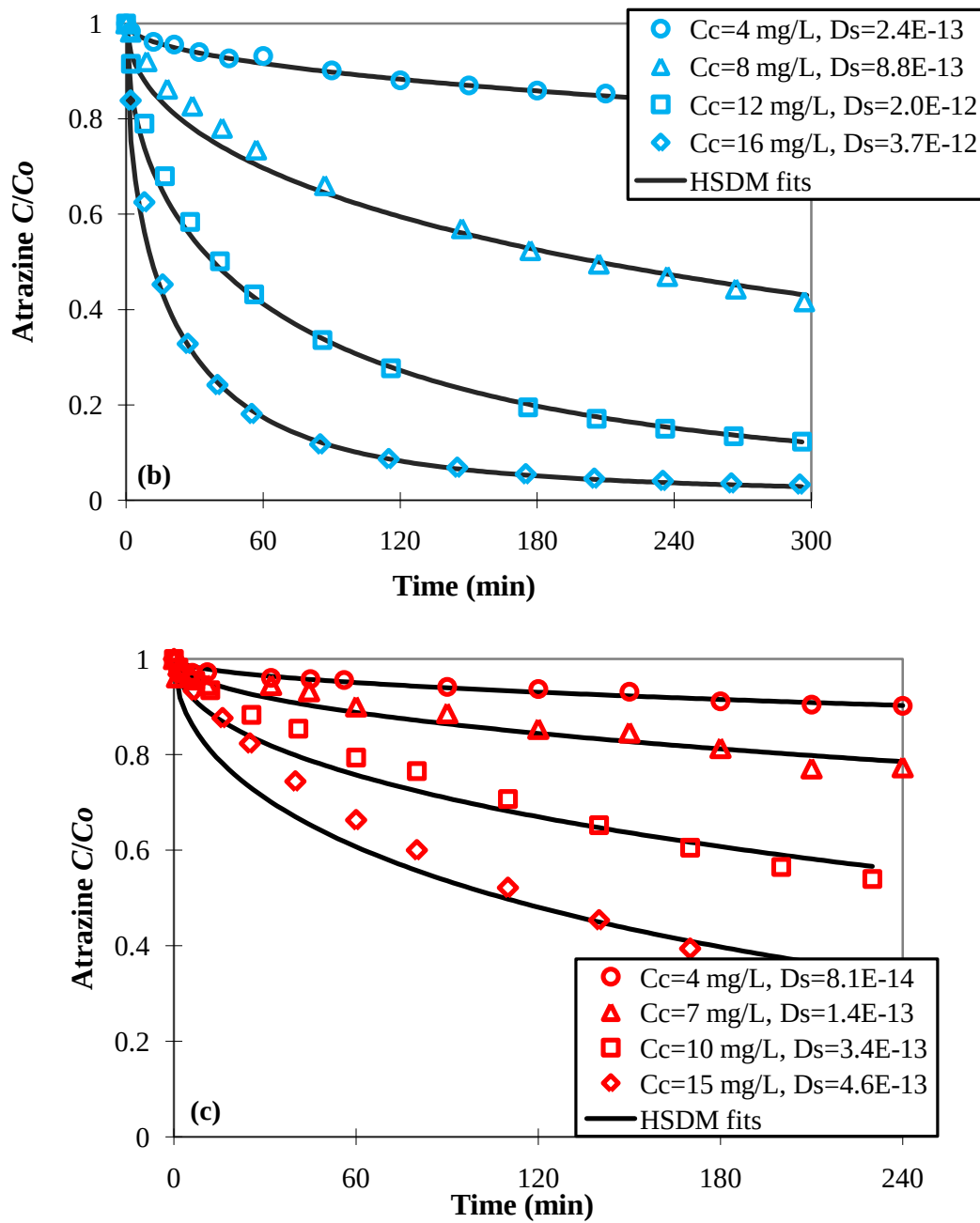


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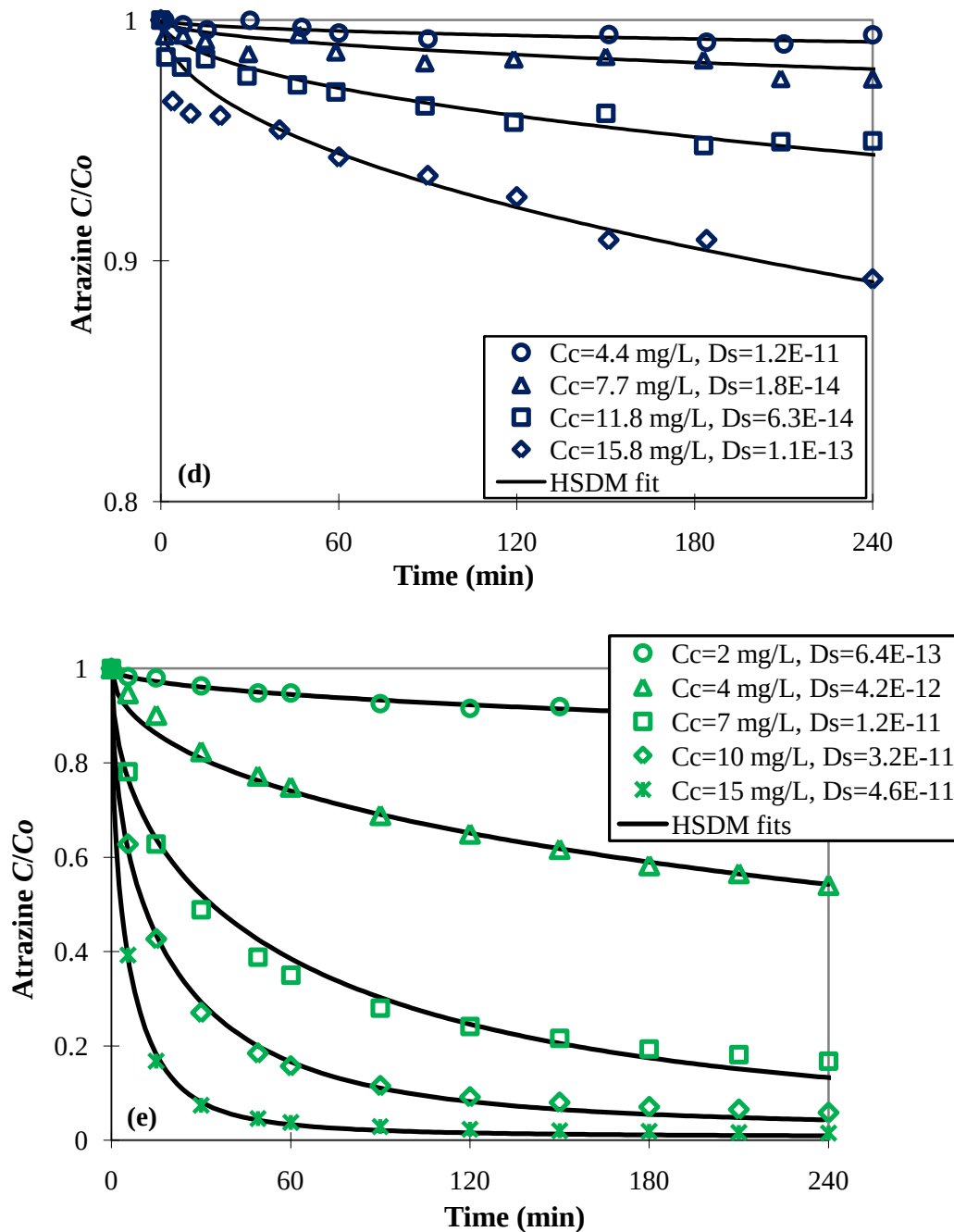


Figure 4.5 Atrazine adsorption kinetics in the presence of preloaded NOM on (a) SA UF, (b) SA Super, (c) W35, (d) W20 and (e) Pellet II (first number in legends is carbon dose in mg/L and second number is HSDM model fitted D_s in cm^2/min)

The surface diffusion coefficients $D_{s,0}$ for single-solute atrazine, which had been derived in a separate set of experiments, are listed in Table 4.2 (data not shown). D_s values obtained at various levels of NOM pre-loading normalized by the corresponding $D_{s,0}$ values are plotted against NOM loading in Figure 4.6. It is necessary to note that even

though surface diffusion is generally applied in the model fitting, the constriction and blockage of the pores by competing compound may have shifted the diffusion mechanism from surface diffusion to pore-surface diffusion. Nevertheless, the HSDM fitted D_s is a valuable parameter for diffusion rate comparison. NOM preloading resulted in logarithmic order of magnitude decreases in the rate of atrazine adsorption, consistent with previous observations (2), and this pore blockage effect varied significantly among carbons with different PSD. The pore blockage effect was most severe for W20, with less than 40 mg/g of NOM causing the surface diffusion coefficient to be reduced by almost three orders of magnitude. In contrast, a NOM loading of more than 180 mg/g on Pellet II was necessary to detect any pore blockage, and 250 mg/g to reduce the surface diffusion coefficient by about two orders of magnitude. Equation 4.1 developed by Li et al. (4) was used to quantitatively describe the pore blockage effect:

$$\frac{D_s}{D_{s,0}} = \begin{cases} 1 & q \leq q_{cr} \\ \exp[-\beta(q - q_{cr})] & q > q_{cr} \end{cases} \quad (4.1)$$

The parameter q_{cr} is the critical (threshold) carbon surface loading at which the pore blockage effect begins to occur, and is shown in Figure 4.6 as the intercept of the regression of the exponential decreasing D_s values as a function of surface loading. The parameter β describes the exponential decrease rate of D_s with increasing surface loading in excess of q_{cr} . Values for β and q_{cr} are summarized in Table 4.3.

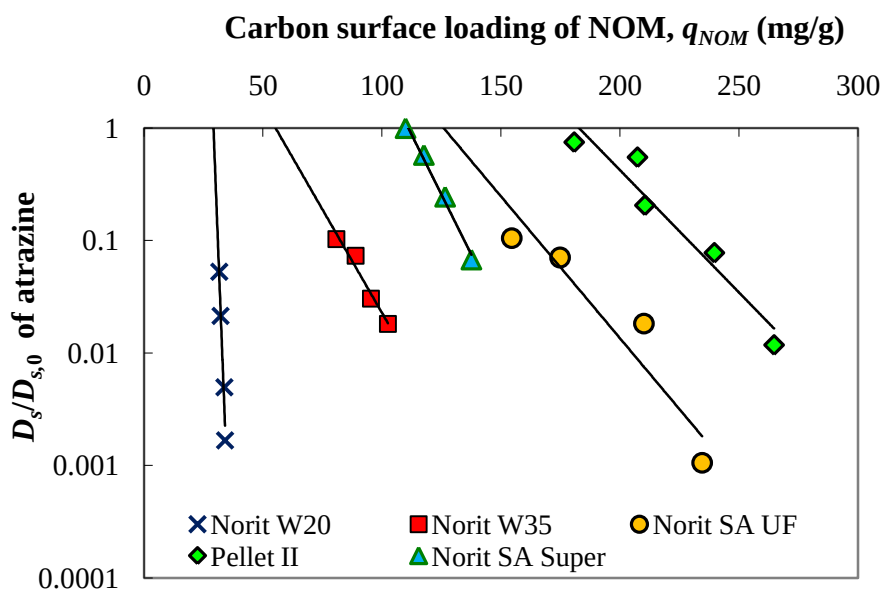


Figure 4.6 Normalized surface diffusion coefficient of atrazine versus extent of NOM preloading

Table 4.2 COMPSORB parameters for the five PACs and CWW water

	<i>SA UF</i>	<i>SA Super</i>	<i>W35</i>	<i>W20</i>	<i>Pellet II</i>
<u>Adsorption parameters for atrazine</u>					
K ($\mu\text{g}/\text{mg})(\text{L}/\mu\text{g})^{(1/n)}$	26.5	29.6	26.0	8.48	18.2
$1/n$	0.409	0.406	0.387	0.339	0.310
$D_{s,0}$ (cm^2/min)	1.70×10^{-11}	3.6×10^{-12}	4.5×10^{-12}	3.0×10^{-12}	5.40×10^{-11}
<u>Adsorption Parameters for SC fraction of NOM</u>					
$C_{0,SC}$ ($\mu\text{g}/\text{L}$)	400	800	600	600	320
K ($\mu\text{g}/\text{mg})(\text{L}/\mu\text{g})^{(1/n)}$	26.5	29.6	26.0	8.48	18.2
$1/n$	0.409	0.406	0.387	0.339	0.310
$D_{s,0}$ (cm^2/min)	1.70×10^{-11}	1.00×10^{-11}	4.57×10^{-12}	3.00×10^{-12}	5.40×10^{-11}
<u>Adsorption Parameters for PB fraction of NOM</u>					
$C_{0,PB}$ ($\mu\text{g}/\text{L}$)	7310	6980	6970	6980	6970
K ($\mu\text{g}/\text{mg})(\text{L}/\mu\text{g})^{(1/n)}$	7.83×10^{-6}	1.15×10^{-2}	1.38×10^{-5}	2.27×10^{-7}	2.38×10^{-3}
$1/n$	1.94	1.07	1.80	2.13	1.33
$D_{s,0}$ (cm^2/min)	2.11×10^{-10}	4.65×10^{-10}	2.81×10^{-11}	1.64×10^{-10}	1.61×10^{-10}
<u>Parameters for PB effects on atrazine adsorption kinetics</u>					
q_{cr} (mg/g)	122	110.0	55.3	28.5	182.7
β	0.055	0.098	0.085	0.99	0.050

The two pore-blockage regression parameters could also be compared with the same four pore size ranges of the PSD. No good correlation was found between β and the surface area for any of these pore size ranges (data not shown). In contrast, the critical NOM loading, q_{cr} , correlated well with surface area for the pore size range of 15-50 Å (Figure 4.7), where most of the NOM was found to adsorb. Thus, by increasing the volume of pores in this size range there should be less severe pore blockage. Again the cut-off sizes for the pore size range are expected to be NOM-specific, although generally speaking, lower-end mesopores are most likely responsible for NOM adsorption.

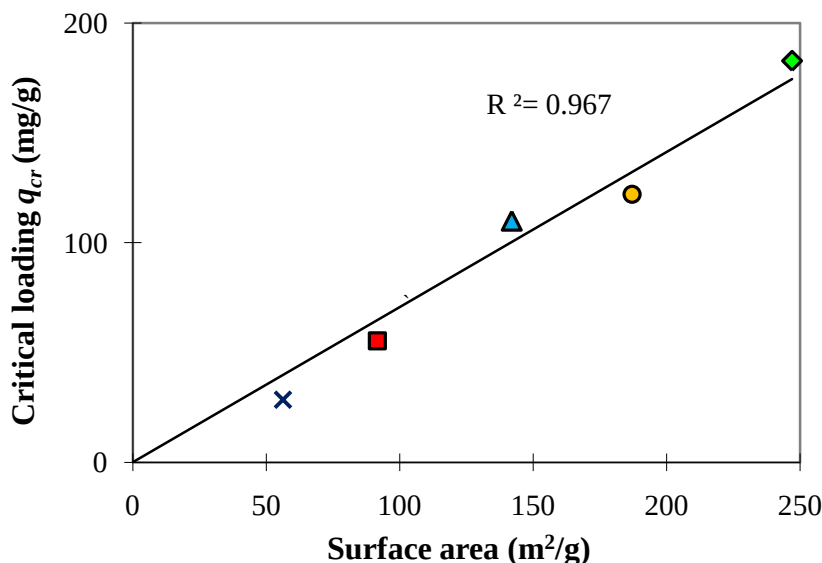


Figure 4.7 Pore blockage (PB) parameter q_{cr} as a function of surface area for pores with diameter in the range of 15-50 Å

Since the above analysis shows that the pores in the size range 15-50 Å are where majority of pore-blocking NOM adsorb, we normalized surface loading of NOM by dividing by the pore surface area in this size range, and called it the surface density of NOM in mg/m². The plot of diffusion coefficient as a function of this modified q_{cr} is shown in Figure 4.8. This approach brought the data sets for the four carbons, SA UF, Pellet II, W35 and SA Super closer together so that they could be fit reasonably well by one line, thus supporting the conclusion that it is the density of NOM molecules in this pore size range that causes the pore blockage effect.

The plot for the W20 carbon in Figure 4.8 is an interesting exception to the other four carbons. A possible reason for this difference may be that the mechanism of pore

blockage is different for this carbon. Its volume of mesopores is very small, and it is possible that the pores of this carbon are constricted or blocked by adsorption at the mouth of the pores on the outer surface of the carbon particle rather than by adsorption inside the pores.

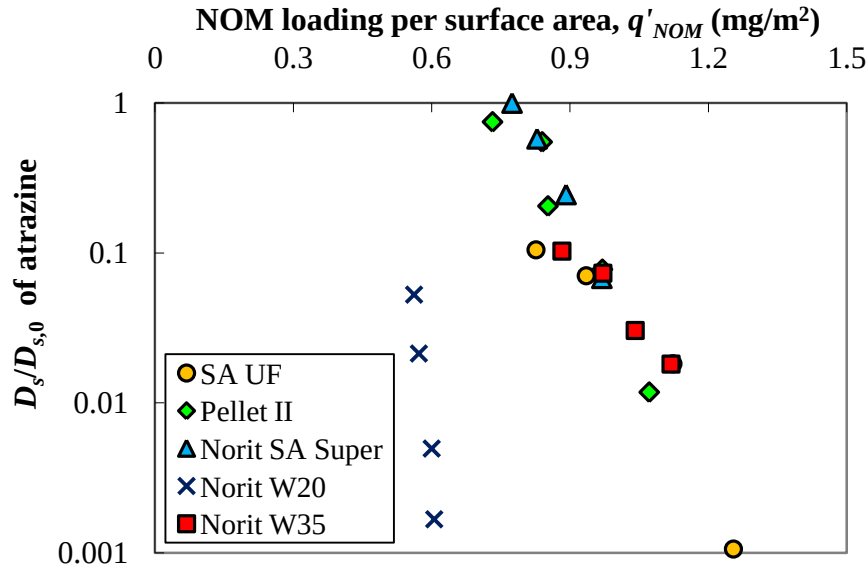


Figure 4.8 Normalized surface diffusivity of atrazine as a function of the NOM loading density in pores with diameter in the range of 15-50 Å

Flow-through PAC/filtration Model Simulation and Experimental Verification

The information that has been determined thus far can be used to predict the performance of PAC in a flow-through hybrid adsorption/membrane filtration process to illustrate the importance of carbon PSD in process efficiency. The COMPSORB mathematical model developed by Li et al. (4, 18) was used to serve the modeling purpose, and the prediction was verified by laboratory experimentation. COMPSORB is based on adsorption/filtration hybrid systems, and it takes into account both direct site competition and pore blockage effects. The model parameters that are required for COMPSORB, in addition to the isotherm and kinetic parameters (Freundlich constants K and $1/n$, diffusivity D_s and preloading parameters q_{cr} and β) determined above, were listed in Table 4.2. “SC fraction” represents the portion of NOM that directly competes with atrazine for adsorption sites, and “PB fraction” represents the portion of NOM involved in blocking pores. These fractions cannot be physically isolated, but their concentrations

and adsorption parameters can be obtained by modeling competitive adsorption experimental data for the best fit, following the same procedures described for a previous study (20). In adsorption/filtration experiments, a pulse input of pre-weighed PAC in the form of slurry was spiked into the stirred chamber of the membrane reactor at the beginning of an operating cycle, while atrazine was added to CWW water and fed continuously. The operation was stopped at 360 minutes, which in practice will correspond to the membrane backwash interval (MBI), when flow was reversed to clean up membrane before another cycle starts. Effluent samples were collected for atrazine and DOC analyses. The amount of PAC added as a pulse input at the beginning of each run was calculated based on influent flow rate, cycle duration and the desired equivalent carbon dose rate in mg/L of water treated.

Model predictions for effluent atrazine concentrations from the PAC/membrane process for carbon doses from 1 to 8 mg/L are shown in Figure 4.9. Here the influent atrazine concentration was 10 µg/L, flow rate was 10 mL/min and the MBI was 360 minutes. Doses of 1, 2, 4 and 8 mg PAC per liter of treated water are equivalent to 3.6, 7.2, 14.4 and 28.8 mg of PAC spikes at the beginning of each operating cycle. W20, which has the lowest adsorption capacity for atrazine and the largest pore blockage effect, shows the worst performance. Pellet II, the activated carbon that removes the most atrazine for a given PAC dose, does not have the highest adsorption capacity for atrazine but it has much less pore blockage than the other carbons. Thus, model simulations tell us that adsorption kinetics can be a more important factor than adsorption capacity in flow-through reactors within which equilibrium with the influent concentration of the target trace contaminant is not reached.

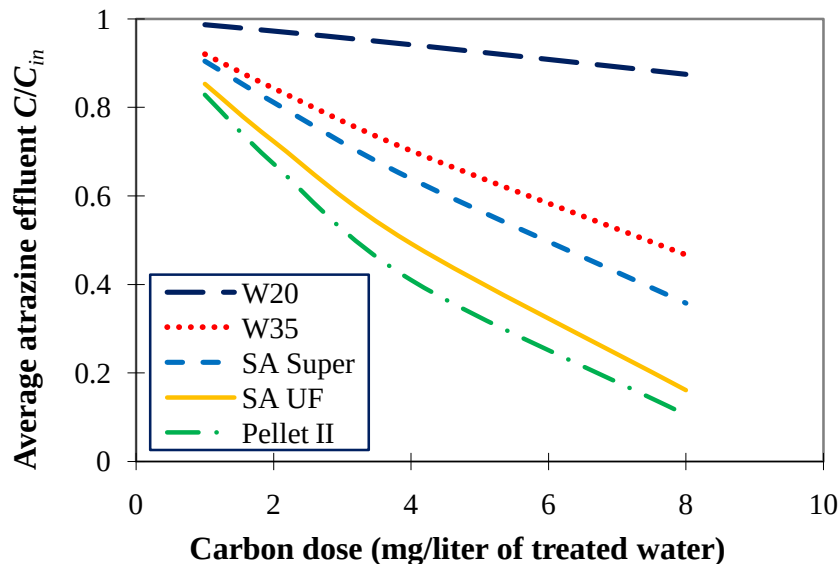


Figure 4.9 Model simulation of atrazine removal in a flow-through hybrid adsorption/membrane filtration system

To verify the model predictions, PAC/membrane process flow-through experiments were carried out for four PACs at one carbon dose of 14.4 mg, equivalent to 4 mg per liter of treated water for the above system. Norit SA Super was not included in this matrix because preliminary experiments (not shown), as well as the above model simulations, have shown it to perform similarly to Norit SA UF carbon.

Experimental results (data points) and model predictions (lines) for each of the four carbons are shown in Figure 4.10. The COMPSORB model was able to predict effluent atrazine concentration profiles reasonably well, although the quality of correspondence between data and model predictions varied among carbons. However, as noted by Ding et al. (20) in a previous study, the COMPSORB model gives a much better prediction compared to those by models that do not take into account both pore blockage and direct competition effects of NOM. However, the effect of pore blockage is not predicted as well as we would like for SA UF, Pellet II and W35. For example, with Pellet II, the predicted curve shows a sharp upturn at about 130 minutes of run time, about at the point that the q_{cr} loading with NOM was reached, whereas the data show a much more gradual increase in concentration. A possible explanation for this effect is that modeling the pore blockage effect using Equation (4.1) is not completely accurate. According to that equation, the PB effect kicks in at a threshold loading; however, it may also follow a

gradual curve instead of this sharp start. Another factor is that the q_{cr} and β values were determined in batch experiments using carbon that had been preloaded with NOM for 4 days, whereas in the bench-scale experiment the NOM adsorbed at the same time as the atrazine over a period of 6 hours. This requires further study.

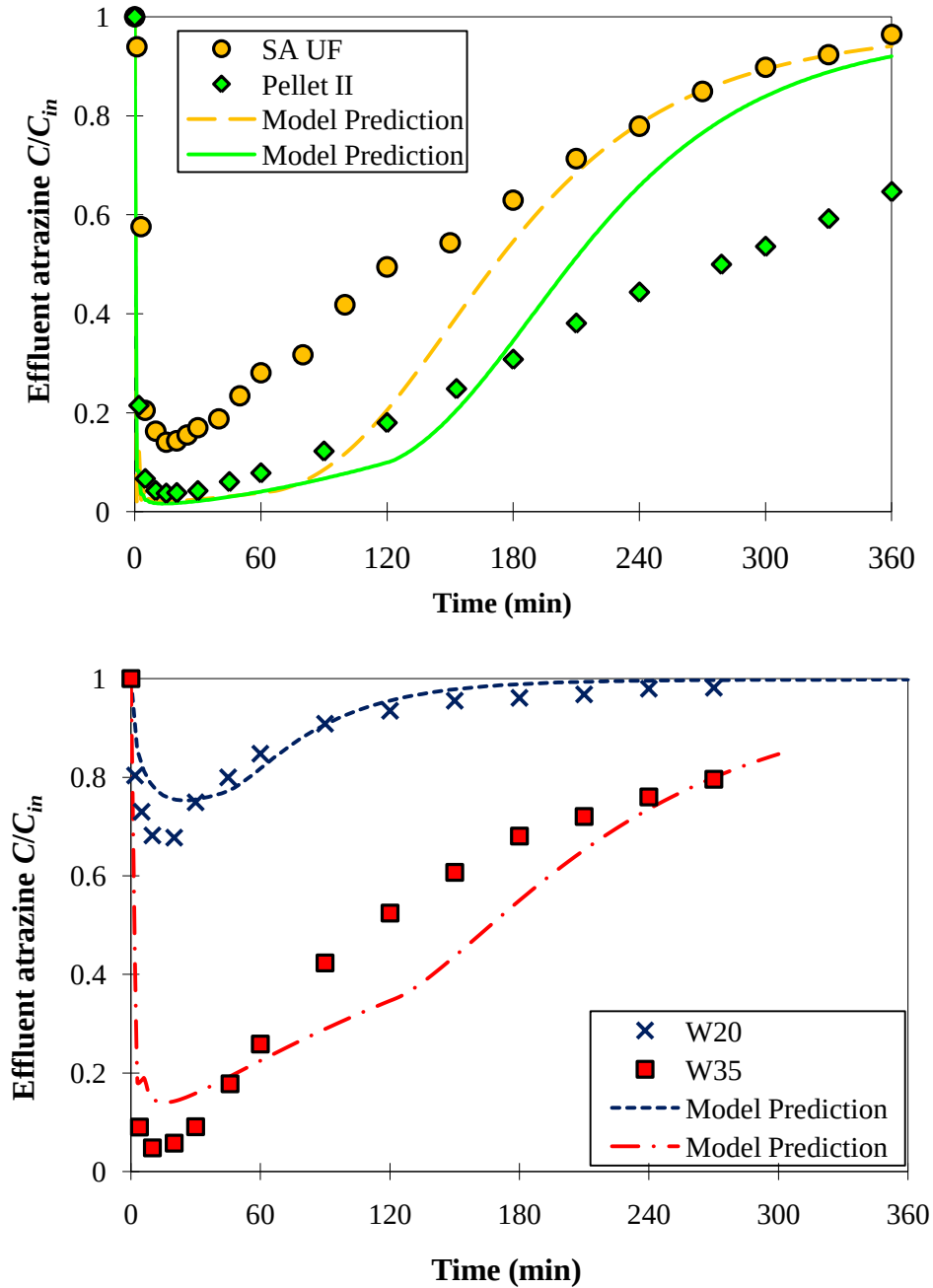


Figure 4.10 Experimental results and model predictions of atrazine removal in CWW water by the flow-through PAC/membrane system
(a) Norit SA UF and Pellet II; (b) Norit W20 and Norit W35

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CHAPTER 5

SITE COVERAGE EFFECT OF COMPETING COMPOUNDS ON TRACE ORGANIC CONTAMINANT SORPTION KINETICS ON ACTIVATED CARBON*

INTRODUCTION

The competition of background organic matter in water is known to hinder the removal of trace organic contaminants by activated carbon. Two major mechanisms of competition are direct competition for the trace compound's adsorption sites by similar-sized molecules (1-3), which causes a reduction in capacity for the target compound, and pore blockage by larger molecular weight organic matter (4-6), which causes a reduction in the rate of adsorption. Compounds that are responsible for the reduction in capacity were named strongly-competing (SC) compounds, and those that reduce the magnitude of the internal diffusion coefficient of the target compound were termed pore blocking (PB) compounds (7).

Another important kinetic mechanism was identified in recent research by To et al. (8, 9) who showed that adsorption of SC compounds caused an increase in the diffusion coefficient of atrazine during both adsorption and desorption (Figure 5.1). This increase was attributed to the reduced diffusion resistance on the pore surface as more and more of atrazine's preferred surface sites were occupied by SC matter, and thus atrazine diffusion could take place with less interaction with the pore surface. These authors developed a kinetic model that incorporated both the increase in diffusion coefficient caused by the SC effect of NOM and the decrease in diffusion coefficient caused by the PB effect of NOM.

* Literature data from references 15, 20 and 21 were used in this study as indicated in this chapter. Some kinetic data from these references were re-analyzed to show the enhanced diffusivity. .

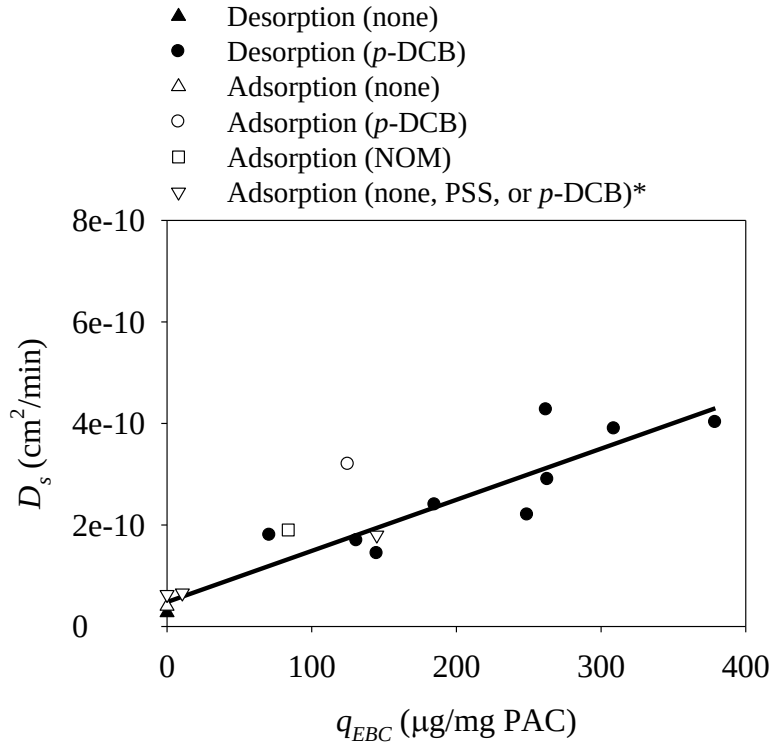


Figure 5.1 Surface diffusion coefficient of atrazine desorption and adsorption versus adsorbed concentration of the SC compound, with the source of SC competition shown in parenthesis (Reproduction of figure 4 in reference 8)

The objective of this study was to determine whether the increase of trace compound's diffusion coefficient due to SC compounds was a general phenomenon that occurs with adsorbents and competing compounds other than those tested by To et al., and to compare the ability of the proposed kinetic model to describe atrazine adsorption/desorption kinetics in the presence of competing compounds on PACs of difference source. Further, it was of interest to determine whether the diffusion coefficient is impacted to a greater extent by the pore blocking effect than by the effect of SC compound loading.

MODEL DESCRIPTION

According to the studies by To et al. (8), the surface diffusion coefficient of the trace compound enhanced by increasing adsorbed amount of the SC compound, $D_{s,SC}$, follows the relationship:

$$D_{s,SC} = D_{s,0} + A \times q_{EBC} \quad (5.1)$$

where $D_{s,0}$ is the atrazine diffusion coefficient in the absence of competition such as in organic-free water (OFW), q_{EBC} is the loading of the SC compound quantified as an equivalent background compound (EBC) (10, 11), and A is the correlation coefficient for the linear fit. Because the value of $D_{s,0}$ varies for different PACs, we modified Equation 5.1 by normalizing D_s over $D_{s,0}$:

$$\frac{D_{s,SC}}{D_{s,0}} = 1 + A' \times q_{EBC} \quad (5.2)$$

where A' is the slope, and $A' = \frac{A}{D_{s,0}}$

The SC factor is then defined as

$$f_{SC} = \frac{D_{s,SC}}{D_{s,0}} \quad (5.3)$$

The diffusion coefficients are derived by fitting each of the kinetic test data sets with the Homogeneous Surface Diffusion Model (HSDM) (12). Further details on the HSDM application to this problem can be found in references (8, 9).

Surface loading of the SC compound (q_{EBC}) is determined by using the EBC-IAST approach (11). This method is based on the representation of the SC NOM fraction as a single Equivalent Background Compound (EBC). As a further simplification, Ding et al. (13, 14) assumed similar adsorbability of the target compound and the EBC, and thus assigned the Freundlich isotherm equilibrium parameters of atrazine to the EBC. Based on these assumptions, the Ideal Adsorbed Solution Theory (IAST) (11) for bi-solute competitive adsorption can be used to determine the expected atrazine and EBC concentrations at equilibrium.

When SC and PB compounds co-exist, or when a single competing compound is able to exert both SC and PB competitive effects, the resulting surface diffusion coefficient of a trace contaminant is influenced by both effects. The procedure that allows separation of SC and PB effects (8) is summarized below.

1) $D_{s,SC}$.

Atrazine adsorption kinetic tests when only the SC effect is present are first conducted.

The SC-only scenario was achieved in simultaneous adsorption of the trace compound with the competing compounds. If there are PB components in the competing compound, especially with mixture like NOM, they tend to be large in size and have slower intra-particle surface diffusivity than the smaller-sized atrazine (15), so in a simultaneous spike of atrazine and competing compounds, the competing compounds were thought not able to cause strong PB effect as what is happening in a preloading test. Our kinetic data on simultaneous adsorption of atrazine and PSS-1.8k (shown later in Figure 5.2 (c)) verified this.

The SC-only scenario was also assumed in preloading experiments with competing compounds that proved to have minimum PB effects. These compounds include methyl orange (MO) and xylenol orange (XO) for atrazine adsorption on WPH carbon (15).

The experiment was designed so that different levels of SC loading, q_{EBC} , are achieved, and HSDM fitting provides the best fit D_s for each of the data sets. Then, $D_{s,\text{SC}}$ versus q_{EBC} was plotted to find the SC kinetic parameter, A' .

2) $D_{s,\text{PB}}$.

Atrazine adsorption kinetic tests on PACs preloaded with competing compounds are then conducted. The resulting diffusion coefficients are under influence of both SC and PB effects.

To separate SC effect from the total effect, q_{EBC} for each of these kinetic sets is calculated based on isotherm information assuming equilibrium conditions; given A' from step 1, the SC factor for each test can be computed using Equation 5.2 and 5.3. Next, the pore-blocking contribution ($D_{s,\text{PB}}$) can be determined by factoring out the SC factor using Equation 5.4.

$$D_{s,\text{PB}} = \frac{D_s}{f_{\text{SC}}} \quad (5.4)$$

The PB kinetic effect can also be related to the loading of the PB component, described in the equation below, developed by Li et al. (17):

$$\frac{D_s}{D_{s,0}} = \begin{cases} 1 & q_{\text{PB}} \leq q_{\text{cr}} \\ \exp[-\beta(q_{\text{PB}} - q_{\text{cr}})] & q_{\text{PB}} > q_{\text{cr}} \end{cases} \quad (5.5)$$

Using $D_{s,PB}$ in place of D_s equation (5.5) can be used to determine the PB kinetic parameters q_{cr} and β . For tests with natural organic matter (NOM), it is assumed that the total concentration of adsorbed NOM is a close approximation to the adsorbed concentration of the PB fraction, since SC NOM makes up a very small percentage of the total NOM mass (13).

RESULTS AND DISCUSSION

Overview of the Literature Data

Atrazine adsorption data in the absence/presence of competing compounds were collected previously by researchers from the Snoeyink research group. Permission was obtained to use their data to achieve research objectives in this study, and we acknowledge their contribution for the raw data. The materials and methods of the experiments that they performed are briefly summarized below and details can be found in their individual doctoral dissertations (15, 20, and 21).

The adsorption data were for 3 commercial PACs: SA UF (20, 21), W35 (21) and WPH (15, 20). Using the same PSD analysis technique that was presented in Chapter 4, the PSD properties for these 3 PACs were obtained and are summarized in Table 5.1.

Table 5.1 Pore volume and surface area properties of W35, SAUF and WPH

	Pore volume (cm³/g)				Surface Area (m²/g)			
Pore Width (Å)	< 15	15-50	50-100	100-300	< 15	15-50	50-100	100-300
W35	0.238	0.126	0.068	0.050	585	83.3	19.6	6.52
SA UF	0.284	0.241	0.150	0.219	619	171	42.1	25.9
WPH	0.205	0.111	0.014	0.015	578	41.4	53.2	17.4

The experimental conditions are summarized in Table 5.2. To be noted is the NOM used here was Suwannee Rive NOM (SR NOM).

Table 5.2 Experimental conditions of atrazine adsorption kinetics on WPH, SA UF and W35

PAC	$C_{0,\text{atrazine}}$ ($\mu\text{g/L}$)	Competing Compound	$C_{0,\text{competing}}$ (mg/L)	Simultaneous or <u>P</u> reload	C_c (mg/L)	Reference
WPH	103	--	--	--	4	20
	100	<i>p</i> -DCB	2	S	2, 14, 25	20
	100	<i>p</i> -DCB	2	P	2, 5, 15	20
	98	PSS-1.8k	10	S	3, 5	20
	97	PSS-1.8k	10	P	2, 4, 8, 20	20
	59	--	--	--	4	15
	61	MO	2	P	5, 12	15
	60	XO	0.22, 0.42, 2	P	4	15
SA UF	103	--	--	--	4	20
	100	<i>p</i> -DCB	2	S	5	20
	100	PSS-1.8k	10	S	2	20
	102	--	--	--	10	21
	85	<i>p</i> -DCB	2.0	P	4	21
	104	<i>p</i> -DCB	2.0	P	6	21
	100	NOM	3.8	P	4	21
	711*	--	--	--	6	21
	100*	<i>p</i> -DCB	0.5-3.0, with interval of 0.5	--	5	21
	50*, 150*	<i>p</i> -DCB	2.0	--	5	21
W35	62	--	--	--		21
	10, 60	NOM	3.9	S		21
	60	NOM	8.0	S		21
	100	NOM	4.0	S		21
	200	NOM	6.1	S		21

* Desorption tests

Determining SC Kinetic Parameters

Atrazine adsorption kinetics on WPH carbon is shown in Figure 5.2 (a) - (c). The raw kinetic data are from Li's dissertation (20) but were re-analyzed with the HSDM model in this study to fit for surface diffusion coefficients, and to determine the SC loadings. Plot (a) is for simultaneous adsorption of atrazine with *p*-DCB, the SC compound, with carbon doses of 2, 14 and 25 mg/L, plot (b) is for atrazine adsorption in the presence of preloaded *p*-DCB with carbon doses of 2, 5 and 15 mg/L, and plot (c) is for atrazine with simultaneous adsorption of PSS-1.8k with carbon doses of 3 and 5 mg/L. These experimental conditions have already been summarized in Table 5.2, and all represent scenarios in which only the SC effect is important. Also included in Figure 5.2 (a) is one data set for atrazine adsorption in the absence of competition for determination of $D_{s,0}$.

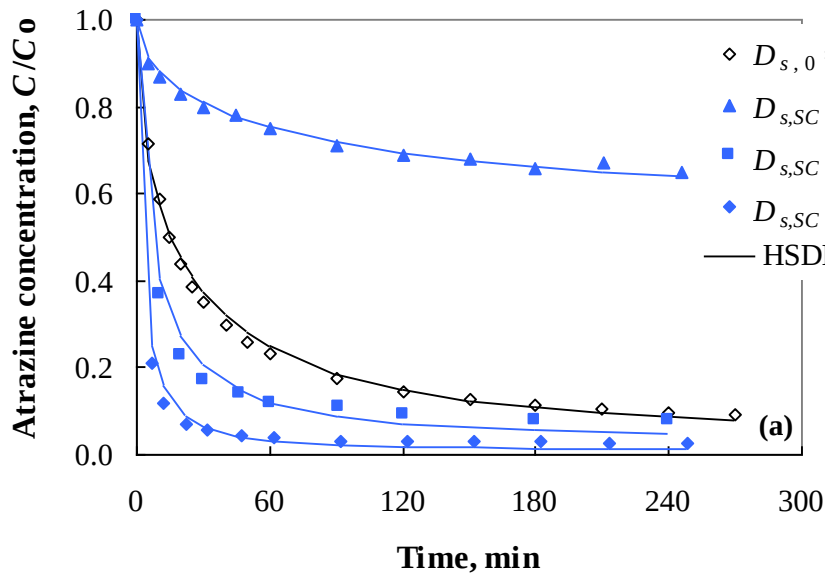


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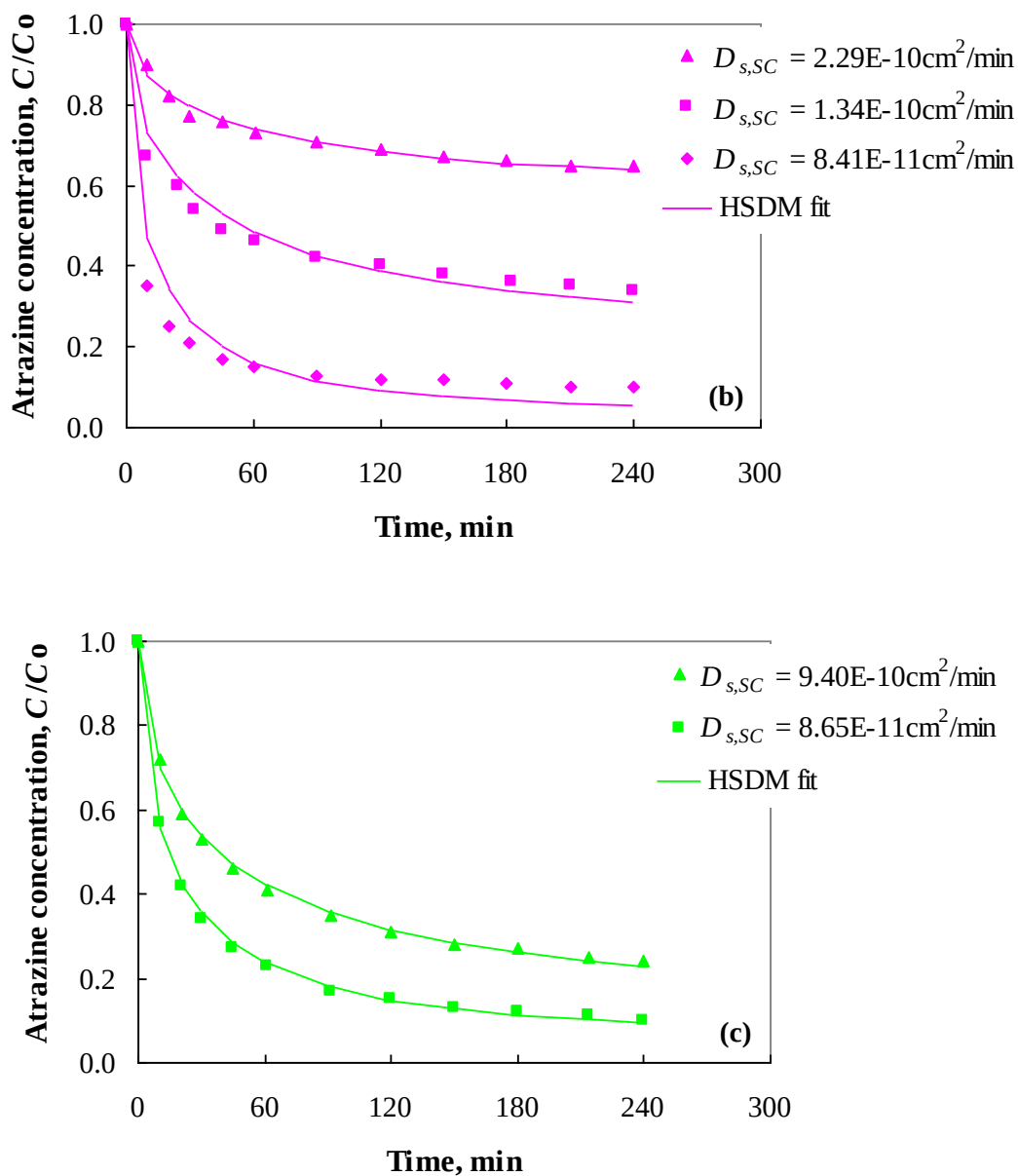


Figure 5.2 Kinetics of atrazine adsorption on WPH carbon in the presence of various competing compounds with corresponding HSDM fits (raw data was from chapter 4 of reference 20 and HSDM fitting was performed in this study)
(a) simultaneous adsorption with p -DCB, $C_{0,\text{atrazine}} = 100 \text{ mg/L}$, $C_{0,p\text{-DCB}} = 2 \text{ mg/L}$, $C_c = 2, 14$ and 25 mg/L ;
(b) adsorption in the presence of pre-sorbed p -DCB, $C_{0,\text{atrazine}} = 100 \text{ mg/L}$, $C_{0,p\text{-DCB}} = 2 \text{ mg/L}$, $C_c = 2, 5$ and 15 mg/L ;
(c) simultaneous adsorption with PSS-1.8k, $C_{0,\text{atrazine}} = 100 \text{ mg/L}$, $C_{0,\text{PSS}} = 10 \text{ mg/L}$, $C_c = 3$ and 5 mg/L .

The experimentally fitted diffusion coefficients are normalized with respect to $D_{s,0}$ and plotted in Figure 5.3 versus the loading of the SC compound expressed as EBC

concentration on PAC, following the method developed earlier (13). Also shown are adsorption kinetic data for atrazine in the presence of pre-adsorbed dyes, MO and XO, for which the D_s fitting had been done by Tang in his dissertation study (15). The SC loadings for the MO and XO preloads were also determined following the same EBC approach. Tang et al. (15) has demonstrated that these two competing compounds had negligible PB effect on atrazine adsorption on WPH carbon, therefore these tests agreed with SC-only scenario.

The EBC fit results are shown in Figure 5.3 (a) and (b). The dash line represents the fitted $C_{0,EBC}$ that gave the best fit for each data set. The fitted concentrations, $C_{0,EBC}$, were listed in the legend. There is slight difference in the K and $1/n$ values between the two sets of experiments. However, the two non-competitive data were very close in the isotherms; however, the log-log scale fit introduced such variation in the values for the Freundlich K .

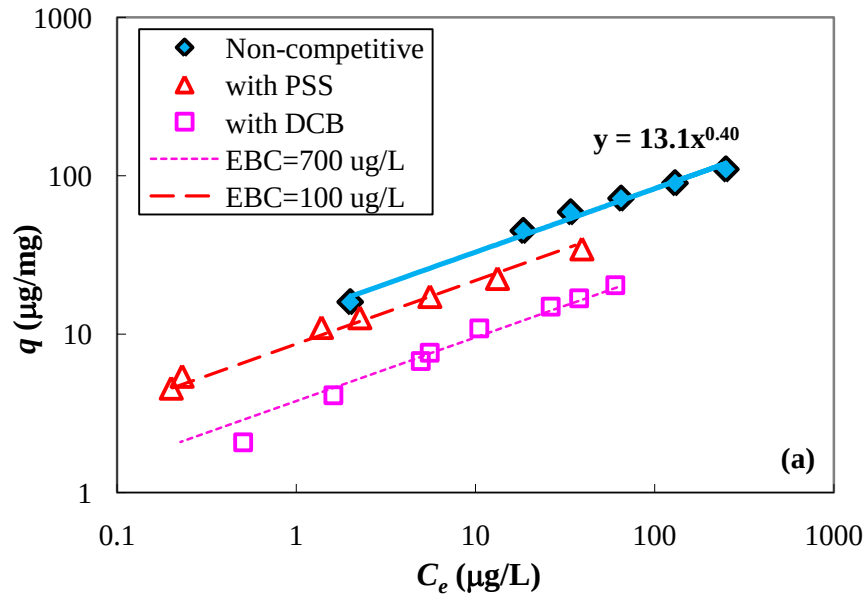


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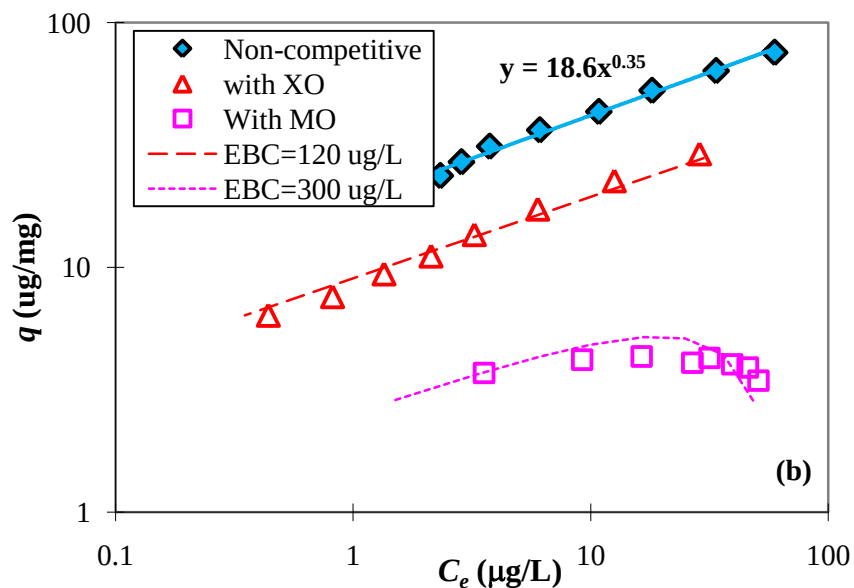


Figure 5.3 IAST-EBC analyses for atrazine adsorption isotherms on WPH in the presence of (a) *p*-DCB and PSS-1.8k; and (b) MO and XO (raw data in plot (a) were from chapter 4 of reference 20 and raw data in plot (b) were from chapter 3 of reference 15, with the EBC fitting performed in this study)

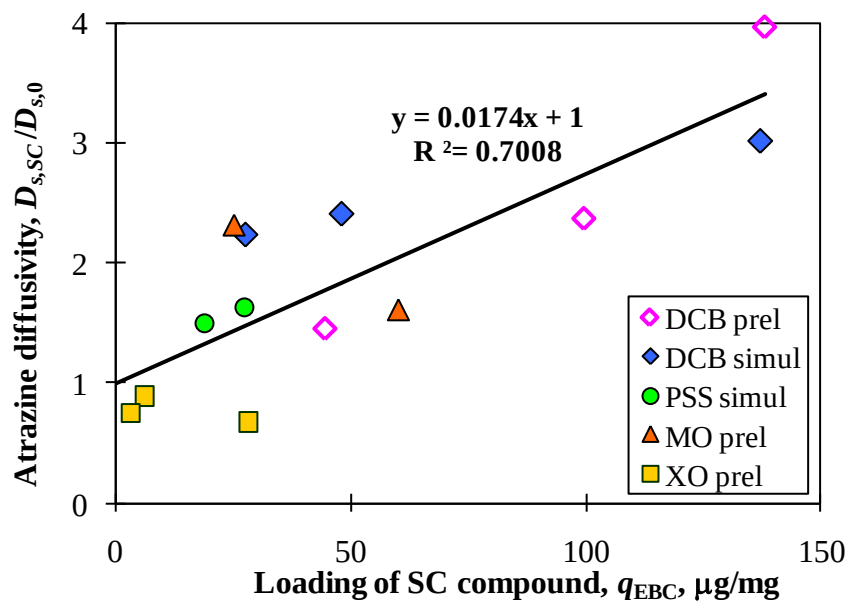


Figure 5.4 Dependency of surface diffusion coefficient of atrazine adsorption on WPH carbon on adsorbed concentration of various SC compounds

Figure 5.4 confirmed the general trend of diffusion rate enhancement with increasing SC loading, as what has been discovered with another PAC (SA UF) by To et al. (8). *p*-DCB

shows the greatest effect to increase diffusivity of atrazine, which is reflected in its highest EBC loadings. The strong competitive effect of *p*-DCB is likely due to its small size and high adsorptive affinity to PACs that it is able to compete with atrazine for adsorption sites. PSS-1.8k shows little increase in atrazine diffusivity because the size exclusion effect that PSS molecules primarily adsorb in sites that atrazine does not interact strongly with. Preloading of XO actually resulted in the normalized diffusion coefficient of atrazine to be a little lower than 1, indicating that PB effect, although minimal, starts to interfere. Despite of the varying competing capacity, a linear trend line can be fitted through the data points of all competing compounds. Besides, the preloaded *p*-DCB data did not show lower surface diffusion coefficients than simultaneous *p*-DCB data, which again confirmed that *p*-DCB has a minimal PB effect.

Enhanced diffusion coefficient data for W35 carbon, as derived by To (21), were also plotted as a function of the SC loading (Figure 5.5). Data WPH carbon and for SA UF carbon that were derived previously are also shown in the same Figure. All data points show positive relationship between the surface diffusion coefficient of atrazine and the SC loading, but what is really an important finding is that a single trend line can be applied to data from all three PACs. The normalized surface diffusion coefficient increases linearly with loading of the SC compound as:

$$\frac{D_{s, SC}}{D_{s,0}} = 1 + 0.0208q_{EBC}$$

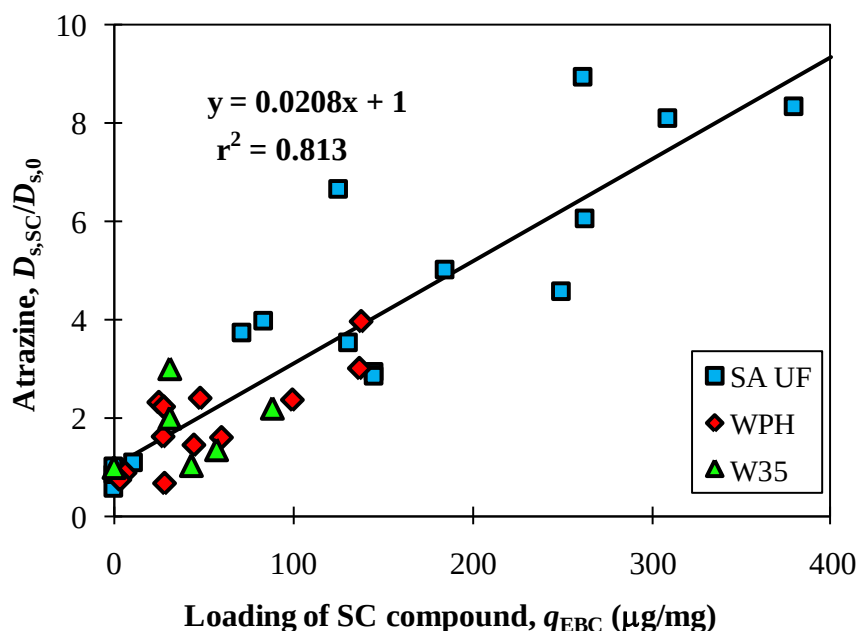


Figure 5.5 Dependency of surface diffusion coefficient of atrazine adsorption/desorption on SC compound loading on PAC (data for SA UF and W35 were re-produced from Chapter 3 and 5 in reference 21)

Despite the diverse properties of PACs as well as those of competing compounds, choosing to quantify the SC as an EBC enabled us to unify data from various PACs and competing compounds into a single plot. This EBC concept does not involve the actual adsorption capacity of a competing compound; instead, it was based on adsorption capacity reduction of a target compound, and competing compounds that cause the same level of capacity loss will be treated as the same EBC with same concentration. In other words, EBC quantifies the portion of competing molecules that occupies the adsorption sites which would be originally taken by atrazine; with those sites being covered, atrazine molecules have less drag force while diffusing into inner pores. On the other hand, competing molecules that adsorb in sites of low affinity to atrazine do not compete directly to reduce adsorption capacity and do not have much impact on atrazine diffusivity. It is important to keep in mind that an EBC loading could be very different from the actual loading of the competing compound, especially when the competing compound is a mixture like NOM, of which only small NOM molecules competes directly for sites while molecules of all sizes adsorb on PAC.

SC compounds resulted in higher degrees of enhancement of the atrazine diffusion

coefficient on SA UF than on WPH or W35, as evidenced by SA UF data points located in the upper left region of the plot. In other words, SC compounds achieved much higher loading on SA UF than on the other two PACs. The pore size distribution of SA UF shows that it has greatest amount of surface area and volume in the micropore and low-end mesopore range, where atrazine adsorption occurs. Consequently competition between atrazine and the SC compound occurs on the surface in this pore size range. These surfaces provide high potential for SC loading, resulting in greater enhancement of the diffusion coefficient

This study confirmed the enhancement of the atrazine diffusion coefficient by surface coverage of competing compounds on two PACs in addition to the SA UF carbon that is used by To (8) in the development of the theory. Further, her proposed equation nicely described the linear correlation between surface diffusivity and loading of the SC compound. More importantly, the work shows that the EBC representation is an appropriate approach to quantify the effect of adsorption site coverage by competing compounds on the target compound diffusion coefficient. Given the correlation determined in this study, the effect of competition on surface diffusivity of a target compound can now be estimated by calculating the loading of EBC for that specific initial condition from isotherm data.

Calculating loadings using isotherm information presumes equilibrium condition for the competing compounds. However this may not always be true, especially in simultaneous adsorption, where the EBC loading increases with time to reach final equilibrium. Using a varying EBC loading and consequently a varying diffusion coefficient will make modeling too complicated and the current approach of a constant equilibrium loading works effectively in our study.

Determining PB Kinetic Parameters

Most competing compounds have dual effects on atrazine adsorption kinetics, including PSS-1.8k (Figure 5.6) and SR NOM. The competing compounds were pre-sorbed before atrazine started to diffuse in, so they exerted both SC and PB effects on atrazine diffusivity, D_s . The experimentally-determined diffusion coefficients were adjusted to represent the contribution due to PB NOM alone by factoring out the SC factor (Equation

5.4). Equation 5.5 is confirmed to be able to describe $D_{s,PB}$ as a function of PB loading (plots not shown).

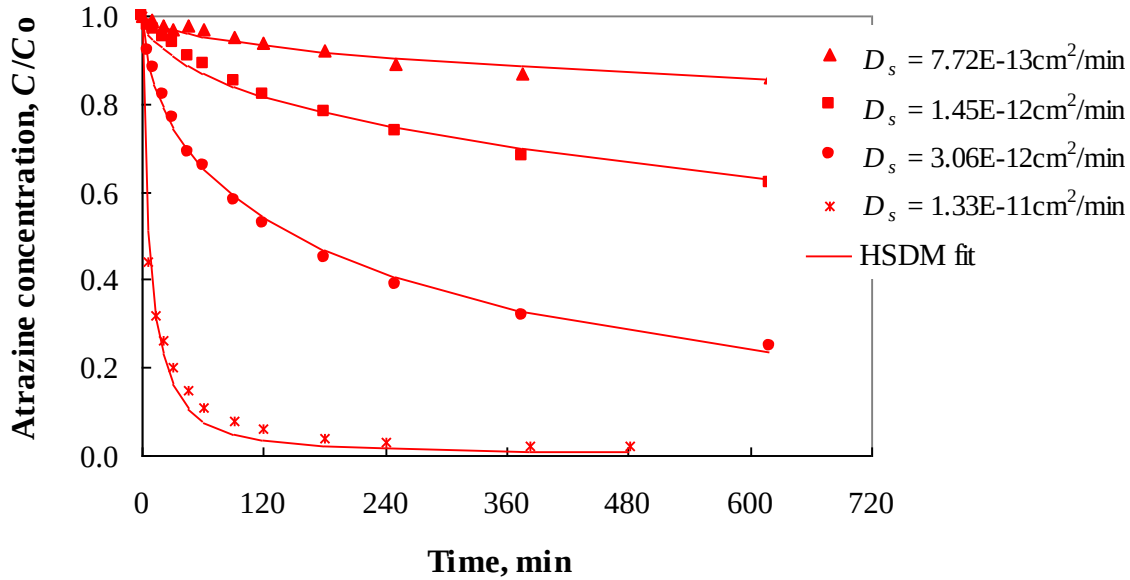


Figure 5.6 Kinetics of atrazine adsorption in the presence of preloaded PSS-1.8k on WPH carbon, with corresponding HSDM fits (raw data were from reference 20 and HSDM fitting was performed in this study)

Competing compounds have a counter-effect on the adsorption kinetics of a target compound; the relative strength of the SC or PB effect is implied by the magnitude of f_{PB} and f_{SC} listed in Table 5.3. An f_{PB} that is greater than f_{SC} signals that the PB effect of NOM has a stronger impact than the SC effect on overall kinetics, and the diffusion rate of atrazine is thus smaller than the original. Shown in Table 5.3, values for f_{SC} are generally below 5 for the conditions tests, while those for f_{PB} can be very different, depending on the actually loading of the competing compound. The ratio of f_{PB} to f_{SC} ranges from a little over 1 to about 80, indicating the observed competitive effects on atrazine diffusivity is the reduction in D_s but the extent is highly dependent on the carbon dose and competing compound concentration. Because the kinetic effect of PB fraction increased more quickly than the kinetic effect of SC fraction as adsorption of the competing compound increased, the SC and PB kinetic factors are roughly in the same order of magnitude at high carbon doses, while the PB factor becomes almost two orders of magnitude larger than the SC factor at low carbon doses. Dominance of PB effect

could be due to the preloading of the competing compounds before atrazine got in contact with PAC. Large competing molecules usually have a slow diffusion rate so if simultaneous adsorption of atrazine was taking place, the same pore blocking effect would not have been observed.

Table 5.3 SC and PB effects caused by preloaded competing compounds (PSS-1.8k for WPH, and SR NOM for W35 and SA UF) on the adsorption kinetic of atrazine on 3 PACs (Data on WPH were based on raw adsorption data from reference 20 and were analyzed to separate the SC and PB effects; data on W35 were from tabulation of data in Chapter 5 of reference 21 ; and data on SA UF were taken from Table 4.2 in reference 21.)

PAC	C_c mg/L	$C_{0,Atra}$ μg/L	$C_{0,competing}$ mg C/L	q_{EBC} μg/mg	q_{PB} mg C/g	D_s cm ² /min	f_{SC} (-)	f_{PB} (-)
WPH	1.9	97	5	35	16	7.7E-13	1.7	141
	4	97	5	22	10	1.5E-12	1.5	63
	7.9	97	5	12	5.7	3.1E-12	1.3	26
	20	97	5	5.0	2.3	1.3E-11	1.1	5.2
W35	2	60	4.0	133	66	3.8E-12	3.8	39
	4	60	4.0	47	56	1.2E-11	2.0	7
	8	60	4.0	20	51	2.7E-11	1.4	2.3
	12.2	60	4.0	13	47	3.7E-11	1.3	1.6
SA UF	2	100	4.1	168	112	2.9E-12	4.5	75
	4	100	4.1	101	105	8.7E-12	3.1	17
	8	100	4.1	48	96	2.4E-11	2.0	4
	9.9	100	4.1	38	93	3.0E-11	1.8	2.8

Thus we see that the relative effects of SC and PB can range from SC effect as the primary effect, such as with *p*-DCB and MO, to the PB effect dominant when the adsorbate is very large.

This study reemphasizes that while the PB effect on kinetics can be significant, the side-by-side adsorption of SC NOM plays its part to offset the decrease in kinetics. The SC effect of increasing kinetics may be a positive phenomenon in trace contaminant adsorption, but direct surface competition has two negative effects of reducing capacity and hastening the release of trace contaminants. Meanwhile, pore blockage has the

beneficial effect of slowing down trace contaminant desorption.

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CHAPTER 6

COMPETITIVE EFFECTS OF BACKGROUND ORGANIC MATTER ON ATRAZINE ADSORPTION ON ACTIVATED CARBON-EFFECTS OF MOLECULAR WEIGHT AND STRUCTURE*

INTRODUCTION

Activated carbon (AC) is an effective material for removing a wide range of organic micropollutants from water. Nonetheless, the efficacy of micropollutant removal by AC decreases substantially in the presence of natural organic matter (NOM) (1-6). NOM, with its heterogeneous nature of organic compounds of molecular weight varying from a few hundred to over 10,000 (2), exerts different competitive effects on target compound adsorption. Carter *et al.* (1) proposed two mechanisms by which NOM could inhibit micropollutant adsorption: direct site competition (SC) and pore blockage (PB). Direct competition for available adsorption sites, and the resulting adsorption capacity reduction, is mainly caused by NOM with molecular weight and size similar to those of the micropollutant (4, 7). In contrast, pore blockage is mainly caused by larger molecules, which adsorb in larger pores and thereby constrict the entrance to smaller pores, and result in slower micropollutant diffusion. Li *et al.* (5) and Ding *et al.* (6) examined this PB effect by studying atrazine adsorption with NOM-preloaded adsorbents and found atrazine D_s reduction with increasing NOM surface loading. In addition to these two effects, a third effect has been discovered recently, by which adsorption of site competing compounds enhanced surface diffusion coefficient of the target compound atrazine.

Despite previous research efforts, the relationship between NOM constituent molecular weight and its competitive effects, particularly pore constriction, has not been fully characterized. This is partially due to the heterogeneous nature of NOM, which makes quantifying the competitive effects and predicting the efficiency of AC under various water qualities difficult. One approach that will lead to an improved understanding of the competitive effects involves the use of synthetic compounds as surrogate for NOM (7-9). An important criterion for selection of surrogates is that the molecular weight of the compounds must resemble the NOM constituents that are commonly found in natural

* This chapter used raw data from chapter 3 of G. Tang's PhD dissertation (12). The kinetic data were re-analyzed in this study to separate the site-covering and pore-blockage effects.

water sources. Li et al. (9) found that for NOM in a groundwater from central Illinois, USA, the number-averaged (MW_n) and weight-averaged (MW_w) molecular weights were 519 and 767 Da, respectively. In another study (5), these authors found evidence that compounds with molecular weights between 200 and 700 Da comprised the NOM fraction mainly responsible for pore constriction affecting atrazine (216 Da) adsorption kinetics. Similarly, Newcombe et al. (4, 10) evaluated the competitive effect of NOM fractions and found that their smallest fraction, with MW_n and MW_w of 670 and 949 Da, respectively, was the most detrimental to 2-methylisoborneol (168 Da) adsorption capacity and removal rates.

The objective of this study was to advance our understanding of the effect of background compound molecular size and structure on the mechanisms of competitive adsorption by NOM. Methyl Orange, Brilliant Yellow, Congo Red, Xylenol Orange, and Evans Blue, with molecular weights in the range of 300-900 Da, were chosen as surrogate compounds for pore-constricting NOM in this study. Their effects on the adsorption of atrazine, an herbicide of environmental concern, onto two activated carbons with different PSD were examined.

RESULTS AND DISCUSSION

Overview of the Literature Data

Data on atrazine adsorption isotherms and kinetics in the absence/presence of NOM surrogates were taken from Chapter 3 in reference 12; the kinetic data were re-analyzed in this study to incorporate the newly-discovered SC (site-covering) effect that affects target compound sorption kinetics. The materials and methods on which the literature data were based were summarized here.

Carbon-14 radio labeled atrazine was again the target contaminant and the competing compounds were five dyes that represented NOM fractions of different molecular weights. They included Methyl Orange (MO), Brilliant Yellow (BY), Congo Red (CR), Xylenol Orange (XO), and Evans Blue (EB). Molecular structure and physical sizes of the five dyes are presented in Figure 6.1 and Table 6.1. Two commercial carbons, WPH from Calgon and SA UF from Norit, were used, for which the amounts of micropore and

mesopore are listed in Table 6.2.

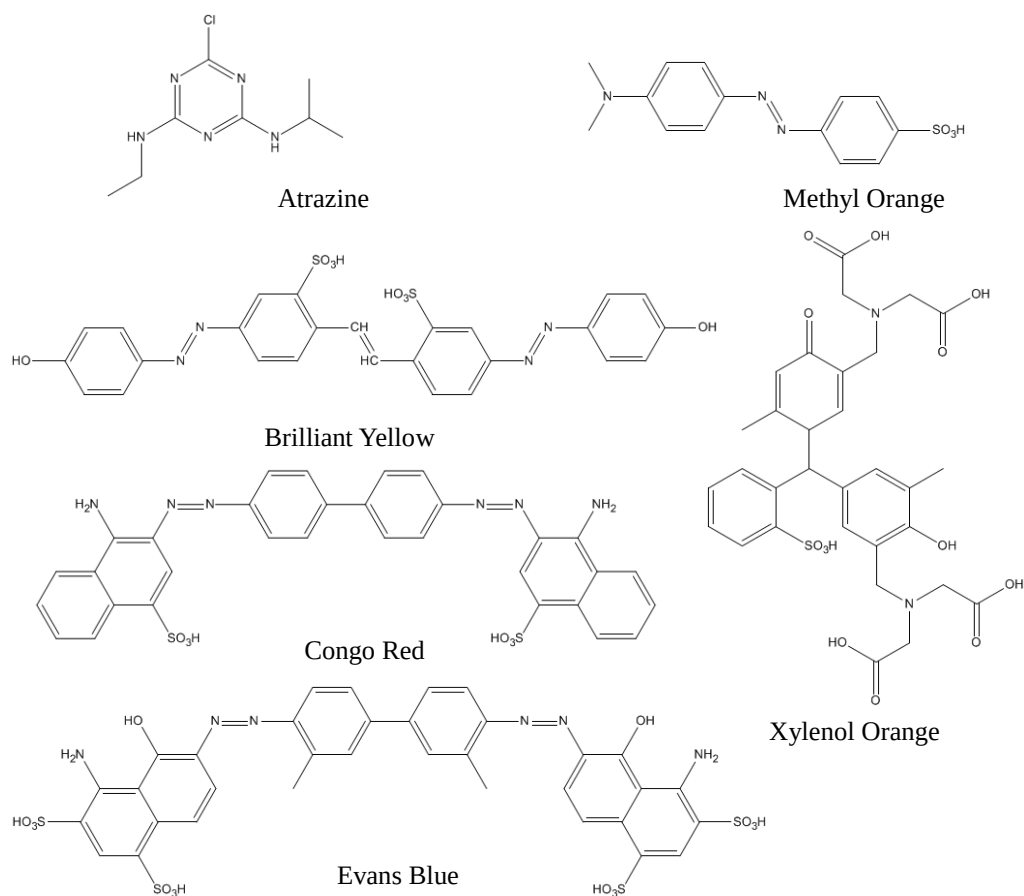


Figure 6.1 Two-dimensional molecular structures of target trace contaminant atrazine, and NOM surrogates Methyl Orange, Xylenol Orange, Brilliant Yellow, Congo Red, and Evans Blue (Reproduction of Figure 3.1 from reference 12)

Table 6.1 Three-dimensional molecular sizes of NOM surrogates (tabulation of the data from Chapter 3 of reference 12)

	Atrazine	MO	XO	BY	CR	EB
Molecular weight (Da)	215.7	304.3	668.7	578.6	650.7	868.9
Width (Å)	5.7	4.9	10.9	6.6	5.6	5.2
Length (Å)	12.7	16.8	15.0	26.3	26.0	28.9
Height (Å)	9.5	7.0	13.4	9.4	10.0	10.1

Table 6.2 Pore size distributions of WPH (11) and SA UF (6)

Property	WPH	SA UF
BET surface area (m ² /g)	903	1114
Micropore (<20 Å)volume (cm ³ /g)	0.420	0.354
Mesopore (20 - 500 Å)volume (cm ³ /g)	0.072	0.265
Micropore surface area (m ² /g)	888	652
Mesopore surface area (m ² /g)	15	410

Effects of Surrogate Compounds on Atrazine Adsorption Equilibrium

Atrazine isotherms for the two PACs preloaded with each surrogate are compared to the corresponding single-solute atrazine isotherm and results were summarized in Table 6.3. The values for Freundlich K were later used in the HSDM fitting for the kinetic data.

Table 6.3 Freundlich parameters for atrazine adsorption in organic free water and in the presence of surrogate compounds (Reproduction of Table 3.2 from reference 12)

	PAC A			PAC B		
	K ($\mu\text{g}/\text{mg})(\mu\text{g}/\text{L})^n$	$1/n$	% decrease in K	K ($\mu\text{g}/\text{mg})(\mu\text{g}/\text{L})^n$	$1/n$	% decrease in K
Single-solute	18.6	0.352	---	29.7	0.354	---
with 2mg/L MO	--	--	--	4.44	0.109	85.1
with 2mg/L BY	6.26	0.381	66.3	8.33	0.393	72.0
with 2mg/L CR	6.95	0.428	62.6	11.5	0.428	61.3
with 2mg/L XO	8.50	0.375	54.3	16.7	0.363	43.8
with 2mg/L EB	13.7	0.369	26.3	22.7	0.341	23.6

SA UF generally has higher capacity for atrazine, both in the single-solute case and in competitive case, presumably due to its larger secondary micropore volumes.

For both adsorbents, MO, the surrogate with the smallest molecular dimensions, caused the largest reduction in atrazine adsorption, i.e., 87-95 % for WPH and 83-94% for SA UF for the range of experimental conditions investigated. This is due to its molecular dimensions being the closest to those of atrazine, and therefore, it has access to the same

adsorption sites as atrazine. Also, compared to the single-solute atrazine isotherm, atrazine isotherms in the presence of MO were characterized by a lower Freundlich parameter $1/n$ and a corresponding large deviation from the OFW Freundlich isotherm at the highest aqueous concentrations. This indicates that MO has a stronger affinity than atrazine for the carbons (17). These effects have also been observed for atrazine adsorption in some natural waters (18).

After MO, BY had the strongest direct competition followed by CR, XO and EB. The decrease in atrazine capacity produced by surrogate compounds with elongated structures (BY and CR) was more pronounced than the more round molecules of XO, even though XO has lower molecular weight and higher OFW capacity (Table 6.4). Previous studies have shown that the smallest pore size that a molecule can adsorb in is largely determined by its width (secondary dimension) (19, 7 and 8). Data in Table 6.2 show that CR and BY have a molecular width of 9.4-10.0 Å, which is about the same as that for atrazine (9.5 Å), and therefore they compete more strongly than XO which has a width of 13.4 Å. The tertiary dimension of XO (10.9 Å) is considerably larger than those for BY, CR and atrazine (6.6, 5.6 and 5.7 Å, respectively) and may contribute to the exclusion of XO from the pores that adsorb atrazine. EB caused the weakest competitive effect on atrazine isotherms due to its low adsorption capacity on both PACs (Table 6.4).

Table 6.4 Freundlich K for dye adsorption on WPH and SA UF carbons (Tabulation of isotherm data in Chapter 3 from reference 12)

		MO	XO	BY	CR	EB
K (mg/g)(mg/L)ⁿ	WPH	289	183	160	105	50
	SA UF	263	223	196	167	109

Single-Solute Atrazine Adsorption Kinetics

The kinetics of atrazine adsorption by fresh adsorbents was determined using batch tests. The carbon doses (C_c) used for both adsorbents were 2 and 4 mg/L, and the initial atrazine concentration for each experiment was 60 µg/L (data now shown; please refer to Tang's dissertation (12)). The resulting single-solute atrazine surface diffusion coefficients ($D_{s,o}$) were 2.8×10^{-11} cm²/min for WPH and 3.0×10^{-11} cm²/min for SA UF.

Atrazine Adsorption Kinetics in the Presence of Pre-adsorbed Surrogates

Experimental conditions including initial concentrations and carbon doses of the preloading tests as well as the fitted surface diffusion coefficient D_s for atrazine are summarized in Table 6.5. Again, figures of the kinetic curves and HSDM simulations can be found in Tang's dissertation (12). Except for MO, loadings of the rest 4 surrogates all caused reduction in atrazine D_s . As discovered in some research (25, 26), a competing compound loading could have both pore blockage effect and enhancement effect at the same time so that a resulted D_s was the combined effect of both. By following the procedure the same group of researchers developed we were able to obtain the enhancement factor and pore blockage factor for each kinetic data set.

The enhancement effect was thought to be positively related to the loading of the site competing compounds (25). It was further demonstrated in Chapter 5 that despite differences in adsorbents or competing compounds, the enhancement relationship between enhanced diffusion coefficient and the SC loading followed the single trend line, if the SC compound loading was expressed as the equivalent background compound (EBC, 20) following the approach developed earlier (6). The EBC was used because this approach allows only the fraction of molecules that compete directly with the atrazine to be considered when determining enhanced diffusion. This was necessary because competition between adsorbates of different sizes in a porous adsorbent results some molecules adsorbing in pores where there is no completion for sites. The enhancement factor f_{SC} and pore blockage factor f_{PB} were then defined in Equations 6.2 and 6.3.

$$\frac{D_{s,SC}}{D_{s,0}} = 1 + A \cdot q_{EBC} \quad (6.1)$$

$$f_{SC} = \frac{D_{s,SC}}{D_{s,0}} \quad (6.2)$$

$$f_{PB} = \frac{D_{s,0}}{D_{s,PB}} = \frac{D_{s,SC}}{D_s} \quad (6.3)$$

From Chapter 5, we have derived the universal slope A of 0.021 for Equation 6.1. The atrazine isotherms in the presence of surrogates were fitted for the EBC concentrations.

As shown in Figure 6.2(a), Evans blue had an equivalent concentration of 30 $\mu\text{g/L}$ that directly competed with atrazine for adsorption capacity of WPH, while other surrogates had a equivalent concentration of 120, 200, 250 and 300 $\mu\text{g/L}$, even though the actual initial concentrations of the surrogates were all 2 mg/L. A higher EBC concentration indicates stronger direct competition. The same observations were made for competitive isotherms on SA UF carbon (Figure 6.2(b)).

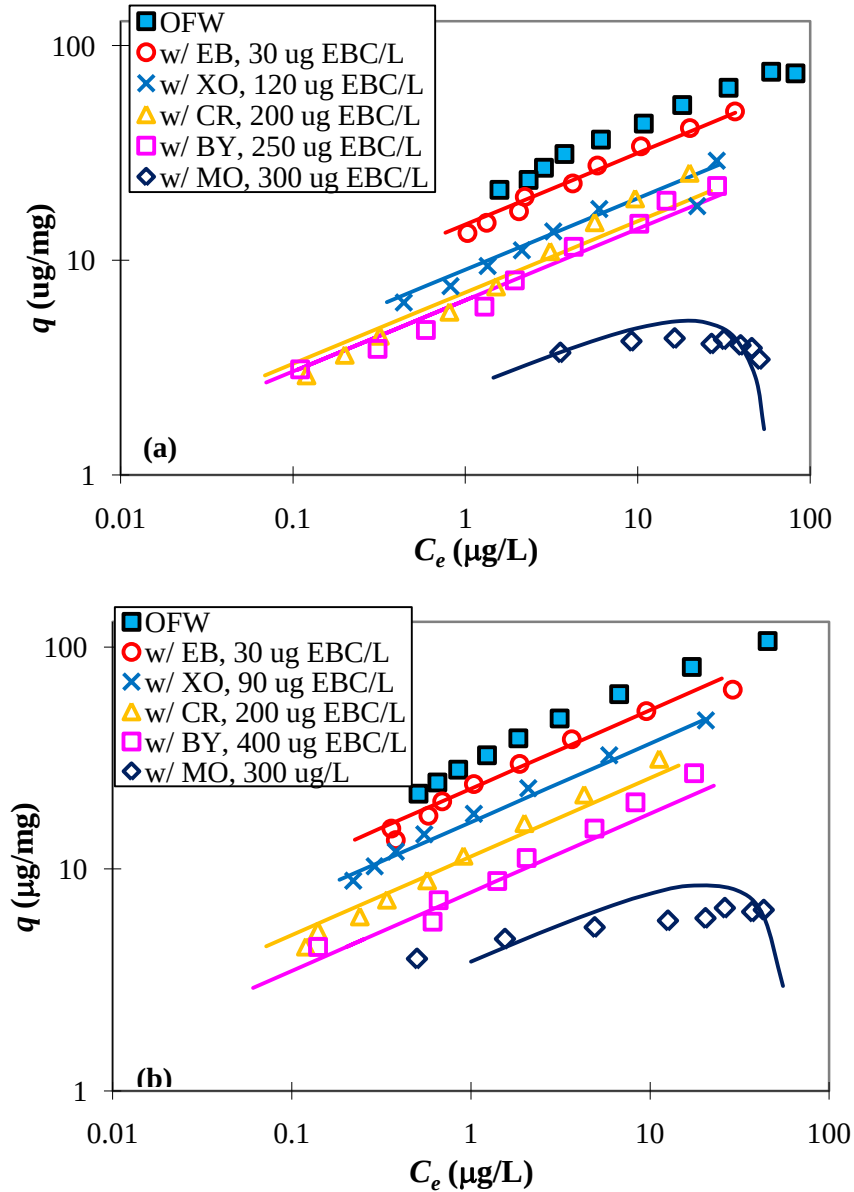


Figure 6.2 IAST-EBC fitting (lines) for atrazine adsorption isotherms on (a) WPH and (b) SA UF in the presence of NOM surrogates (Raw isotherm data were from Chapter 3 of reference 12, and the EBC fitting was done in this study)

By knowing the initial concentration of the EBC, the EBC loading at each carbon dose, q_{EBC} , was determined. Therefore the enhancement factors and pore blocking factors were calculated using Equations 6.1-6.3. This procedure was carried out for all 5 surrogates and 2 PACs, with obtained values list in Table 6.5.

For all surrogates, the amount of the enhancement effect is within one order of magnitude, while the PB effect is very different for different competing compounds. MO, which has the small molecular size and strongly competed with atrazine for adsorption sites, exhibited the greatest effect to increase atrazine diffusivity, but was not effective at blocking pores to reduce atrazine diffusion rate, so the overall competitive effect on atrazine kinetics was a subtle change in atrazine's surface diffusion coefficient. The resulting atrazine D_s value were comparable to those obtained for single-solute and in certain cases the diffusion coefficients in the presence of preloaded MO were actually greater than those in the absence of competition ($D_{s,0} = 2.8 \times 10^{-11} \text{ cm}^2/\text{min}$ for WPH and $D_{s,0} = 3.0 \times 10^{-11} \text{ cm}^2/\text{min}$ for SA UF).

Atrazine diffusivity was found to decrease with increasing surface loading of BY or CR for both adsorbents. At the highest solid phase concentration achieved in this study, atrazine $D_{s,\text{PB}}$ decreased by two to three orders of magnitude compared to that of the corresponding fresh carbon in OFW ($D_{s,0}$).

XO did not cause as much pore blocking effect on atrazine diffusion rate as BY or CR at the same surrogate loading, despite their similarity in molecular weight and adsorbability. This indicates that molecular dimensions of competing compounds may also play a significant role on the extent of pore constriction, in addition to direct competition. The microstructure of activated carbon is often described as disordered arrangements of defective crystallites of graphite (Thompson and Gubbins, 2000) with pores in the form of slits and voids between adjacent graphene sheets. Elongated molecules such as CR and BY could block access to slits and voids with linear openings more effectively than compact molecules such as XO, thus resulting in more severe hindrance for atrazine diffusion at lower concentration.

Table 6.5 Atrazine D_s under various adsorbent surface loadings of surrogate compounds
(the values for D_s were from a tabulation of data in Chapter 3 of reference 12; the determination of SC and PB factors were done in this study)

PAC A (WPH) $D_{s,o} = 2.8 \times 10^{-11} \text{ cm}^2/\text{min}$					PAC B (SA UF) $D_{s,o} = 3.0 \times 10^{-11} \text{ cm}^2/\text{min}$				
[MO] ₀ = 2mg/L									
C_c (mg/L)	q_e (mg/g)	D_s (cm ² /min)	f_{SC}	f_{PB}	C_c (mg/L)	q_e (mg/g)	D_s (cm ² /min)	f_{SC}	f_{PB}
5	281	4.50E-11	4.03	3.41	5	294	4.10E-11	6.60	3.34
12	158	6.50E-11	2.90	1.25	12	166	1.80E-11	3.66	4.53
[BY] ₀ = 2mg/L									
C_c (mg/L)	q_e (mg/g)	D_s (cm ² /min)	f_{SC}	f_{PB}	C_c (mg/L)	q_e (mg/g)	D_s (cm ² /min)	f_{SC}	f_{PB}
9	129	9.00E-13	1.68	52.4	8	181	1.10E-13	2.17	486
14	127	1.40E-12	1.45	29.0	12	167	4.00E-13	1.76	114
18	111	4.70E-12	1.35	8.04	14	144	1.80E-12	1.65	24.2
20	96.4	8.70E-12	1.32	4.24	16	125	4.40E-12	1.56	9.50
23	87	1.20E-11	1.27	2.97	20	101	9.80E-12	1.43	4.03
[CR] ₀ = 2mg/L									
C_c (mg/L)	q_e (mg/g)	D_s (cm ² /min)	f_{SC}	f_{PB}	C_c (mg/L)	q_e (mg/g)	D_s (cm ² /min)	f_{SC}	f_{PB}
9	114	1.70E-12	1.46	24.1	8	170	1.20E-13	1.76	381
14	112	1.90E-12	1.30	19.1	12	154	1.90E-13	1.49	213
18	103	2.30E-12	1.23	15.0	14	135	6.90E-13	1.41	56.5
20	95.8	4.90E-12	1.21	6.91	16	120	1.80E-12	1.35	21.0
23	83.5	9.20E-12	2.82	8.60	20	95.6	6.30E-12	1.27	5.76
XO, $C_c = 4\text{mg/L}$					XO, $C_c = 3\text{mg/L}$				
[XO] ₀ (mg/L)	q_e (mg/g)	D_s (cm ² /min)	f_{SC}	f_{PB}	[XO] ₀ (mg/L)	q_e (mg/g)	D_s (cm ² /min)	f_{SC}	f_{PB}
2	213	1.90E-11	6.92	10.20	2	231	5.10E-12	7.13	41.95
0.42	106	2.50E-11	2.30	2.58	0.42	132	1.20E-11	1.13	2.83
0.22	51.8	2.10E-11	1.68	2.25	0.22	72.2	2.10E-11	1.07	1.5
EB, $C_c = 4\text{mg/L}$					EB, $C_c = 3\text{mg/L}$				
[EB] ₀ (mg/L)	q_e (mg/g)	D_s (cm ² /min)	f_{SC}	f_{PB}	[EB] ₀ (mg/L)	q_e (mg/g)	D_s (cm ² /min)	f_{SC}	f_{PB}
2	58.2	1.30E-11	1.15	2.49	2	110	7.90E-12	1.26	3.80
0.8	60.8	1.20E-11	1.06	2.48	0.8	114	9.70E-12	1.07	3.09
0.3	57.1	1.30E-11	1.02	2.20	0.3	96.6	1.40E-11	1.00	2.14
0.2	47.6	1.30E-11	1.02	2.19	0.2	64.4	1.80E-11	1.00	1.67
0.1	25.2	1.40E-11	1.01	2.02	0.1	34	2.20E-11	1.00	1.36

EB did not cause much reduction in atrazine diffusion coefficients either. However, this relatively low pore constriction effect is mainly due to the low adsorbability of EB and the consequent low EB loading on the PACs.

The comparison of the pore blockage effect by the various surrogate compounds on atrazine adsorption kinetics is shown in Figures 6.3(a) for WPH and 6.3(b) for SA UF in terms of normalized atrazine diffusivities. As depicted in the figures, preloading of round sized XO molecules caused weak pore blockage effect for atrazine adsorption kinetics on both PACs. In contrast, atrazine surface diffusivity decreased quickly with increasing preloading of either BY or CR for both PACs. Interestingly, BY and CR (as well as EB within its more limited surface loading range) appeared to have a similar effect as characterized by the same slope and the same critical surface loading of approximately 80 mg/L (WPH) or 100 mg/L (SA UF). Critical loading is the minimum loading above which the atrazine diffusivity begins to decrease exponentially with increasing surface loading. Also shown in figure 6.3 are the effects on atrazine D_s resulting from preloading the adsorbents with several natural waters, reported in several other studies. In these studies, carbon was first exposed to Fresh Lake Decatur water (FLDW) (5), one-year-old Lake Decatur water (DLDW) (5) or Clinton Water Works water (CWW) (6) before atrazine adsorption. As depicted in the figure, the overall pore blockage effect caused by natural water NOM was generally less pronounced than that caused by surrogate compounds BY, CR and EB, and the difference was more obvious for SA UF. NOM is a mixture of molecules with different physical and chemical properties and its molecular weight varies from just a couple of hundred to over ten thousand Dalton, while the surrogates that we used in this study generally represent a relatively narrow span of NOM molecular weight distribution. Based on the study that showed that the pore-blocking fraction of NOM is mostly in the MW range of 200 to 700 Dalton (5), the unrepresented portion of NOM of higher molecular weight did not cause as much PB effects as surrogates. Therefore a single surrogate compound may not be able to model the real effects caused by NOM mixture; a combination of surrogates of various sizes may work better for quantitative modeling. Nevertheless that among the surrogates investigated in this study BY and CR could be used as conservative surrogates to represent the pore blockage effect of NOM.

The difference between the two PACs may be rooted from their pore size distribution. SA UF, with its extensive mesopore and macropore volume (9), provided more adsorption capacity for NOM molecules and so induce lesser competitive effect for a given NOM loading than WPH, a primarily microporous adsorbent, did not have this buffer effect so the PB effect increased faster once it reached the threshold loading.

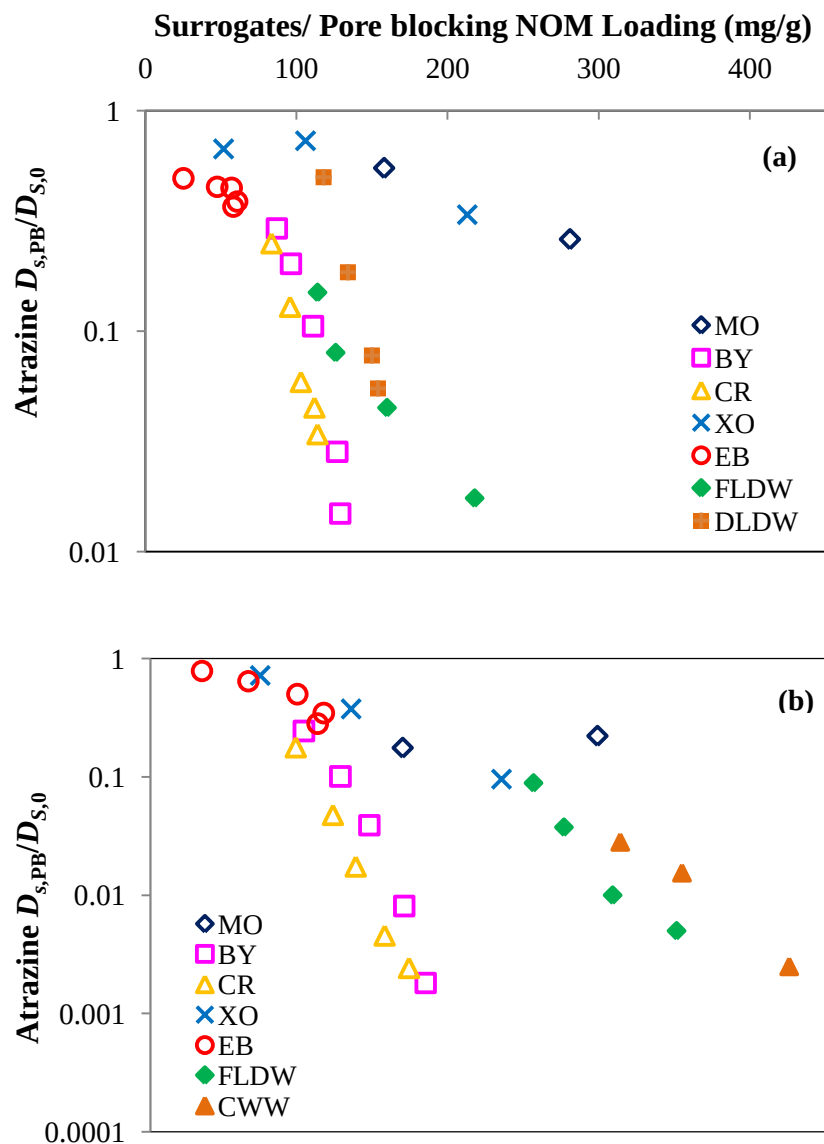


Figure 6.3 Normalized atrazine D_s as a function of surface loading of surrogate compounds and NOM (DLDW (5), FLDW (5), CWW (6)) for (a) WPH and (b) SA UF

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CHAPTER 7

ENHANCED ADSORPTION KINETICS: SURFACE DIFFUSION COEFFICIENT AS A FUNCTION OF LOADING HISTORY

INTRODUCTION

Chapter 5 and 6 show that loadings of site-competing compounds increased the surface diffusion coefficient of atrazine adsorption on activated carbon, and this enhancement effect was observed for various competing compounds and PACs. An important remaining question is whether previous loadings of atrazine itself also has a kinetic effect on itself, and if yes, whether the effect is the same as that observed when different species compete with atrazine.

Enhancement of surface diffusivity of atrazine adsorption on an activated carbon in the presence of preloaded competing compounds was discovered by To *et al.* (1, 2). They proposed the site coverage theory to explain the observed increase in surface diffusion coefficient. According to their theory, adsorbed site-competing (SC, 3-4) compounds occupied the active sites that would otherwise interact strongly with atrazine molecules as they diffused inside the pore, resulting in weaker surface resistance to atrazine diffusion and a faster diffusion rate. The enhancement of the diffusion coefficient was directly related to the loading of the SC compound. The EBC (equivalent background compound) model (5) was used to quantify the amount of the competing compound that competed with atrazine for adsorption sites, following the procedure developed by Ding *et al.* (6). This analysis was based on the concept that only a portion of the adsorbed competing compound completes directly with the target compound because of chemical and physical differences between the target compound and the competing compound. To simplify the analysis, the EBC fraction of the competing compound was assigned the same isotherm parameters as the target compound atrazine. The EBC, then, represents the competing compound expressed in atrazine equivalents. The EBC loading represented the coverage of adsorption sites available to atrazine that were occupied by competing compounds.

Knowing that the enhancement effect is caused by surface coverage, the effect should be observed if the coverage is either by the competing molecule or by the target compound

itself. A literature review did not find conclusive evidence of this, however. Some studies have shown that the diffusion coefficient of a target compound is dependent on its initial concentration, carbon dose or adsorbed concentration, and others have not (7, 8), thus indicating the need for more definitive research. .

A better understanding of the effect of competition on adsorption kinetics can help to better understand the adsorption process in the sophisticated internal structure of activated carbon, and eventually allow us to build more complete adsorption models to better predict adsorption efficiency of various reactor designs. This is especially pertinent to GAC adsorbers, which generally have a service life of 2-5 years and therefore get loaded with various contaminants. Adsorption and desorption are very common in GAC adsorption processes, in response to changes in influent concentrations. Kinetics generally is a more important controlling factor than equilibrium in such systems. A better understand on how diffusivity of a specific adsorbate changes throughout the service life will be a valuable addition to present models.

The objectives of this study were to investigate the dependency of the atrazine surface diffusion coefficient on atrazine surface loading and to investigate the mechanism of the enhanced adsorption kinetics.

MATERIALS AND METHODS

Water

Distilled de-ionized (DDI) water was used in this study as organic free water (OFW). The natural water used was groundwater from Clinton Water Works (CWW), Clinton, IL. Details can be found in Chapter 3.

Adsorbent

One commercial PAC, NORIT SA UF, was used. Details can be found in Chapter 3. This one has been shown in previous research to have high capacity for atrazine adsorption and had a lot of experimental data for reference.

Trace Organic Compound

Carbon-14 radio-labeled atrazine (Syngenta Crop Protection, Inc., Greensboro, NC) was used as the target trace compound, consistent with previous research. A stock solution with a concentration of 12.4 mg/L was prepared using DDI water and kept at 4°C until use. On the test day, this stock solution was diluted to make up the test solutions. The sampling technique and analysis of concentration of radioactive atrazine is described in Chapter 3.

Atrazine Adsorption Kinetic Tests on Fresh PAC

Atrazine adsorption kinetic tests on fresh SA UF carbon were conducted on fresh PAC in OFW following the procedure provided in Chapter 3. The data were used to establish a baseline for comparison with subsequent tests using preloaded carbon. Test solution with a concentration of 65 µg/L was made by adding 4.72 mL of atrazine stock solution to each of the 1-L amber bottles that contained 900 mL of DDI water using a 5-mL auto pipette. The test solution was mixed on stir plates. The initial concentrations were measured before PAC doses of 2, 3 and 4 mg/L were added into individual bottles and atrazine concentrations were monitored over the following 4 hours. The sampling procedure for atrazine can also be found in Chapter 3.

Atrazine Adsorption Kinetic Tests on Partially Loaded PAC

Atrazine adsorption kinetics on PAC that has been partially loaded with atrazine is termed “presorb kinetics”. To achieve the atrazine loading, atrazine stock solution was added to 900 mL of DDI in 1-L amber isotherm bottles, the initial concentration of atrazine, C_1 , was measured, and then PAC was dosed to the bottles. The amount of the atrazine stock and/or carbon mass was varied in order to realize different atrazine loadings at the end of the preloading period. The test solutions were continuously mixed in a shaker for 4 days, at the end of which the equilibrium concentration of atrazine, $C_{e,1}$, was determined. Bottles were then moved onto magnetic stir plates, where stir bars were put into each bottle and another spike of atrazine stock solution was added. Atrazine concentrations were monitored over the following 4 hours. The sampling procedure for atrazine was described in Chapter 3. Details of the experimental conditions including carbon dose and

concentrations of the first spike and second spike of atrazine are listed in Table 7.1 in the Results and Discussion section.

Presorb kinetic tests were also carried out on PAC that was loaded with both atrazine and CWW NOM to investigate the effects of combined loading. The experiments were conducted in a very similar manner to the tests with presorbed atrazine, except that DDI was replaced by CWW water.

HSDM Model Fitting for Surface Diffusion Coefficient

Homogeneous Surface Diffusion Model (HSDM) was used to model adsorption kinetic (9, 10) and the surface diffusion coefficient D_s can be obtained by fitting model prediction to experimental data for each kinetic data set. The HSDM requires isotherm parameters of atrazine in DDI water and in CWW water, which had been determined earlier (Table 4.1, Chapter 4). The FORTRAN program that was used in Chapters 4-6 was valid only for virgin carbon kinetics, so it was necessary to write a new HSDM model that incorporated the partial loading as an initial condition. This model was developed using MATLAB and is presented in the Results and Discussion section.

RESULTS AND DISCUSSION

HSDM for Partially Loaded Carbon (PL-HSDM)

The MATLAB program was built to solve the HSDM to get an aqueous concentration vs. time profile for carbon that has been partially preloaded with adsorbate, q_0 . The program was based on the governing equation for adsorption kinetics on spherical particle (11), with the initial and boundary conditions

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \quad (7.1)$$

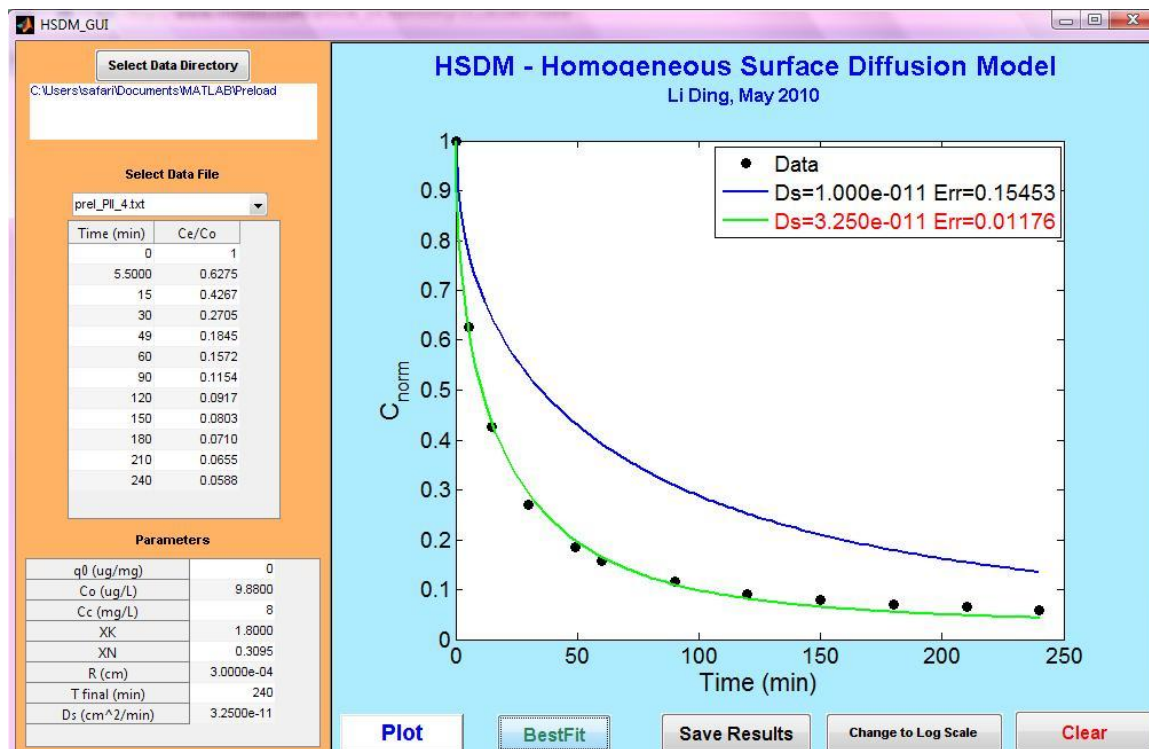
$$q(r, t = 0) = q_0 \quad (7.2)$$

$$\frac{\partial q}{\partial r}(r = 0, t) = 0 \quad (7.3)$$

$$q(r = R, t) = q_s(t) = KC(t)^{1/n} \quad (7.4)$$

This set of partial differential equation can be solved numerically, but it also has an analytical solution (12). The Matlab code was formulated based on the analytical solution. Details on the analytical solution and the MATLAB code can be found in Appendix A.

The model outputs were normalized and non-normalized aqueous concentrations and solid concentration of the adsorbate as a function of time. The model also calculates the difference between the model prediction and the experimental data. Elements such as a graphic user interface (GUI) and visual output were incorporated into the program to make it more user-friendly.



**Figure 7.1 Work space of the HSDM_GUI model
(Plot shows the improved data fit by modifying D_s)**

Figure 7.1 is an example of how the HSDM_GUI is used to determine the surface diffusion coefficient. For details on how to work with the model, please refer to Appendix A.

All D_s values discussed below were derived with the new HSDM program.

Atrazine Adsorption Kinetics on Virgin PAC

Data for atrazine adsorption kinetic from DDI water on virgin SA UF carbon set the baseline for comparison of the kinetic effect caused by preloading. The initial concentration of 65 $\mu\text{g/L}$ and carbon doses of 2, 3 and 4 mg/L were used. Each of the 4-hour data sets was fitted with the HSDM to give the best-fit surface diffusion coefficient, D_s (Figure 7.2). A loading, q_0 , of zero was used for fresh PAC. As shown in the legend, the D_s for different carbon doses varies only slightly, indicating that the surface diffusion coefficient of atrazine is not dependent on carbon dose. The average value for the atrazine diffusion coefficient on fresh PAC is $1.14\text{E-}11 \text{ cm}^2/\text{min}$, which is approximately the same as that obtained in another study for the same PAC (6).

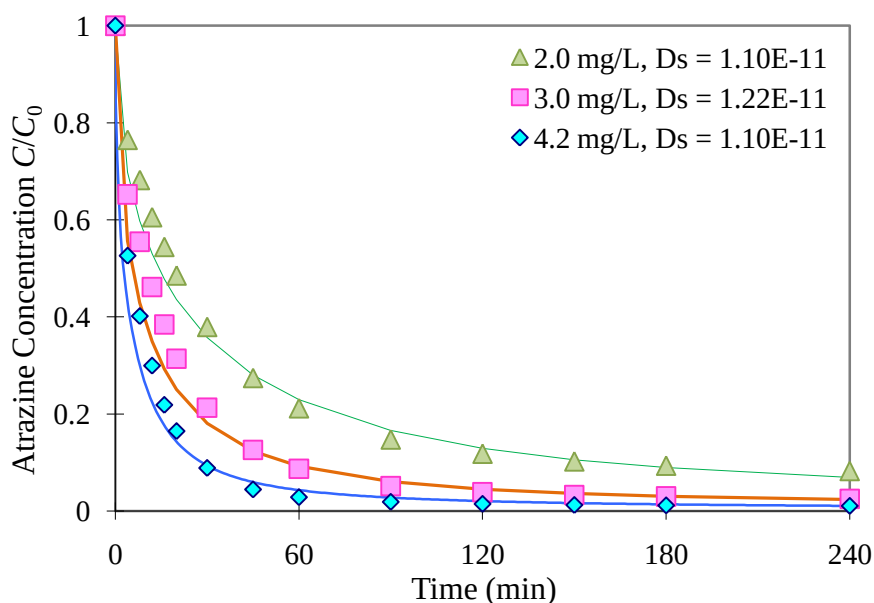


Figure 7.2 Adsorption kinetics of atrazine on virgin SA UF in DDI water with HSDM fit ($C_0 = 65 \mu\text{g/L}$, $C_c = 2, 3$ and 4 mg/L)

Enhanced Atrazine Adsorption Kinetics on Partially-Loaded PAC

Adsorption kinetics of atrazine on SA UF that was partially loaded with atrazine was conducted to investigate the effect of presorbed atrazine on atrazine diffusion rate. Experimental conditions and results are listed in Table 7.1. C_c is the carbon dose and C_1 and C_2 are equivalent aqueous concentrations for the test solutions that resulted from the first and second additions of atrazine stock.

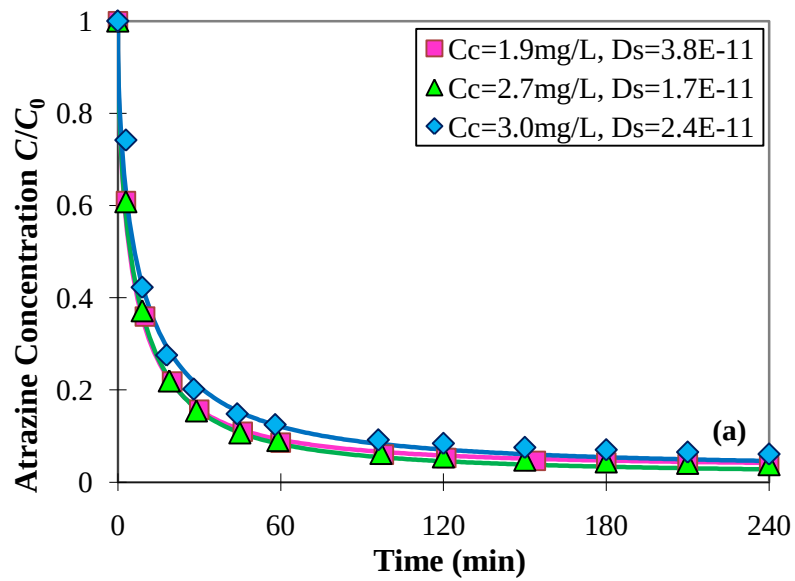
Table 7.1 Experimental conditions and results of the presorb kinetic tests

C_c (mg/L)	C_1 ($\mu\text{g/L}$)	q_0 ($\mu\text{g/mg}$)	C_2 ($\mu\text{g/L}$)	D_s (cm^2/min)	$D_s/D_{s,0}$
2.7	15	5.5	50	1.7E-11	1.49
1.4	15	7.8	50	3.8E-11	3.33
2.7	30	9.9	50	2.4E-11	2.11
4.3	50	11.5	15	2.00E-11	1.75
3.0	50	16.6	15	1.40E-11	1.23
2.0	50	24.8	15	3.10E-11	2.73
4.0	100	24.8	15	1.00E-11	0.88
3.0	100	32.8	15	1.20E-11	1.05
3.7	210	56.8	50	8.0E-11	7.02
2.9	210	71.0	50	9.0E-11	7.89

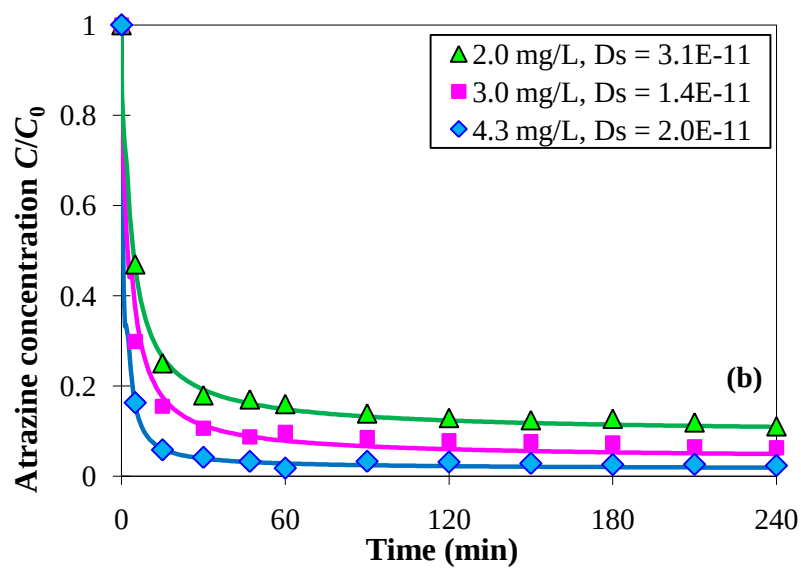
q_0 is the amount of presorbed atrazine from the 4-day adsorption of the first atrazine addition. It was calculated using the 4-day equilibrium concentration ($C_{e,1}$) and the mass balance equation,

$$q_0 = \frac{C_1 - C_{e,1}}{C_c} \quad (7.5)$$

Also listed in Table 7.1 is the HSDM-fitted surface diffusion coefficient D_s for each of the kinetic runs. The atrazine diffusion coefficient was found to be generally greater on PACs that had partial loadings of atrazine than on virgin PAC, which has a D_s of 1.14E-11 cm^2/min ($D_{s,0}$). The last column in Table 7.1 is $D_s/D_{s,0}$, which gives a more direct comparison of the enhancement. Experimental data and fitting curves are shown in Figure 7.3, (a) - (d).

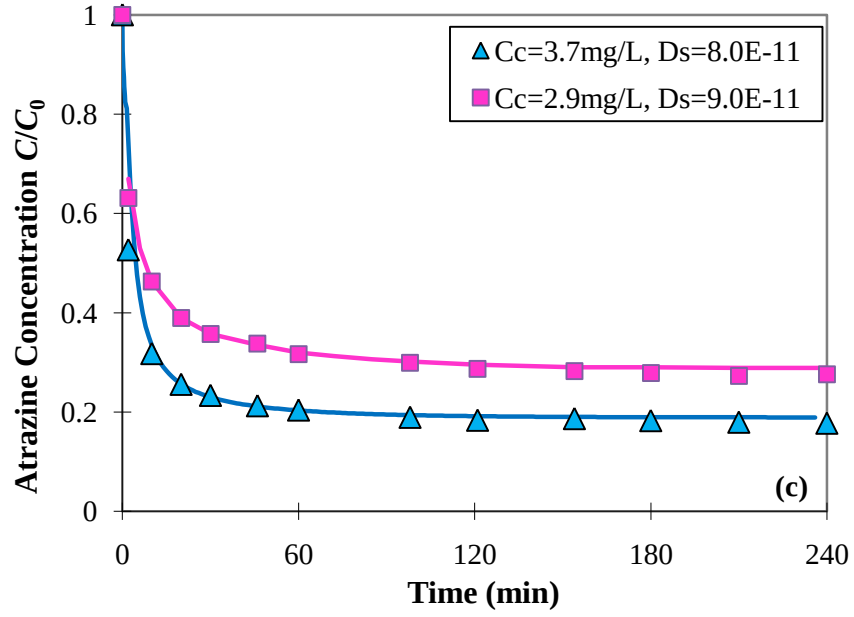


(a)

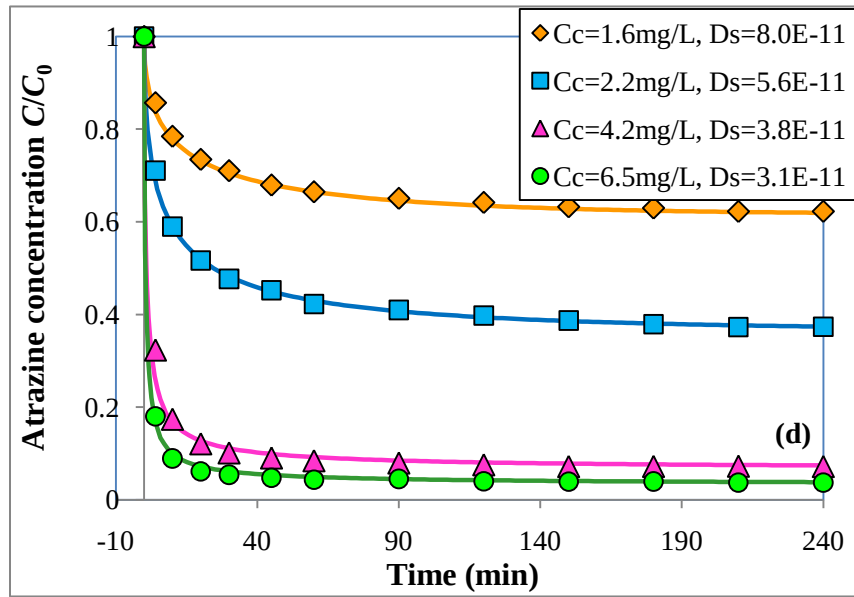


(b)

Figure 7.3 continued on next page



(c)



(d)

Figure 7.3 Adsorption kinetics of atrazine on preloaded SA UF in DDI with individual HSDM fits (lines)

- (a) $C_1 = 15 \mu\text{g/L}$ ($30 \mu\text{g/L}$ for C_c of 3.0), $C_2 = 50 \mu\text{g/L}$
- (b) $C_1 = 50 \mu\text{g/L}$, $C_2 = 15 \mu\text{g/L}$
- (c) $C_1 = 210 \mu\text{g/L}$, $C_2 = 50 \mu\text{g/L}$
- (d) $C_1 = 160 \mu\text{g/L}$, $C_2 = 40 \mu\text{g/L}$

In addition, similar presorb tests were carried out on one another PAC, W35, and the data

are shown in Figure 7.4.

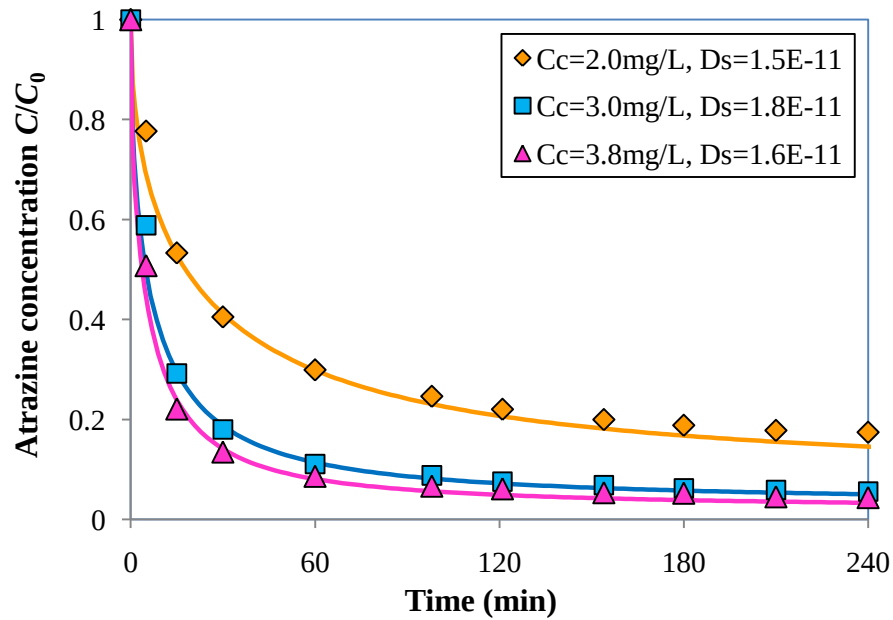


Figure 7.4 Adsorption kinetics of atrazine on atrazine preloaded W35 with HSDM fits (lines)

$C_1 = 50 \mu\text{g/L}$, $C_2 = 50 \mu\text{g/L}$

The experiments confirmed the expectation of the enhancement effect caused by atrazine loadings. The adsorbed atrazine molecules covered active adsorption sites to reduce the interaction between diffusing molecules and the internal carbon surface, thereby resulting in a faster diffusion rate for diffusing molecules.

Figure 7.5 compares the enhancement effect by atrazine with that caused by other competing compounds as presented in Chapter 5. The actual loading of atrazine was used for the EBC loading on the x-axis since we modeled EBC as a compound that had the same adsorption properties as atrazine.

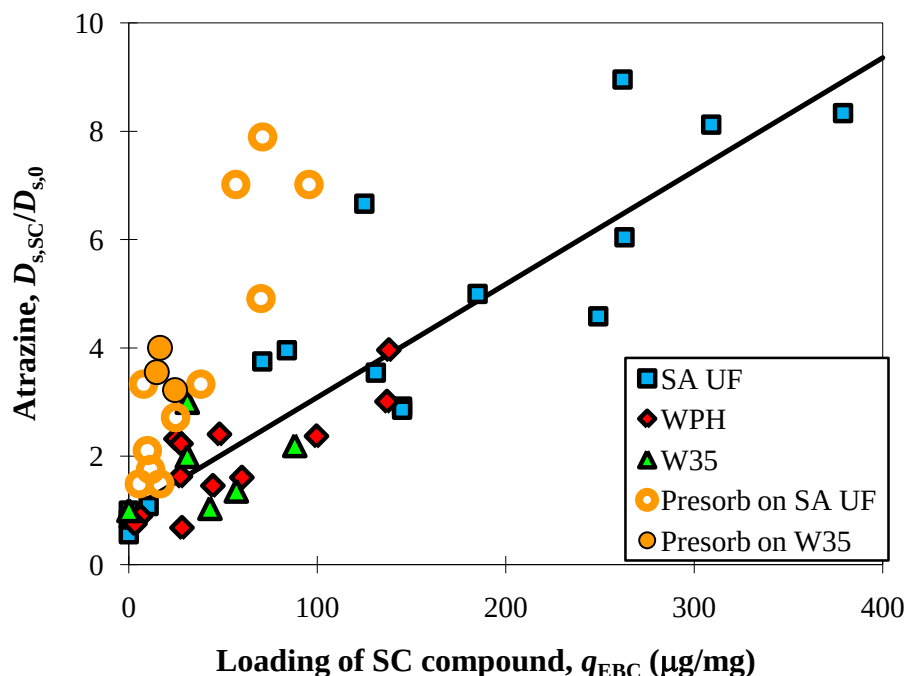


Figure 7.5 Enhanced diffusivity as a function of the EBC loading – comparison of atrazine loadings to the competing compound loadings (data for SA UF, WPH and W35 were re-produced from Figure 5.5 of Chapter 5)

In Figure 7.5, the first 3 sets of data are reproduced from Chapter 5, which show the enhancement effects caused by competing compounds on atrazine adsorption kinetics on SA UF, WPH and W35 carbons. The trend line was created based on competing compound data, showing the same enhancement effect in spite of the differences in adsorbents and competing compounds. Compared to competing compound data, the atrazine loading, although a little scattered, seems to induce a stronger enhancement effect than other competing compounds.

Several explanations were proposed for the difference between atrazine loading (same-species loading) and competing compound loading, as discussed below.

One possible cause for the difference is the absence of the displacement in the same-species sequential loading, or to be more accurate, the inability to distinguish between molecules from the first loading and those of the second loading. Even for the same species, the dynamic nature of the adsorption process means there is exchange between pre-adsorbed atrazine and atrazine that is introduced later. However, this displacement was not measured in the atrazine-preloading tests because we were not able to

differentiate between the first and second spike since both spikes were radiolabeled and our monitoring of the bulk solution concentration was only based on radioactivity. The combined effect of desorption and adsorption atrazine introduced zero net flux at the locations where exchange occurred, which consequently produced a kinetic plateau earlier than in the other desorption/adsorption cases. Another way to understand this problem is to consider that the first spike of atrazine filled micropores and this atrazine was not displaced by the second atrazine spike. Therefore the second spike of atrazine only needed to travel in big micropores and mesopores to reach its adsorption sites. This artifact, together with what has been named “site covering” effect, contributed to the enhanced diffusivity of atrazine in the same-species loading experiments. In contrast, in the competing compound loading scenario, only the atrazine molecules were radiolabeled so we were able to monitor the diffusion of just atrazine that was introduced after the preloading period. The competing molecules that have pre-occupied micropores would be partially displaced by atrazine molecules, in accordance with the adsorption equilibrium relationship. Atrazine molecules would then travel into the then-occupied micropores where diffusion is slower. Therefore the observed atrazine diffusion coefficient was expected to be smaller on PACs that were loaded with competing compounds. If differentiation can be made between the pre-loaded atrazine and the subsequent atrazine spike, for example, by using one non-labeled and one labeled atrazine for each step, or by using different isotope-labeled atrazine, we would expect to see the enhancement effect to be similar to that caused by the preloading with compounds other than atrazine.

Another possibility is that an artifact was introduced when we treated the compounds other than atrazine as an equivalent background compound (EBC). The EBC was first introduced for competitive adsorption between a target contaminant and natural organic matter (NOM). NOM, as a complex mixture of organics, cannot be characterized as an individual compound, nor do the adsorption parameters based on a lumped concentration such as total organic carbon work well for competitive isotherm prediction of the target contaminant. This is mainly due to only a portion of NOM components that effectively competes with the target compound. The EBC approach treats NOM as a fictive compound that could cause the same level of competition with the target compound as

the NOM itself. The adsorption parameters as well as the concentration of the EBC are then obtained by fitting of the competitive isotherms.

A further simplification was made by Ding et al. (6) who treated EBC of NOM to be similar to the target compound in terms of adsorption parameters because they thought the NOM component that is close to the target compound in size and adsorption strength competed most strongly. This approach was also used here. However, this may not be a proper assumption to use in kinetic studies to quantify the site-covering effect, because quantification of competition for sites for adsorption capacity and that of covering of sites for reduced surface diffusion resistance may not be identical. Also as can be noticed in Figure 7.5, the highest atrazine-like EBC loading was close to 400 $\mu\text{g}/\text{mg}$, while the actually atrazine loading that was ever achieved in my isotherms tests was a little over 100 $\mu\text{g}/\text{mg}$ (Figure 7.6).

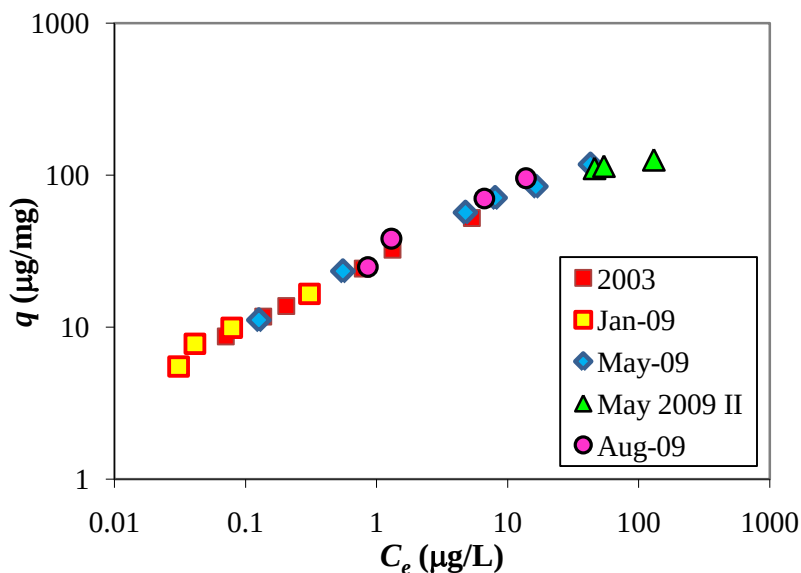


Figure 7.6 Single-solute atrazine adsorption isotherms on SA UF carbon (legends show when the isotherm tests were conducted)

Shown in Figure 7.6, atrazine isotherms on SA UF performed at different time are very consistent, assuring the reliability of the data. The isotherm data in the middle concentration range are a straight line, which can be perfectly described with the Freundlich isotherm equation (Equation 7.6). However, the data reach a plateau at the high concentration end, which is not uncommon for adsorption isotherms. Therefore, to

use Freundlich parameters generated in the mid-concentration range to estimate EBC loading at high concentration may have introduced errors in EBC loadings. Again this could have contributed to the difference in the enhancement effect caused by atrazine loadings and atrazine-analogous EBC loadings.

$$q = KC_e^{1/n} \quad (7.6)$$

An additional factor in the enhancement effect study is the molecular interaction between adsorbed phase and diffusing phase and also the interaction between adsorbates and adsorbents. There is an underlying assumption that the interaction between diffusing molecules and adsorbed molecules is weaker than that between diffusing molecules and the adsorbent surface. Otherwise the surface resistance could even be higher due to molecular drag forces. This assumption is generally valid due to strong adsorption bonds between adsorbate and adsorbent. However, differences in molecular interaction forces may result in different level of enhancement, and the site-covering compound that is closest to atrazine in adsorption characteristics may cause the greatest enhancement effect as it would more effectively cover the sites that interact strongly with diffusing atrazine molecules.

Additional research is needed to better understand enhancement mechanisms and to determine which of the above are applicable explanations of the data.

The increase in atrazine diffusion coefficient caused by site competition is generally within one order of magnitude for the loading range studied, in contrast to the pore blockage effect, which could cause a decrease of up to 4 orders of magnitude (6) (Chapter 4). To see the combined effect of these two contradicting influences, PAC was preloaded with both atrazine and natural organic matter (NOM) for 4 days before kinetic runs before the second spike of atrazine was started. The fitted D_s as a function of pore-blocking NOM loading is shown in Figure 7.7 below.

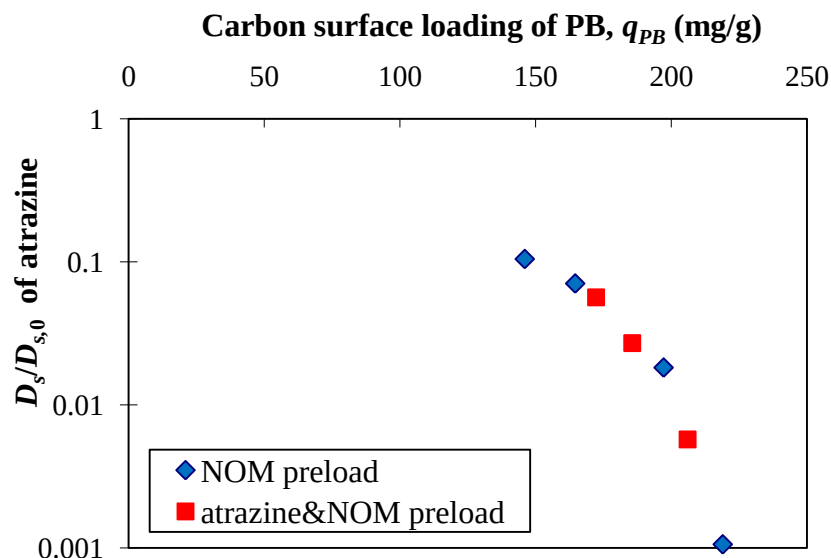


Figure 7.7 Kinetic Effect of atrazine and CWW NOM loadings on surface diffusion coefficient of atrazine adsorption on SA UF carbon

NOM has been known to cause severe pore blockage for atrazine adsorption, with the atrazine diffusion coefficient decreasing as NOM loading increases (20, 6). This is clearly shown in Figure 7.5 by the “NOM preload” data that are reproduced from Chapter 4. Loadings of both atrazine and NOM caused as much reduction in the diffusion coefficient of atrazine as the NOM-only loading, even though atrazine alone tests have shown it enhanced diffusion rate. In order to estimate how much enhancement effect was caused by atrazine loading in this combined loading tests, we calculated the atrazine loadings for the three data points to be 3.0, 3.8 and 5.3 $\mu\text{g}/\text{mg}$, which are too small to cause a significant enhancement of the atrazine diffusion coefficient (Figure 7.4). Atrazine isotherm data that were collected in previous years revealed that the highest atrazine loading achieved in the presence of CWW NOM was 11 $\mu\text{g}/\text{mg}$, which is still not high enough to counter the PB effect caused by the same NOM. The limited atrazine loading due to strongly competing NOM explains why enhancement effect gets masked by the PB effect.

There may be circumstances that adsorption of a target compound is strong enough, for example, the target compound has high influent concentration or strong affinity to the adsorbent, to cause significant enhancement effect to partially compensate the PB effect. An adsorption model that takes into account both effects should be able to improve

performance predictions, especially for GAC columns that usually stay in service for extended period, get loaded with various compounds and encounter many changes in influent concentration. In such a transient system, adsorption kinetics, rather than adsorption equilibrium, is a key factor to determine how much a contaminant can be removed by adsorption. How to formulate a simple yet effective model to simulate such competitive adsorption kinetics is important future work.

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CHAPTER 8

SUMMARY, CONCLUSIONS AND FUTURE RESEARCH

This dissertation research investigated the effects caused by competing compounds on the target compound adsorption on porous adsorbents. Atrazine, a widely used herbicide in the United States, was used as the trace-level target contaminant and natural organic matter (NOM) from different sources as well as NOM surrogates were used as the competing compounds. Both equilibrium and kinetics of atrazine adsorption under the influence of various competing compounds were studied for experimental quantification, mechanistic study and mathematical modeling, with the emphasis on the kinetic effects.

Previous research discovered three effects that competition may have on target compound adsorption on activated carbon: reduction in adsorption capacity caused by direct site competition (SC), reduction in diffusion rate caused by pore blockage (PB) and enhancement in diffusion rate caused by site coverage. Most compounds, especially the mixture of compounds that makes up NOM, are able to exert more than one effect at the same time. These competitive effects were further investigated in this study and better understandings were achieved.

The study with activated carbons of different pore size distribution (PSD) discovered that PSD had great influence on NOM adsorption and the pore blockage effect caused by NOM. The NOM used in this study was found to primarily adsorb in mesopores and its adsorption capacity was directly correlated to the amount of pores of diameter 15-50 Å. Consequently, activated carbon that has more surface area in this pore size range had a smaller PB effect on atrazine adsorption kinetics at the same NOM loading. This finding suggested mesopore is equally important as micropores in providing adsorption capacity for trace compound removal and provided a direction for activated carbon production toward more mesopores in addition to micropores in order to control the adverse competitive effect.

The enhancement effect, in which competing compounds decreased surface resistance for atrazine diffusion by occupying adsorption sites, was observed in experiments with two other PACs and other competing compounds. More important, the equation that

describes the enhanced surface diffusion coefficient for atrazine as a function of the loading of the site-covering compounds was found to be independent of either the PAC type or the competing compound type. The key component was to quantify the SC compound as the equivalent background compound (EBC) that had same adsorption parameters as atrazine. By doing this, the EBC loading was thought to reflect the amount of atrazine-active sites being covered by the competing compound, which was the direct cause of enhanced diffusion. .

For compounds that exert both the PB effect and the enhancement effect, the two effects can be separated following the procedure developed by To et al (ref). Atrazine adsorption data in the presence of NOM surrogates that were collected in past years were re-analyzed using this procedure to study relationship between molecular structure and the competitive effects. The smaller molecules were generally more effective in reducing the equilibrium capacity of the target compound. However, for molecules of similar molecular weight, elongated molecules tended to have more equilibrium effect than round molecules. Kinetic wise, large-sized surrogates caused much stronger PB effect, while the enhancement effect caused by all surrogate compounds was generally with one order of magnitude. Therefore, the overall kinetic effect was also dependent on molecular weight and the PB effect was usually dominant except for very small molecules.

Consistent with the enhanced atrazine diffusivity resulted from site coverage by pre-adsorbed competing compounds, preloading with atrazine was found to also increase the diffusion coefficient of atrazine, and the extent of enhancement caused by atrazine preloading seemed greater than that caused by competing compounds. The same-species loading was thought to be different from the competing-species loading due to the absence of the displacement, and “Micropore Filling” was proposed to describe the mechanism for the enhanced diffusivity caused by the same species loading. According to this hypothesis, pre-adsorbed atrazine occupies and stays on the favorable sites located in micropores, so later atrazine only travels in larger pores where diffusion coefficient was considered to be faster than in smaller pores.

Future work can be focused on further elucidating the enhancement effect and on how to

make use of these findings in practical water treatment processes. Details on potential research tasks are proposed below.

- Why atrazine preloading caused stronger diffusivity enhancement than other competing compounds is not fully understood yet, although several possible explanations have been proposed. Therefore additional atrazine kinetic experiments need to be conducted with this SA UF carbon, as well as for several other activated carbons. In addition, it may be necessary to study the effect of the preloading time because a short loading time may not allow diffusion to micropores and the micropore filling assumption may not be valid in that case. The purpose of this study is to expand our understanding of distribution of adsorbed molecules and to quantify the surface diffusion coefficient of atrazine as a function of history loading.
- To study the inter-molecular interaction for adsorbate molecules. The hypothesis that coverage of adsorption sites can reduce the diffusion resistance actually had a default assumption that the interaction between adsorbate-adsorbate is weaker than the interaction between adsorbate and adsorbent (active sites); therefore covering active sites with adsorbate molecules reduces interaction between diffusing molecules and stagnant phase. So if the adsorbed compound has a strong interaction with the diffusing compound, do we expect to the enhancement effect to be compromised or even reversed? This research should start with a careful selection of a series of compounds that have graduated molecular forces and experimental verification of this. These compounds are then put to the preloading tests to see whether a strong molecular force affects extent of the enhancement effect.
- To verify and possibly quantify the dependency of surface diffusivity on adsorbent pore sizes. Activated carbon fiber (ACF), whose pores are relatively uniform in size and oriented along the fiber axis, can be used as the single pore size material. For ACF that are made using the same raw materials and similar activation technique, the difference in kinetics can be contributed to the difference in pore sizes. Regular adsorption kinetic tests will probably suffice for this purpose.
- To evaluate the effect the changes in surface diffusion coefficient can have on the

overall adsorption performance. Adsorption scenario can vary from the basic batch kinetics to flow-through membrane reactors and to GAC columns and removal for each configuration will be compared for different D_s values. This will give us an estimation of how much changes in diffusion coefficient would cause significant effect on the final removal efficiency, and therefore helps to determine whether a fixed D_s is sufficient for modeling purposes. Of special interest is the evaluation of adsorption/desorption kinetics on aged activated carbon columns that have been loaded with various organics. Varied influent water quality, intermittent contaminant loading and other operation conditions will consistently change the equilibrium relationship on the column and kinetics is as important in such a transient process.

- To model the surface diffusion coefficient as a function of previous loadings. The 3-component flow-through model (COMPSORB) can be good start to work with to incorporate the enhancement effect into the modeling. It will then be necessary to incorporate the knowledge on pore size distribution (PSD) in order to know the location for adsorbed molecules as well as diffusing molecules, because covering a strong site is expected to have more enhancement effect than covering a weak site, while the distribution of sites is related to PSD. Certain simplifications of the porous structure needs to be made for this purpose; for example, some research modeled activated carbon as a dual-zone material in which small pores (or hole-filling domain) branch off the large pores (diffusion domain) and different values were assigned for diffusion coefficients in small pores and large pores. The relative strength of the SC effect to the PB effect is also a variation to be studied. Most data favor an overall effect of reduced diffusivity especially with NOM competition. However, there are certain surrogate data showing the enhanced diffusivity as the primary effect or a limited reduction in diffusivity. Is it safe to assume that all NOM would cause stronger PB effect than the SC effect so we expect reduced diffusivity anyway, or we should treat it case by case and be advised to watch for enhanced diffusivity? More data may be needed to get a more comprehensive view.
- To apply the findings obtained on PAC studies to GAC systems. The loadings in a

GAC system are much more complicated than what we had in the batch study. The carbon in a GAC system is constantly exposed to influent that contains NOM and various contaminants, whose concentrations fluctuate with time. This continuous feeding of adsorbates results in constantly changing loadings of competing compounds and also introduces the loading time effect, for which we still have not gained a definite knowledge on its effect on the competition. Another thing to keep in mind is that although GAC particles may not behave just like giant PAC particles also they seem so, because they are being applied to packed beds/columns that are very different than PAC application regarding flow rate, contact time and mixing conditions. Small-scale column tests may be necessary too.

APPENDIX A

COMPUTER FORMULATION OF THE HSDM (HOMOGENEOUS SURFACE DIFFUSION MODEL) SOLUTION

MATHEMATICS OF THE ANALYTICAL SOLUTION

The governing equation for the diffusion inside an spherical particle is,

$$\frac{\partial q}{\partial t} = -\frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \quad (\text{A.1})$$

In the most general form, the adsorbent particles have a pre-existing concentration profile, which would result in the following initial conditions and boundary conditions:

$$q = q_0(r) \quad \text{for } t = 0 \quad \text{and } 0 \leq r \leq R \quad (\text{A.2a})$$

$$\frac{\partial q}{\partial r} = 0 \quad t \geq 0 \quad r = 0 \quad (\text{A.2b})$$

$$q = q_s(t) \quad t \geq 0 \quad r = R \quad (\text{A.2c})$$

The analytical solution for the set of equations is (),

$$q(r,t) = \frac{2}{Rr} \sum_{i=1}^{\infty} e^{-i^2 \pi^2 \frac{D_s}{R^2} t} \sin \frac{i\pi r}{R} \left[\int_0^R r' q_0(r') \sin \frac{i\pi r'}{R} dr' - i\pi D_s (-1)^i \int_0^t e^{i^2 \pi^2 \frac{D_s}{R^2} \lambda} q_s(\lambda) d\lambda \right] \quad (\text{A.3})$$

where q_s is the solid phase loading at the carbon particle surface $q(r = R, \lambda)$, and it is related to the bulk solution concentration by the isotherm equilibrium, which in our case is the Freundlich isotherm,

$$q_s(\lambda) = KC(\lambda)^{\frac{1}{n}} \quad (\text{A.4})$$

The average loading in one carbon particle at any given time t , $q_t(t)$ can be defined as,

$$\frac{4}{3} \pi R^3 q_t(t) = \iiint_V q(r,t) dV = 4\pi \int_0^R q(r,t) r^2 dr \quad (\text{A.5})$$

Even though $q_t(t)$ cannot be measured directly, it is related to the bulk solution

concentration that can be easily monitored:

$$q_t(t) = \frac{C_0 - C(t)}{C_c} \quad (\text{A.6})$$

For carbons with a evenly distributed loading, $q_0(r) = q_0$, the $q_t(t)$ is:

$$q_t(t) = \frac{6}{R^2} \sum_{i=1}^{\infty} e^{-i^2 \pi^2 \frac{D_s}{R^2} t} \left[\frac{R^2}{i^2 \pi^2} q_0 + D_s \int_0^t e^{i^2 \pi^2 \frac{D_s}{R^2} \lambda} q_s(\lambda) d\lambda \right] \quad (\text{A.7})$$

Equation set (A.4), (A.6) and (A.7) can then be solved numerically.

MATLAB PROGRAM CODE

The solution was formulated using MATLAB program, and the code, called “HSDM_GUI” is provided below.

```
%=====
% Initialization code - DO NOT EDIT %
%=====
function varargout = HSDM_GUI(varargin)
% HSDM_GUI M-file for HSDM_GUI.fig
%   HSDM_GUI, by itself, creates a new HSDM_GUI or raises the
existing
%   singleton*.
%
%   H = HSDM_GUI returns the handle to a new HSDM_GUI or the handle
to
%   the existing singleton*.
%
%   HSDM_GUI('CALLBACK',hObject,eventData,handles,...) calls the
local
%   function named CALLBACK in HSDM_GUI.M with the given input
arguments.
%
%   HSDM_GUI('Property','Value',...) creates a new HSDM_GUI or
raises
%   the existing singleton*. Starting from the left, property value
pairs are
%   applied to the GUI before HSDM_GUI_OpeningFcn gets called. An
%   unrecognized property name or invalid value makes property
application
%   stop. All inputs are passed to HSDM_GUI_OpeningFcn via varargin.
%
%   *See GUI Options on GUIDE's Tools menu. Choose "GUI allows only
one
%   instance to run (singleton)".
%
% See also: GUIDE, GUIDATA, GUIHANDLES
```

```

% Edit the above text to modify the response to help HSDM_GUI

% Last Modified by GUIDE v2.5 24-Mar-2010 13:11:15

% Begin initialization code - DO NOT EDIT
gui_Singleton = 1;
gui_State = struct('gui_Name',       mfilename, ...
    'gui_Singleton',  gui_Singleton, ...
    'gui_OpeningFcn', @HSDM_GUI_OpeningFcn, ...
    'gui_OutputFcn',  @HSDM_GUI_OutputFcn, ...
    'gui_LayoutFcn',  [], ...
    'gui_Callback',    []);
if nargin && ischar(varargin{1})
    gui_State.gui_Callback = str2func(varargin{1});
end

if nargout
    [varargout{1:nargout}] = gui_mainfcn(gui_State, varargin{:});
else
    gui_mainfcn(gui_State, varargin{:});
end
% End initialization code - DO NOT EDIT

%=====
% --- Executes just before HSDM_GUI is made visible. %
%=====
function HSDM_GUI_OpeningFcn(hObject, eventdata, handles, varargin)

% Choose default command line output for HSDM_GUI
handles.output = hObject;

initialize_gui(hObject, handles, false);

% retrieve updated handles
handles = guidata(hObject);

% Update handles structure
guidata(hObject, handles);

% UIWAIT makes HSDM_GUI wait for user response (see UIRESUME)
% uiwait(handles.figure1);

%=====
% --- Outputs from this function are returned to the command line. %
%=====
function varargout = HSDM_GUI_OutputFcn(hObject, eventdata, handles)

% Get default command line output from handles structure
varargout{1} = handles.output;

```

```

%=====
% --- Executes on button press in Clear. %
%=====
function Clear_Callback(hObject, eventdata, handles)

% The Clear button clears the lines in the plot, but leaves the dots
that
% showing the measurement data.
% It also clears the data in the handles.data so the next plot will
start
% anew.

% set the flags to indicate future plot will be new one
handles.data.newplot=true;
handles.data.replot=false;

% clear out current model data
handles.data.nplot=0;
handles.data.nplot_current=0;
handles.data.x={};
handles.data.y={};
handles.data.Ds=[];

% get measurement data from the table
data = get(handles.data_table, 'Data');
xm = data(:,1);
ym = data(:,2);

% Determine if to plot in linear or log scale, then plot the data
% This effectively clears out the original plot
if handles.data.plotlog
    h=semilogy(xm,ym);
else
    h=plot(xm,ym);
end

% Add x y labels
xlabel('Time (min)', 'FontSize', 16);
ylabel('C_{norm}', 'FontSize', 16);
% Set font size of axes numbers
set(gca, 'FontSize', 14);

% set Mark style of the measured data
set(h(1), 'LineStyle', 'o', 'MarkerFaceColor', 'k', 'MarkerEdgeColor', 'k');

% Add legend named 'Data'
legend('Data');

% Set the Clear button to gray since there is no line to clear now
set(handles.Clear, 'String', 'Clear', 'ForegroundColor', [.8 .8 .8]);

% update the
guidata(hObject, handles);

```

```

%=====
% Initialize GUI %
%=====
function initialize_gui(hObject, handles, isreset)

% Default parameter values
% They are listed here for reference only
% Cc = 3.0;      %carbon dose, mg/L
% Ds = 1.1e-11; %initial guess of Ds, in cm^2/min
% Co = 15;       %ug/L atrazine
% q0 = 0;        % ug/mg
% R  = 0.0003;   % radius, cm
% K  = 26.5;     % Freundlich K value
% kn = 0.41;     % Freundlich 1/n value

% Set initial values for some parameters
handles.data.plotlog = false;
handles.data.newplot = false;
handles.data.nplot = 0;
handles.data.nplot_current=0;
handles.data.x={};
handles.data.y={};
handles.data.xm=0;
handles.data.ym=0;
handles.data.replot = false;

% Set Clear button color to gray
set(handles.Clear, 'String', 'Clear', 'ForegroundColor', [.8 .8 .8]);

% save current directory as the data directory.
% It will be changed if user selects a different directory through GUI
datadir = pwd;

% Save the selected directory to handles.param
handles.param.datadir=datadir;

% Update the text display of data directory
set(handles.datadir, 'String', handles.param.datadir);

% refresh data and parameter using first data file in current directory
refresh_file(hObject, handles);

% retrieve updated handles
handles = guidata(hObject);

% Set up line color, width and style for each line.
% Up to 16 lines are defined
linewidth{1} = 1.5; linestyle{1} = '-'; linecolor{1} = [0 0 1];
linewidth{2} = 1.5; linestyle{2} = '-'; linecolor{2} = [0 1 0];
linewidth{3} = 1.5; linestyle{3} = '-'; linecolor{3} = [1 0 0];
linewidth{4} = 1.5; linestyle{4} = '-'; linecolor{4} = [0 1 1];
linewidth{5} = 1.5; linestyle{5} = '-'; linecolor{5} = [1 0 1];
linewidth{6} = 1.5; linestyle{6} = '-'; linecolor{6} = [0.49 1 0.83];
linewidth{7} = 1.5; linestyle{7} = '-'; linecolor{7} = [.5 .5 .5];

```

```

linewidth{8} =1.5; linestyle{8} ='-'; linecolor{8} =[1 .62 .40];
linewidth{9} =1.5; linestyle{9} ='-'; linecolor{9} =[0 0 1];
linewidth{10}=1.5; linestyle{10}='--'; linecolor{10}=[0 1 0];
linewidth{11}=1.5; linestyle{11}='--'; linecolor{11}=[1 0 0];
linewidth{12}=1.5; linestyle{12}='--'; linecolor{12}=[0 1 1];
linewidth{13}=1.5; linestyle{13}='--'; linecolor{13}=[1 0 1];
linewidth{14}=1.5; linestyle{14}='--'; linecolor{14}=[0.49 1 0.83];
linewidth{15}=1.5; linestyle{15}='--'; linecolor{15}=[.5 .5 .5];
linewidth{16}=1.5; linestyle{16}='--'; linecolor{16}=[1 .62 .40];

% Save the line style setting into handles.data
% Set the maximum lines that can be plotted to be the maximum of number
of
% line styles defined
handles.data.linewidth=linewidth;
handles.data.linestyle=linestyle;
handles.data.linecolor=linecolor;
handles.data.nplotmax=length(linewidth);

% update handles in GUI
guidata(hObject, handles);

%=====
% --- Executes on button press in plot. %
%=====
function plot_Callback(hObject, eventdata, handles)
% hObject      handle to plot (see GCBO)
% eventdata    reserved - to be defined in a future version of MATLAB
% handles      structure with handles and user data (see GUIDATA)

% Determine if this is just a replot using current data
% If so, no calculation is needed.  Otherwise calculate model with
current
% parameters.
replot = handles.data.replot;
if (~replot)
    % calculate using model
    Calculate(hObject,handles);
    % retrieve updated handles
    handles = guidata(hObject);
end

% number of lines in current plot
nplot = handles.data.nplot;
% index of the newest line plotted previously
nplot_current = handles.data.nplot_current;

% Since the initial time steps vary with different set of parameters in
% each model calculation, the (time,C_nom) pair has different lengths
for
% different parameters.  The variables x and y are cell arrays that
store
% these model simulations.

```

```

% add new data to handles if there is a newly added model calculation
if (~replot)
    if handles.data.newplot
        % if this is a new plot, clear original model data and start
        anew
            nplot = 1;
            nplot_current=1;
            clear x y;
        else
            % if this is a model simulation to be added to existing lines
            % increase the count 'nplot', retrieve current data, then add
            the
                % new one.
                if nplot < handles.data.nplotmax
                    % increase the line count if the maximum is not reached
                    nplot = nplot+1;
                    nplot_current=nplot_current+1;
                else
                    % if the maximum number of lines are reached, replace the
                    oldest
                        % with the newest one. The most current one before this is
                        % indicated by nplot_current. So nplot_current+1 is the
                        oldest
                            % one to replace. If nplot_current reaches maximum, then
                            % replace the 1st one.
                            if nplot_current==handles.data.nplotmax
                                nplot_current=1;
                            else
                                nplot_current=nplot_current+1;
                            end
                        end
                    % retrieve original data
                    x=handles.data.x;
                    y=handles.data.y;
                end

            % add current data
            x{nplot_current} = handles.data.time;
            y{nplot_current} = handles.data.C_nom;

            % update data in handle
            handles.data.newplot = false;
            handles.data.nplot = nplot;
            handles.data.nplot_current = nplot_current;
            handles.data.x=x;
            handles.data.y=y;
            handles.data.Ds(nplot_current)=handles.param.Ds;

        end

    %%%% Start Plotting %%%%

    % get measurements

```

```

data = get(handles.data_table, 'Data');
xm = data(:,1);
ym = data(:,2);

% get model data
x = handles.data.x;
y = handles.data.y;

% plot measurement
if handles.data.plotlog
    h = semilogy(xm,ym);
else
    h = plot(xm,ym);
end
% set style of the measured data
set(h, 'LineStyle', 'none', 'Marker', 'o', 'MarkerFaceColor', 'k', 'MarkerEdgeColor', 'k');

% add lines to plot from model data, using pre-defined line styles
for i=1:nplot
    line(x{i},y{i}, ...
        'LineStyle',handles.data.linestyle{i}, ...
        'Color', handles.data.linecolor{i}, ...
        'LineWidth',handles.data.linewidth{i});
end

% Add x and y labels, and set axes font size
set(gca, 'FontSize',12);
xlabel('Time (min)', 'FontSize',16);
ylabel('C_{norm}', 'FontSize',16);
set(gca, 'FontSize',14);

% calculate the errors
errs=zeros(1,nplot);
for i=1:nplot
    errs(i)=getErr(x{i},y{i},xm,ym);
end

% plot the rms error in the legend
% highlight the line with minimum error using red text
legend_labels=cell(nplot+1,1);
legend_labels{1}='Data';
for i=1:nplot
    legend_labels{i+1}=sprintf('Ds=%8.3e\nErr=%7.5f',handles.data.Ds(i),errs(i));
end
[dummy,imin]=min(errs);
[LEGH,OBJH,OUTH,OUTM]=legend(legend_labels);

set(OBJH(imin+1), 'Color', 'r');

% Now there are lines plotted, so we should activate the 'Clear' button
by
% setting it to red.
set(handles.Clear, 'String', 'Clear', 'ForegroundColor', 'r');

```

```

% Now the plot is current, so we set 'replot' to be true. Next time
the
% button 'Plot' is pressed, it will only replot without model
calculation
handles.data.replot=true;

guidata(hObject, handles);

%=====
% Model Calculation %
%=====
function Calculate(hObject, handles)
%
% calculate C_nom and C
%

% retrieve parameters
q0      = handles.param.q0;
Co      = handles.param.Co;
Cc      = handles.param.Cc;
K       = handles.param.K;
kn      = handles.param.kn;
R       = handles.param.R;
t_final = handles.param.t_final;
Ds      = handles.param.Ds;

G=6*Ds/(R^2);

% Determine how many terms are needed for the summation.
% The summation is essentially sum(1/n^2) for n=1 to Inf. The exact
% value of this summation is pi^2/6. The error of the summation is
% proportional to (1/N). For N=5000;, 1-sum(1/(1:n)^2)*6/pi=1.2e-4.
%
n=5000; % for summation i=1 to infinity
Bi=(1:n).^2*pi^2*Ds/(R^2);

del_tmax = 2; % define maximum time step

it=1; % current step number

% determine initial time step, in min
del_t = min([1e-11/Ds,del_tmax]); %time step, at most del_tmax min, can
be smaller when Ds is large

t(it)=0;

I_i(it,:) = zeros(1,n);

C_ans(it) = Co;

while t(it)<t_final

    it=it+1;

```

```

t(it)=t(it-1)+del_t;

alpha_i = (1-exp(-Bi*del_t))./(2*Bi);
alpha = sum(alpha_i);

gamma_i = exp(-Bi*del_t) .* I_i(it-1,:);
gamma = sum(gamma_i);

Q_i = exp(-Bi*t(it)) * q0 ./ Bi;
Q(it) = sum(Q_i);

C_guess=[Co 0];
C_ans(it) = fzero(@(C)C+Cc*G*(Q(it)+K*(gamma+alpha*(C^kn+C_ans(it-1)^kn)))-Co-Cc*q0,C_guess);

I_i(it,:) = gamma_i + alpha_i*(C_ans(it)^kn + C_ans(it-1)^kn);

I(it)=sum(I_i(it,:));

% determine next time step according to the change of C
% only double time step when the change is less than 10%
if (abs(C_ans(it)-C_ans(it-1))/C_ans(it-1) < 0.1)
    del_t=min(del_t*2,del_tmax);
end

end

% Save results in handles
handles.data.I = I;
handles.data.C_nom = C_ans/Co;
handles.data.C = C_ans;
handles.data.qt = G*(K*I+Q);
handles.data.qtc = G*(K*I);

handles.data.time=t;

guidata(hObject, handles);

%=====
% --- Executes on selection change in fileSelect. %
%=====
function fileSelect_Callback(hObject, eventdata, handles)
% hObject    handle to fileSelect (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: contents = get(hObject,'String') returns fileSelect contents
as cell array
%         contents{get(hObject,'Value')} returns selected item from
fileSelect
datadir = handles.param.datadir;

```

```

% fn = get(handles.fileSelect, 'String');
% if ~isempty(fn)
%
%     % get current selection
%     i = get(handles.fileSelect, 'Value');
%
%     % read in parameters
%     fid=fopen([datadir '/' fn{i}], 'r');
%     Co=fscanf(fid, '%f', 1)*1e3; fgetl(fid);
%     Cc=fscanf(fid, '%f', 1)*1e3; fgetl(fid);
%     Ds=fscanf(fid, '%f', 1); fgetl(fid);
%     K=fscanf(fid, '%f', 1); fgetl(fid);
%     kn=fscanf(fid, '%f', 1); fgetl(fid);
%     R=fscanf(fid, '%f', 1); fgetl(fid);
%     t_final=fscanf(fid, '%f', 1); fgetl(fid);
%     q0=fscanf(fid, '%f', 1); fgetl(fid);
%
%     % read rest of the data file in as measurements
%     data=fscanf(fid, '%f', [2 inf]);
%     data=data';
%     fclose(fid);
%
%     handles.param.q0=q0;
%     handles.param.Co=Co;
%     handles.param.Cc=Cc;
%     handles.param.K=K;
%     handles.param.kn=kn;
%     handles.param.R=R;
%     handles.param.t_final=t_final;
%     handles.param.Ds=Ds;
%
%     % update data list in the table
%     set(handles.data_table, 'Data', data);
%
%     % construct matrix of parameters to update the parameter table
%     param=[q0;Co;Cc;K;kn;R;t_final;Ds];
%     set(handles.param_table, 'Data', param);
%
% end

refresh_data(hObject, handles);
% retrieve updated handles
handles = guidata(hObject);

handles.data.newplot = 1;
handles.data.replot = false;

guidata(hObject, handles);

%=====
% --- Executes during object creation, after setting all properties. %
%=====
function fileSelect_CreateFcn(hObject, eventdata, handles)
% hObject    handle to fileSelect (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB

```

```

% handles      empty - handles not created until after all CreateFcns
called

% Hint: popupmenu controls usually have a white background on Windows.
%      See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
get(0,'defaultUiControlBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

%=====
%=====
function plotScale_Callback(hObject, eventdata, handles)

% Swith between log scale and linear scale when this button is pressed
if (handles.data.plotlog)
    % switch to linear scale
    set(hObject, 'String', 'Change to Log Scale');
    handles.data.plotlog = false;
else
    % switch to log scale
    set(hObject, 'String', 'Change to Linear Scale');
    handles.data.plotlog = true;
end
handles.data.replot=true;

guidata(hObject,handles);

% Call plot to re-plot using current scale setting
plot_Callback(hObject, eventdata, handles)

%=====
%=====
function Save_Callback(hObject, eventdata, handles)

% Open a diaglog box for saving the current model data and parameters
% The default file name to save is the same as the input data file with
the
% extensiion changed from 'txt' to 'out', in the same directory.

% get all file names listed in the menu
fn = get(handles.fileSelect,'String');
if ~isempty(fn)
    % get current file selection
    i = get(handles.fileSelect,'Value');
    fnin = fn{i};
else
    % use the following name is there is no input file name available.
    % this usually shouldn't happen.
    fnin = 'model_output';
end

% change the output file name extension from 'txt' to 'out'

```

```

fnout = regexp(fnin, '.txt', '.out');

% obtain current data file directory
datadir = get(handles.datadir, 'String');

% open a dialogue window asking file name to save model result
[fnout,path] = uiputfile('', 'Save Parameter and Model Result', [datadir
 '/' fnout]);

% If the diaglog box is canceled, no file name is provided. Then
simply
% return to previous function.
if fnout==0
    return;
end

fid = fopen([path fnout], 'w');

q0      = handles.param.q0;
Co      = handles.param.Co;
Cc      = handles.param.Cc;
K       = handles.param.K;
kn      = handles.param.kn;
R       = handles.param.R;
t_final = handles.param.t_final;
Ds      = handles.param.Ds;

% save parameters
fprintf(fid, 'Co=\t%g\n', Co/1e3);
fprintf(fid, 'Cc=\t%g\n', Cc/1e3);
fprintf(fid, 'Ds=\t%g\n', Ds);
fprintf(fid, 'K=\t%g\n', K);
fprintf(fid, 'kn=\t%g\n', kn);
fprintf(fid, 'R=\t%g\n', R);
fprintf(fid, 't_final=\t%g\n', t_final);
fprintf(fid, 'g0=\t%g\n', q0);

% save model results
% using tab as delimiter for easy import into Excel
fprintf(fid, 'Time (min)\tC_nom\tC\tqt\n');
for i=1:length(handles.data.time)

fprintf(fid, '%g\t%g\t%g\t%g\n', handles.data.time(i), handles.data.C_nom(
i), handles.data.C(i), handles.data.qt(i));
end
fclose(fid);

%=====
% Update parameters when they are changed in the param table %
%=====
function param_table_CellEditCallback(hObject, eventdata, handles)

data=get(hObject, 'Data');

handles.param.q0      = data(1);

```

```

handles.param.Co      = data(2);
handles.param.Cc      = data(3);
handles.param.K       = data(4);
handles.param.kn      = data(5);
handles.param.R       = data(6);
handles.param.t_final = data(7);
handles.param.Ds      = data(8);

% The plot should be updated when parameters are changed
handles.data.replot = false;

guidata(hObject,handles);

% --- Executes during object creation, after setting all properties.
function param_table_CreateFcn(hObject, eventdata, handles)
% hObject    handle to param_table (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns
called

%=====
% Button to select data directory %
%=====
function dirSelect_Callback(hObject, eventdata, handles)

% Press this button brings up a dialog, asking for the directory where
the
% data files are located

% Display dialog asking for data directory
datadir=uigetdir;

if datadir

    % Save the selected directory to handels.param
    handles.param.datadir=datadir;

    % Update the text display of data directory
    set(handles.datadir, 'String', handles.param.datadir);

    refresh_file(hObject, handles);

    % retrieve updated handles
    handles = guidata(hObject);

end

guidata(hObject,handles);

%=====
% Update data file list using currently selected data directory %
%=====

```

```

function refresh_file(hObject, handles)
%
% retrieve '*.txt' files in the current data directory
% and list
%

% Look for '*.txt' files in current data directory
fns = dir([handles.param.datadir '/*.txt']);

if ~isempty(fns)
    % create pop up menu filled with data file names
    popmenu = cell(size(fns));
    for i=1:length(fns)
        popmenu{i}=fns(i).name;
    end
    set(handles.fileSelect, 'String', popmenu);
    % refresh parameter and data tables
    refresh_data(hObject, handles);
    % retrieve updated handles
    handles = guidata(hObject);
else
    set(handles.fileSelect, 'String', {'Data File List Empty'});
    set(handles.data_table, 'Data', []);

end

guidata(hObject, handles);

%=====
% Update parameters and data using currently selected data file %
%=====
function refresh_data(hObject, handles)
%
% The handles.fileSelect is first checked to see if there are valid
files
% and which one is currently selected. If none, then the data list and
% cleared. The parameter list is not touched.
%

% get all file names listed in the menu
fn = get(handles.fileSelect, 'String');

if ~isempty(fn)

    % get current file selection
    i = get(handles.fileSelect, 'Value');

    % read in parameters
    fid = fopen([handles.param.datadir '/' fn{i}], 'r');
    Co = fscanf(fid, '%f', 1)*1e3; fgetl(fid);
    Cc = fscanf(fid, '%f', 1)*1e3; fgetl(fid);
    Ds = fscanf(fid, '%f', 1); fgetl(fid);
    K = fscanf(fid, '%f', 1); fgetl(fid);
    kn = fscanf(fid, '%f', 1); fgetl(fid);

```

```

R          = fscanf(fid,'%f',1); fgetl(fid);
t_final    = fscanf(fid,'%f',1); fgetl(fid);
q0         = fscanf(fid,'%f',1); fgetl(fid);

% read the rest of the data as measurements
data = fscanf(fid,'%f',[2 inf]);
data = data';
fclose(fid);

% save parameters into handles
handles.param.q0 = q0;
handles.param.Ds = Ds;
handles.param.Cc = Cc;
handles.param.Co = Co;
handles.param.R  = R;
handles.param.K  = K;
handles.param.kn = kn;
handles.param.t_final = t_final;

% Update measurement data in data table for display
set(handles.data_table,'Data',data);

% Construct matrix of parameters and use it to update the parameter
table
param=[q0;Co;Cc;K;kn;R;t_final;Ds];
set(handles.param_table,'Data',param);

else

    set(handles.data_table,'Data',[]);

end

guidata(hObject,handles);

%=====
% Find the bset fit by varying Ds to minimize the error %
%=====
function bestFit_Callback(hObject, eventdata, handles)

% get current value of Ds
Ds = handles.param.Ds;

% change the button label to indicate that the minimum search is still
% working on it
set(handles.bestFit,'String','working ...');

% save current figure window so we can come back to it after the
following
% fminsearch function creating another plot
maingui = gcf;

options = optimset('Display','none','TolFun',1e-5,'TolX',1e-
5,'PlotFcns',@optimplotfval);

```

```

% create a function handle to the error function
fh = @(Ds) myerrfun(Ds,hObject,handles);

% search for the minimum error with initial value being current Ds
Dsmin = fminsearch(fh,Ds,options);

% After the search is done, close current figure. Compare it to the
% maingui to make sure the main gui is not accidentally closed. This
% could happen if the search function does not create its own figure.
if (gcf ~= maingui)
    close(gcf);
end

handles.param.Ds = Dsmin;

% Now the plot is needs to be updated, so we set 'replot' to be false.
% The plot_Callback function is called to plot again. This is
equivalent
% to pressing the 'Plot'. It will add an additional line
handles.data.replot=0;
guidata(hObject, handles);

% switch back to the main GUI before plotting the result
figure(maingui);

handles.param.Ds=Dsmin;
param = get(handles.param_table,'Data');
param(8)=Dsmin;
set(handles.param_table,'Data',param);

% change the button label back after this is done.
set(handles.bestFit,'String','BestFit');

plot_Callback(hObject, eventdata, handles)

% retrieve updated handles
% handles = guidata(hObject);

%=====
% Error fuction used for fminbnd to find Ds that minimize error %
%=====
function err = myerrfun(Ds,hObject,handles)

% get current Ds
handles.param.Ds=Ds;

% calculate using model
Calculate(hObject,handles);
% retrieve updated handles
handles = guidata(hObject);

x0 = handles.data.time;

```

```

y0 = handles.data.C_nom;

% get measurements
data = get(handles.data_table, 'Data');
xm = data(:,1);
ym = data(:,2);

err=getErr(x0,y0,xm,ym);

% fprintf(1,'Ds=%12.5e  err=%10.7f \n',Ds,err);

function err=getErr(x0,y0,xm,ym)

% discard points where y0 doesn't change with x0
noc = ( abs(y0(2:end)-y0(1:end-1)) < 1e-6 );
x0 = x0(~[0 noc]);
y0 = y0(~[0 noc]);

% interpolate model data to measurement data in both x and y
y1 = interp1(x0,y0,xm,'pchip');
x1 = interp1(y0,x0,ym,'pchip');

% range in x and y
rx=max(xm)-min(xm);
ry=max(ym)-min(ym);

% normalize x and y differences using their ranges
dx=abs(x1-xm)/rx;
dy=abs(y1-ym)/ry;

dx2dy2=dx.^2+dy.^2;

% the shortest distance of measurement to model curve
d = sqrt( (dx.*dy).^2./dx2dy2 );
d(dx2dy2==0)=0;

% define the error as the rms of d
err = sqrt( mean(d.^2) );

```

HOW TO RUN THE MODEL

The simulation window is shown in Figure A.1, which can be activated by executing “HSDM_GUI” command in the command window of the MATLAB program.

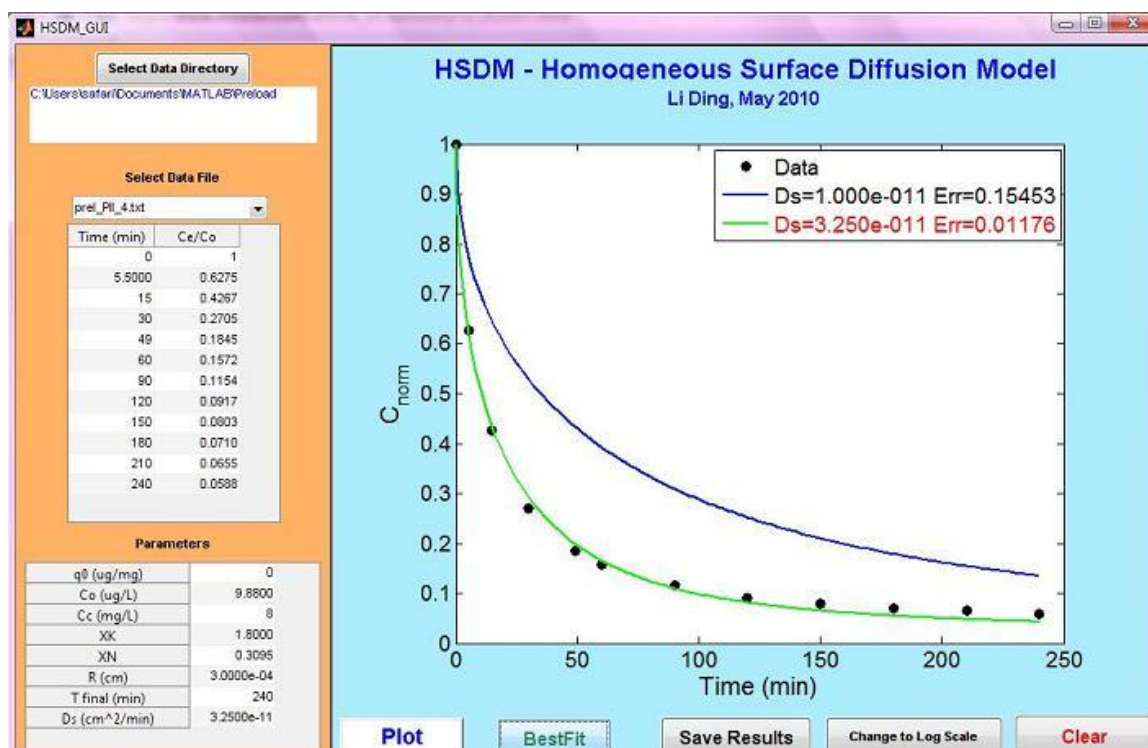


Figure A.1 Example work window of HSDM_GUI model in MATLAB

The orange area in the left is the input region consisting of three blocks. The top block is data directory, which defines the directory where the data files are located. By pressing “Select Data Directory” the data file pathway can be changed in the pop-up window. A data file is a text file that contains experimental data as well as adsorption parameters. An example for data files is shown below in Figure A.2. Right below the “data directory” block is the drop-down menu in which a data file can be selected to work on. Once a data file is selected, its experimental data as well as adsorption parameters will be read and displaced in the middle and bottom blocks, as shown in Figure A.1.

0.00988	/C0 (initial concentration in mg/L)
8.0E-3	/CCONC (carbon concentration in g/l)
3E-11	/DS (surface diffusion coefficient in cm ² /min)
1.8	/XK (Freundlich K value in (mg/g)(ug/l) ^{-1/n})
0.3095	/XN (Freundlich 1/n)
3.0E-04	/RADP (particle radius in cm)
240	/TFINAL (final time in min)
0	/q0
0	1
5.5	0.627487636
15	0.426702004
30	0.270474928
49	0.184457749
60	0.157220947
90	0.115407369
120	0.091743771
150	0.080314253
180	0.070990795
210	0.06550084
240	0.058804042

Figure A.2 Example of the data file for the “HSDM_GUI” program

To the right is the blue output region, where experimental data as well as model simulation using the parameters from left will be displayed in the concentration vs. time plot once the “Plot” button is clicked. Shown in the upper right corner of the plot, legends display values for the surface diffusion coefficient, D_s , and the error of the fit.

The initial guess usually will not land on a good fit so parameters in the left can be changed by simply typing in new values in the simulation window. The original numbers in the input file will not be altered. A simulation curve using the new set of parameters will be generated by pressing the “Plot” button again and be added next to the previous curves for easy comparison and fit evaluation (Figure A.2), until the “Clear” button is pressed. Instead of manual trial and error method to look for the best fit D_s , the best fit can be carried out automatically by pressing the “BestFit” button. The fitting window looks like the example in Figure A.3. The X-axis is number of iterations, and Y-axis is the error from each fitting iteration. The fitting continues as the error gets smaller and stops when the minimum value for the error is reached. The model simulation with the

best fit D_s will then be plotted next to the initial guess curve (Figure A.1).

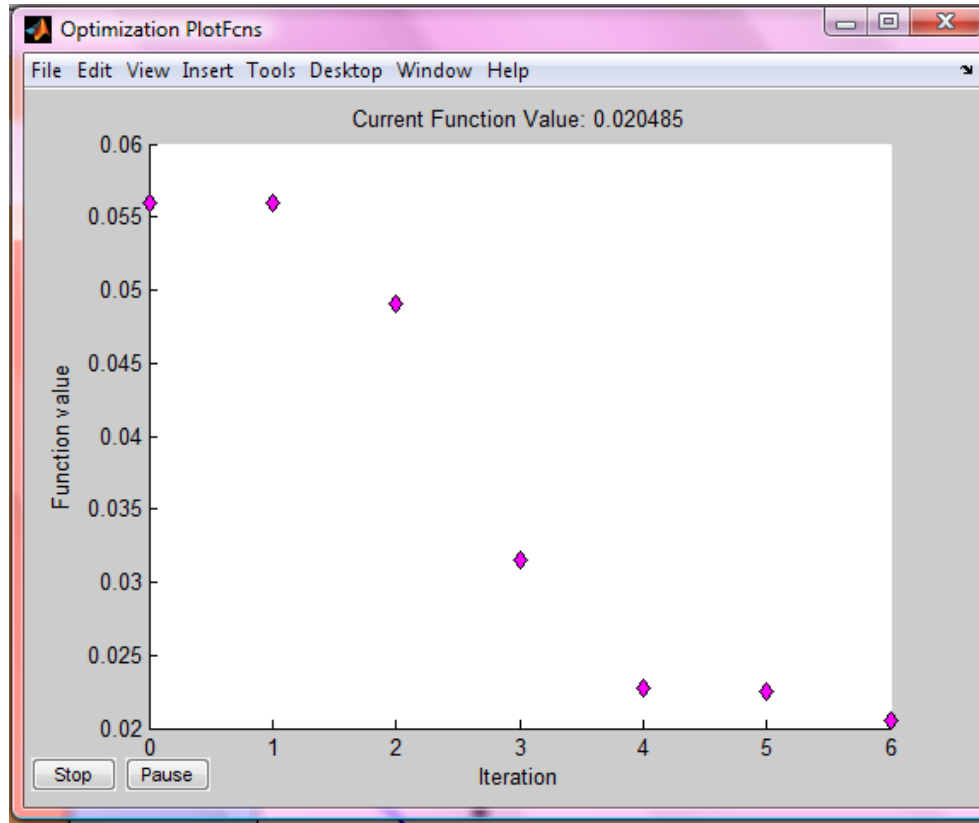


Figure A.3 Optimazation windown of the “HSDM_GUI” program (data shows decreasing fitting errors as the number of iteration increases)

The other two buttons in the output window is “change to log scale”, which switches between linear scale and semi-log scale for y axis, and “Save result” button, which saves the set of parameters that gives the best fit and the fitted result to a text file. The model simulation using this set of parameters will also be saved to the output file, which facilitate data transfer to other spreadsheet programs such as Microsoft Office Excel.

APPENDIX B

EXPERIMENTAL DATA

ADSORPTION ISOTHERMS

Single-solute Atrazine Adsorption Isotherms

PAC = SA UF; Water = DDI; Atrazine batch = VIII, $C_{0,\text{atrazine}} = 292.6 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	4.2	10.7	66.8
400	5.5	5.3	52.3
900	6.8	3.2	42.7
400	9.0	1.3	32.4
400	12.0	0.78	24.3
400	21.3	0.20	13.8
400	25.0	0.14	11.7
400	33.8	0.07	8.67

PAC = SA UF; Water = DDI; Atrazine batch = R, $C_{0,\text{atrazine}} = 202.8 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	0.89	72.0	147.2
900	2.33	17.0	79.7
900	4.11	2.80	48.7
400	6.50	0.80	31.1
400	15.3	0.18	13.3
200	21.0	0.12	9.65
200	30.0	0.075	6.76
200	39.0	0.048	5.20
200	50.5	0.043	4.02

PAC = SA UF; Water = DDI; Atrazine batch = S, $C_{0,\text{atrazine}} = 364.2 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	0.78	196.5	215.7
900	1.7	137.3	136.2
900	3.0	37.9	108.8
900	4.8	7.73	74.6
400	7.0	3.82	51.5
400	9.5	1.19	38.2
400	19.5	0.12	18.7
400	33.8	0.034	10.8
400	47.8	0.027	7.6

PAC = SA UF; Water = DDI; Atrazine batch = V

Volume (ml)	C_c (mg/L)	C_0 ($\mu\text{g/L}$)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	2.9	49.4	0.48	16.9
900	1.4	49.4	2.0	32.8
900	1.0	98.7	22.6	76.1
900	2.1	49.4	0.78	23.0
400	2.3	98.7	3.23	42.5
400	3.1	197.5	8.96	60.3
400	2.3	197.5	16.0	80.7

PAC = SA UF; Water = DDI; Atrazine batch = X; $C_{0,\text{atrazine}} = 213.2 \mu\text{g}$

Volume (ml)	C_c (mg/L)	C_0 ($\mu\text{g/L}$)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	1.4	213.2	42.9	117.9
900	2.3	213.2	16.4	84.3
900	2.9	213.2	8.0	71.0
900	3.7	213.2	4.8	56.8
900	4.1	96.6	0.55	23.4
900	9.6	106.6	0.13	11.1

PAC = SA Super; Water = DDI; Atrazine batch = T1; $C_{0,\text{atrazine}} = 110.5 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
2000	1.5	6.18	71.9
900	2.6	1.93	42.5
900	4.0	0.89	27.4
400	5.5	0.37	20.0
400	7.3	0.22	15.2

PAC = SA Super; Water = DDI; Atrazine batch = V; $C_{0,\text{atrazine}} = 94.9 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	1.6	5.74	57.3
400	8.3	0.093	11.5

PAC = W35; Water = DDI; Atrazine batch = T1; $C_{0,\text{atrazine}} = 110.5 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
2000	1.1	16.7	85.2
900	2.4	3.68	43.7
900	3.1	1.29	35.1
400	4.8	0.83	23.1
400	6.5	0.25	17.0

PAC = W35; Water = DDI; Atrazine batch = V; $C_{0,\text{atrazine}} = 94.9 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	2.0	4.91	45.0
400	8.3	0.13	11.5

PAC = W20; Water = DDI; Atrazine batch = VIII; $C_{0,\text{atrazine}} = 45.0 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	1.8	19.3	14.4
900	4.1	1.82	10.5
400	8.0	0.54	5.6
400	11.5	0.24	3.9
400	15.5	0.16	2.9
200	21.5	0.17	2.1
200	25.5	0.10	1.8
200	34.5	0.10	1.3

PAC = W20; Water = DDI; Atrazine batch = V; $C_{0,\text{atrazine}} = 94.9 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	2.6	34.9	23.5
900	5.9	3.5	15.5
400	9.8	0.82	9.6
400	15.5	0.28	6.1
400	20.0	0.18	4.7
400	30.3	0.13	3.1

PAC = Pellet II; Water = DDI; Atrazine batch = V; $C_{0,\text{atrazine}} = 201.4 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	1.3	107	70.8
900	1.9	56.1	76.9
900	3.0	18.3	61.0
900	3.3	19.6	54.5
400	5.3	6.1	37.2
400	7.3	4.2	27.2
400	10.5	1.1	19.1
200	15.5	0.33	13.0
200	25.0	0.09	8.0

Atrazine Adsorption Isotherms in the Presence of Competition

PAC = SA UF; Water = CWW; Atrazine batch = VIII; $C_{0, \text{NOM}} = 7.0 \text{ mg DOC/L}$;
 $C_{0, \text{atrazine}} = 10.6 \text{ } \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	2.1	1.62	4.24
900	4.2	0.57	2.37
900	6.0	0.20	1.73
400	8.3	0.10	1.27
400	9.8	0.057	1.08
400	14.8	0.025	0.72
400	20.0	0.009	0.53
400	25.5	0.005	0.41
200	30.0	0.009	0.35

PAC = SA UF; Water = CWW; Atrazine batch = VIII; $C_{0, \text{NOM}} = 7.0 \text{ mg DOC/L}$;
 $C_{0, \text{atrazine}} = 60.5 \text{ } \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	1.7	30.7	17.9
400	6.8	1.94	8.64
400	9.5	0.72	6.29
400	15.0	0.24	4.02
400	19.5	0.12	3.10
400	24.0	0.080	2.52
200	30.0	0.040	2.02

PAC = SA Super; Water = CWW; Atrazine batch = V; $C_{0, \text{NOM}}$ = mg DOC/L;
 $C_{0, \text{atrazine}} = 9.44 \text{ } \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	3.3	1.38	2.42
900	6.0	0.36	1.51
400	10.3	0.11	0.91
400	15.8	0.013	0.60

PAC = SA Super; Water = CWW; Atrazine batch = V; $C_{0, \text{NOM}}$ = mg DOC/L;
 $C_{0, \text{atrazine}} = 48.7 \text{ } \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	2.9	16.8	11.1
900	6.0	3.23	7.58
400	10.3	0.81	4.67
400	15.5	0.28	3.13
400	19.3	0.13	2.52
400	25.8	0.062	1.89

PAC = W20; Water = CWW; Atrazine batch = V; $C_{0, \text{NOM}}$ = mg DOC/L
 $C_{0, \text{atrazine}}$ = 9.44 $\mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	3.00	7.19	0.75
900	6.44	3.58	0.91
400	10.75	1.76	0.71
400	20.75	0.31	0.44
400	28.50	0.07	0.33

PAC = W20; Water = CWW; Atrazine batch = V; $C_{0, \text{NOM}}$ = mg DOC/L; $C_{0, \text{atrazine}}$ = 48.7 $\mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	2.9	38.7	3.48
900	7.1	24.2	3.45
400	10.8	14.1	3.22
400	14.8	6.40	2.87
400	21.5	2.08	2.17
400	30.0	0.91	1.59

PAC = W20; Water = CWW; Atrazine batch = VIII; $C_{0, \text{NOM}}$ = mg DOC/L, $C_{0, \text{atrazine}}$ = 44.3 $\mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	3.0	41.3	0.99
900	5.9	31.8	2.12
400	10.5	19.7	2.35
400	16.0	7.76	2.28
400	19.5	3.09	2.11
200	26.5	1.66	1.61
200	32.0	0.96	1.35
200	39.0	0.69	1.12
200	49.5	0.44	0.89
200	75.0	0.18	0.59

PAC = W35; Water = CWW; Atrazine batch = V; $C_{0, \text{NOM}}$ = mg DOC/L
 $C_{0, \text{atrazine}} = 48.9 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	3.1	15.5	10.8
900	5.9	3.40	7.73
900	9.8	1.08	4.91
400	14.8	0.31	3.30
400	20.3	0.13	2.41
400	25.0	0.082	1.95

PAC = W35; Water = CWW; Atrazine batch = V; $C_{0, \text{NOM}}$ = mg DOC/L
 $C_{0, \text{atrazine}} = 9.44 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	2.8	1.73	2.77
900	6.2	0.272	1.47
900	9.5	0.089	0.98
400	15.5	0.014	0.61

PAC = Pellet II; Water = CWW; Atrazine batch = V; $C_{0, \text{NOM}}$ = mg DOC/L

$C_{0, \text{atrazine}} = 9.74 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	1.9	4.84	2.59
900	3.9	1.71	2.06
900	6.1	0.60	1.49
400	10.5	0.051	0.92
400	15.3	0.019	0.64

PAC = Pellet II; Water = CWW; Atrazine batch = V; $C_{0, \text{NOM}}$ = mg DOC/L

$C_{0, \text{atrazine}} = 48.6 \mu\text{g/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	3.2	18.2	9.43
900	6.1	6.37	6.91
400	10.0	1.59	4.70
400	14.5	0.41	3.32
400	19.8	0.15	2.45
400	25.5	0.069	1.90

CWW NOM Adsorption Isotherms

PAC = SA UF; Water = CWW; $C_{0,NOM} = 7.5 \text{ mg/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	2.1	6.5	414
900	4.2	6.2	283
900	6.0	6.0	237
400	8.3	5.9	184
400	9.8	5.8	171
400	14.8	5.4	136
400	20.0	5.0	120
400	25.5	4.7	108
400	30.0	4.4	100

PAC = SA UF; Water = CWW; $C_{0,NOM} = 7.5 \text{ mg/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	1.7	6.9	339
400	9.5	5.9	162
400	15.0	5.4	134
400	19.5	5.0	123
400	24.0	4.8	111
200	30.0	4.4	100

PAC = SA Super; Water = CWW; $C_{0,NOM} = 7.0 \text{ mg/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	2.9	6.6	141
900	6.0	6.2	128
400	10.3	5.7	123
400	15.5	5.3	110
400	19.3	4.9	107
400	25.8	4.5	96

PAC = SA Super; Water = CWW; $C_{0,NOM} = 7.0 \text{ mg/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	3.3	6.5	148
900	6.0	6.2	135
400	10.3	5.8	115
400	15.8	5.3	109
400	20.3	4.9	102

PAC = W35; Water = CWW; $C_{0,NOM} = 7.5 \text{ mg/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	3.0	7.1	122
400	16.0	6.3	76
400	19.5	6.1	74
200	26.5	5.7	67
200	32.0	5.4	66
200	39.0	5.1	62
200	49.5	4.6	59
200	75.0	3.7	51

PAC = W35; Water = CWW; $C_{0,NOM} = 7.0 \text{ mg/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	3.1	6.6	119
900	5.9	6.4	94
400	9.8	6.2	80
400	14.8	5.8	76
400	20.3	5.6	69
400	25.0	5.4	64

PAC = W35; Water = CWW; $C_{0,NOM} = 7.0 \text{ mg/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	2.8	6.4	214
900	6.2	6.3	102
400	9.5	6.1	87
400	15.5	5.7	80
400	20.0	5.5	72
400	24.0	5.3	69
400	29.3	5.0	66

PAC = W20; Water = CWW; $C_{0,NOM} = 7.5 \text{ mg/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	3.4	7.34	47
900	5.6	7.22	50
400	9.5	7.06	46
400	14.8	6.95	37
400	19.8	6.79	36
200	31.5	6.52	31
200	40.0	6.29	30
200	50.0	6.13	27
200	74.5	5.61	25

PAC = W20; Water = CWW; $C_{0,NOM} = 7.0 \text{ mg/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	2.9	6.8	47
900	7.1	6.7	36
400	10.8	6.6	34
400	14.8	6.5	34
400	21.5	6.3	32
400	30.0	6.2	27

PAC = Pellet II; Water = CWW; $C_{0,NOM} = 7.0 \text{ mg/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	1.9	6.4	300
900	3.9	5.9	266
900	6.1	5.4	247
400	8.3	5.3	198
400	10.5	4.6	227
400	15.3	4.3	173

PAC = Pellet II; Water = CWW; $C_{0,NOM} = 7.0 \text{ mg/L}$

Volume (ml)	C_c (mg/L)	C_e ($\mu\text{g/L}$)	q ($\mu\text{g/mg}$)
900	3.2	6.0	291
900	6.1	5.5	241
400	10.0	5.0	200
400	14.5	4.4	176
400	19.8	4.0	150
400	25.5	3.6	130

ADSORPTION KINETICS

Single Solute Atrazine Adsorption Kinetics

PAC = SA UF; Water = DDI; Atrazine batch = T1; $C_c = 4.2$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	62.1	1.00
4	32.7	0.53
8	24.9	0.40
12	18.6	0.30
16	13.6	0.22
20	10.2	0.16
30	5.52	0.089
45	2.77	0.045
60	1.78	0.029
90	1.18	0.019
120	0.92	0.015
150	0.78	0.013
180	0.73	0.012
240	0.66	0.011

PAC = SA UF; Water = DDI; Atrazine batch = T1; $C_c = 3.0$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	63.3	1.00
4	41.3	0.65
8	35.1	0.55
12	29.2	0.46
16	24.3	0.38
20	19.9	0.31
30	13.5	0.21
45	7.98	0.13
60	5.52	0.087
90	3.26	0.051
120	2.46	0.039
150	2.09	0.033
180	1.90	0.030
240	1.61	0.025

PAC = SA UF; Water = DDI; Atrazine batch = T1; $C_c = 2.0$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	63.2	1.00
4	48.3	0.76
8	43.1	0.68
12	38.3	0.61
16	34.4	0.54
20	30.7	0.49
30	24.0	0.38
45	17.3	0.27
60	13.4	0.21
90	9.33	0.15
120	7.48	0.12
150	6.49	0.10
180	5.93	0.094
240	5.24	0.083

PAC = SA Super; Water = DDI; Atrazine batch = V; $C_c = 1.8$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	46.3	1.00
1.5	42.7	0.92
7.5	38.7	0.84
15.5	33.2	0.72
31	26.2	0.57
45.5	21.4	0.46
60	17.9	0.39
90	13.3	0.29
120	12.0	0.26
150	8.62	0.19
180	7.74	0.17
210	6.72	0.15
240	6.23	0.13

PAC = SA Super; Water = DDI; Atrazine batch = V; $C_c = 3.8$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	46.3	1.00
1.5	36.3	0.78
7	30.8	0.67
15	21.2	0.46
30.5	12.3	0.27
45	7.83	0.17
60	5.14	0.11
90	2.35	0.051
120	1.34	0.029
150	0.94	0.020
180	0.78	0.017
210	0.72	0.016
240	0.67	0.014

PAC = W35; Water = DDI; Atrazine batch = V; $C_c = 1.95 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	49.5	1.00
5	40.7	0.82
15	32.9	0.66
30	26.3	0.53
45	21.6	0.44
60	18.4	0.37
90	14.3	0.29
120	11.9	0.24
150	10.0	0.20
180	8.8	0.18
210	7.8	0.16
240	7.3	0.15

PAC = W35; Water = DDI; Atrazine batch = V; $C_c = 1.15 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	49.4	1.00
5	42.2	0.85
15	36.2	0.73
30	31.7	0.64
45	27.8	0.56
60	24.9	0.50
90	20.2	0.41
120	17.7	0.36
150	15.8	0.32
180	15.0	0.30
210	14.2	0.29
240	13.2	0.27

PAC = W35; Water = DDI; Atrazine batch = V; $C_c = 2.25$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	50.2	1.00
5	42.0	0.84
15	33.9	0.68
30	25.2	0.50
45	20.0	0.40
60	16.6	0.33
90	12.1	0.24
120	9.2	0.18
150	7.9	0.16
180	7.0	0.14
210	6.4	0.13
240	6.0	0.12

PAC = W20; Water = DDI; Atrazine batch = T1; $C_c = 2.0$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	9.59	1.00
2	9.12	0.95
5	8.79	0.92
9.5	8.47	0.88
20	7.80	0.81
30	7.31	0.76
44	6.93	0.72
60	6.40	0.67
90	6.09	0.64
119	5.78	0.60
180	5.19	0.54
240	4.88	0.51

PAC = W20; Water = DDI; Atrazine batch = V; $C_c = 1.55$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	49.5	1.00
5	47.2	0.95
15	45.2	0.91
30	43.3	0.87
45	42.3	0.85
60	41.0	0.83
90	39.8	0.80
120	38.7	0.78
150	37.9	0.77
180	37.6	0.76
210	36.6	0.74
240	36.4	0.73

PAC = W20; Water = DDI; Atrazine batch = V; $C_c = 1.9 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	46.3	1.00
1.5	47.5	1.03
7.5	45.2	0.98
15.5	43.4	0.94
31	41.7	0.90
45.5	39.4	0.85
60	38.8	0.84
90	37.2	0.80
120	36.2	0.78
150	35.7	0.77
180	34.9	0.75
210	34.5	0.75
240	33.9	0.73

PAC = W20; Water = DDI; Atrazine batch = V; $C_c = 4.0 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	46.3	1.00
1.5	45.8	0.99
7.5	42.5	0.92
15.5	38.9	0.84
31	34.3	0.74
45.5	31.4	0.68
60	29.1	0.63
90	26.3	0.57
120	24.3	0.52
150	22.7	0.49
180	21.2	0.46
210	20.1	0.43
240	19.4	0.42

PAC = Pellet II; Water = DDI; Atrazine batch = V; $C_c = 2.3$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	52.2	1.00
1.5	35.3	0.68
10	17.8	0.34
20	12.7	0.24
30	9.60	0.18
50	6.54	0.13
70	5.05	0.10
90	4.08	0.078
120	3.28	0.063
150	2.80	0.054
180	2.53	0.049
210	2.26	0.043
240	2.12	0.041

PAC = Pellet II; Water = DDI; Atrazine batch = V; $C_c = 1.9$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	57.1	1.00
5	39.9	0.70
10.5	35.7	0.62
15	32.6	0.57
25	29.2	0.51
60	23.5	0.41
90	22.0	0.39
120	21.5	0.38
150	20.9	0.37
180	20.4	0.36
210	20.5	0.36
240	20.4	0.36

PAC = Pellet II; Water = DDI; Atrazine batch = V; $C_c = 2.0$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	57.1	1.00
5	37.5	0.66
10.5	32.0	0.56
15	24.6	0.43
25	20.5	0.36
60	18.3	0.32
90	16.2	0.28
120	15.7	0.27
150	15.8	0.28
180	14.6	0.26
210	14.5	0.25
240	14.2	0.25

Atrazine Adsorption Kinetics in the Presence of Preloaded CWW NOM

PAC = SA UF; Water = CWW; Atrazine batch = VIII; $C_c = 2.0$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	11.4	1
0.5	11.1	0.98
17	11.2	0.99
27	11.2	0.99
37	11.3	0.99
48	11.1	0.98
60	11.2	0.99
80	11.1	0.98
100	11.1	0.98
120	11.1	0.97
150	11.0	0.97
180	11.0	0.97
210	10.9	0.96
240	10.9	0.96

PAC = SA UF; Water = CWW; Atrazine batch = VIII; $C_c = 4.0$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	11.4	1
0.5	11.0	0.97
16	10.5	0.92
26	10.3	0.91
36	10.2	0.89
48	9.9	0.87
60	9.7	0.86
80	9.7	0.86
100	9.3	0.82
120	9.2	0.81
150	8.9	0.79
180	8.8	0.78
210	8.7	0.77
240	8.4	0.74

PAC = SA UF; Water = CWW; Atrazine batch = VIII; $C_c = 8.3$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	11.4	1.00
0.5	10.4	0.92
16	8.4	0.74
26	7.8	0.68
35.5	7.1	0.62
48	6.5	0.57
60	6.0	0.53
80	5.4	0.48
100	4.9	0.43
120	4.5	0.40
150	4.0	0.35
180	3.5	0.31
210	3.2	0.28
240	2.9	0.26

PAC = SA UF; Water = CWW; Atrazine batch = VIII; $C_c = 11.8$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	11.4	1.00
0.5	9.7	0.86
15	6.1	0.54
25	5.1	0.45
35	4.4	0.38
48	3.7	0.32
60	3.3	0.29
80	2.7	0.24
100	2.3	0.20
120	2.1	0.18
150	1.7	0.15
180	1.5	0.13
210	1.3	0.11
240	1.1	0.10

PAC = SA Super; Water = CWW; Atrazine batch = V; $C_c = 3.8$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	10.1	1.00
2	9.89	0.98
12	9.66	0.96
21	9.61	0.96
32	9.45	0.94
45	9.32	0.93
60	9.37	0.93
90	9.07	0.90
120	8.86	0.88
150	8.75	0.87
180	8.64	0.86
210	8.57	0.85
240	8.43	0.84

PAC = SA Super; Water = CWW; Atrazine batch = V; $C_c = 7.9$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	10.1	1.00
2	9.88	0.98
9	9.25	0.92
18	8.68	0.86
29	8.32	0.83
42	7.85	0.78
57	7.39	0.74
87	6.64	0.66
147	5.73	0.57
177	5.27	0.52
207	4.99	0.50
237	4.72	0.47

PAC = SA Super; Water = CWW; Atrazine batch = V; $C_c = 11.9$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	10.1	1.00
2	9.21	0.92
8	7.94	0.79
17	6.83	0.68
28	5.87	0.58
41	5.04	0.50
56	4.34	0.43
86	3.38	0.34
116	2.78	0.28
176	1.96	0.19
206	1.72	0.17
236	1.51	0.15

PAC = SA Super; Water = CWW; Atrazine batch = V; $C_c = 16.1$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	10.1	1.00
2	8.43	0.84
8	6.28	0.63
16	4.55	0.45
27	3.30	0.33
40	2.43	0.24
55	1.82	0.18
85	1.18	0.12
115	0.87	0.087
145	0.69	0.069
175	0.55	0.055
205	0.46	0.046
235	0.41	0.041

PAC = W35; Water = CWW; Atrazine batch = V; $C_c = 1.9 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	10.1	1.00
1.5	10.1	1.00
6.5	10.0	0.99
11.5	10.1	1.00
30	10.0	0.98
45	10.0	0.99
56	9.9	0.98
90	10.0	0.99
120	9.9	0.98
150	9.9	0.98
180	9.9	0.98
210	9.9	0.98
240	10.0	0.99

PAC = W35; Water = CWW; Atrazine batch = V; $C_c = 4.0 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	10.1	1.00
1.5	9.86	0.97
6	9.82	0.97
11	9.84	0.97
32	9.72	0.96
45	9.69	0.96
56	9.67	0.96
90	9.52	0.94
120	9.48	0.94
150	9.42	0.93
180	9.22	0.91
210	9.15	0.90
240	9.13	0.90

PAC = W35; Water = CWW; Atrazine batch = V; $C_c = 6.9$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	10.1	1.00
2	9.78	0.97
40	9.26	0.92
60	9.00	0.89
80	8.94	0.88
110	8.73	0.86
170	8.18	0.81
200	7.93	0.78
230	7.71	0.76

PAC = W35; Water = CWW; Atrazine batch = V; $C_c = 7.0$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	10.1	1.00
1	9.73	0.96
5.5	9.79	0.97
11	9.58	0.95
32	9.57	0.95
44.5	9.44	0.93
56	9.11	0.90
90	8.97	0.89
120	8.64	0.85
150	8.56	0.85
180	8.23	0.81
210	7.80	0.77
240	7.82	0.77

PAC = W35; Water = CWW; Atrazine batch = V; $C_c = 10.2$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	10.1	1.00
1.5	9.93	0.98
7	9.66	0.95
12	9.46	0.93
25.5	8.94	0.88
41	8.64	0.85
60	8.03	0.79
80	7.75	0.77
110	7.15	0.71
140	6.60	0.65
170	6.12	0.60
200	5.71	0.56
230	5.46	0.54

PAC = W35; Water = CWW; Atrazine batch = V; $C_c = 15.1$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	10.1	1.00
1.5	9.79	0.97
6.5	9.45	0.93
16	8.87	0.88
25	8.33	0.82
40	7.53	0.74
60	6.71	0.66
80	6.07	0.60
110	5.27	0.52
140	4.59	0.45
170	3.99	0.39
200	3.49	0.35
230	3.12	0.31

PAC = W20; Water = CWW; Atrazine batch = V; $C_c = 4.4$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	100.9	1.00
1.3	100.9	1.00
7.5	100.7	1.00
15.5	100.5	1.00
30	100.9	1.00
47.5	100.6	1.00
60	100.3	0.99
90	100.1	0.99
120	101.2	1.00
151	100.3	0.99
184	100.0	0.99
210	99.9	0.99
240	100.3	0.99

PAC = W20; Water = CWW; Atrazine batch = V; $C_c = 7.7$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	100.9	1.00
1.3	100.2	0.99
7.5	100.3	0.99
15	100.0	0.99
29.5	99.5	0.99
46.5	100.3	0.99
59	99.5	0.99
89	99.1	0.98
119	99.3	0.98
150	99.4	0.98
183	99.2	0.98
209	98.4	0.98
240	98.4	0.98

PAC = W20; Water = CWW; Atrazine batch = V; $C_c = 11.8 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	100.9	1.00
1.7	99.3	0.98
7	98.9	0.98
15	99.3	0.98
29	98.5	0.98
46	98.2	0.97
59	97.9	0.97
89	97.3	0.96
119	96.6	0.96
150	97.0	0.96
183	95.6	0.95
209	95.8	0.95
240	95.8	0.95

PAC = W20; Water = CWW; Atrazine batch = V; $C_c = 15.8 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	10.1	1.00
4	9.8	0.97
10	9.7	0.96
20	9.7	0.96
40	9.6	0.95
60	9.5	0.94
90	9.4	0.94
120	9.4	0.93
151	9.2	0.91
184	9.2	0.91
240	9.0	0.89

PAC = Pellet II; Water = CWW; Atrazine batch = V; $C_c = 2.2$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	9.88	1.00
5.5	9.70	0.98
15	9.68	0.98
30	9.51	0.96
49	9.37	0.95
60	9.36	0.95
90	9.14	0.93
120	9.04	0.92
150	9.08	0.92
180	8.94	0.91
210	8.88	0.90
240	8.88	0.90

PAC = Pellet II; Water = CWW; Atrazine batch = V; $C_c = 4.4$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	9.88	1.00
5.5	9.35	0.95
15	8.90	0.90
30	8.14	0.82
49	7.63	0.77
60	7.40	0.75
90	6.80	0.69
120	6.42	0.65
150	6.10	0.62
180	5.75	0.58
210	5.59	0.57
240	5.34	0.54

PAC = Pellet II; Water = CWW; Atrazine batch = V; $C_c = 7.6$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	9.88	1.00
5.5	7.71	0.78
15	6.20	0.63
30	4.82	0.49
49	3.83	0.39
60	3.45	0.35
90	2.77	0.28
120	2.38	0.24
150	2.13	0.22
180	1.91	0.19
210	1.79	0.18
240	1.66	0.17

PAC = Pellet II; Water = CWW; Atrazine batch = V; $C_c = 8.0$ mg/L

Time (min)	C ($\mu\text{g/L}$)	C/C_0
0	9.88	1.00
5.5	6.20	0.63
15	4.21	0.43
30	2.67	0.27
49	1.82	0.18
60	1.55	0.16
90	1.14	0.12
120	0.91	0.092
150	0.79	0.080
180	0.70	0.071
210	0.65	0.066
240	0.58	0.059

PAC = Pellet II; Water = CWW; Atrazine batch = V; $C_c = 12 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	9.88	1.00
5.5	3.88	0.39
15	1.65	0.17
30	0.73	0.074
49	0.45	0.046
60	0.37	0.038
90	0.29	0.029
120	0.23	0.023
150	0.20	0.020
180	0.19	0.019
210	0.16	0.016
240	0.15	0.015

Atrazine Adsorption Kinetics on PAC preloaded with Atrazine (Presorb Tests)

PAC = SA UF; Water = DDI; Atrazine Batch = V; $C_{1,\text{atrazine}} = 50 \mu\text{g/L}$, $C_{2,\text{atrazine}} = 15 \mu\text{g/L}$, $C_c = 4.3 \text{ mg/L}$

Time (min)	$C (\mu\text{g/L})$	C/C_0
0	15.1	1.000
5	2.45	0.163
15	0.88	0.058
30	0.63	0.041
47	0.49	0.032
60	0.27	0.018
90	0.49	0.033
120	0.47	0.031
150	0.43	0.028
180	0.39	0.026
210	0.39	0.026
240	0.35	0.023

PAC = SA UF; Water = DDI; Atrazine Batch = V; $C_{1,\text{atrazine}} = 50 \mu\text{g/L}$, $C_{2,\text{atrazine}} = 15 \mu\text{g/L}$, $C_c = 3.0 \text{ mg/L}$

Time (min)	$C (\mu\text{g/L})$	C/C_0
0	15.3	1.000
5	4.6	0.299
15	2.4	0.155
30	1.6	0.106
47	1.3	0.087
60	1.5	0.098
90	1.3	0.086
120	1.2	0.079
150	1.2	0.077
180	1.1	0.074
210	1.0	0.065
240	1.0	0.063

PAC = SA UF; Water = DDI; Atrazine Batch = V; $C_{1,\text{atrazine}} = 50 \mu\text{g/L}$, $C_{2,\text{atrazine}} = 15 \mu\text{g/L}$, $C_c = 2.0 \text{ mg/L}$

Time (min)	$C (\mu\text{g/L})$	C/C_0
0	15.4	1.00
5	7.2	0.47
15	3.9	0.25
30	2.8	0.18
47	2.6	0.17
60	2.5	0.16
90	2.1	0.14
120	2.0	0.13
150	1.9	0.12
180	2.0	0.13
210	1.8	0.12
240	1.7	0.11

PAC = SA UF; Water = DDI; Atrazine Batch = V; $C_{1,\text{atrazine}} = 100 \mu\text{g/L}$, $C_{2,\text{atrazine}} = 15 \mu\text{g/L}$, $C_c = 4.0 \text{ mg/L}$

Time (min)	$C (\mu\text{g/L})$	C/C_0
0	15.9	1.00
3	9.18	0.58
7	6.85	0.43
11.5	5.19	0.33
20	3.45	0.22
30	2.55	0.16
47	2.05	0.13
60	1.81	0.11
90	1.58	0.10
120	1.52	0.096
150	1.37	0.086
180	1.44	0.091
210	1.38	0.087
240	1.39	0.088

PAC = SA UF; Water = DDI; Atrazine Batch = V; $C_{1,\text{atrazine}} = 100 \text{ } \mu\text{g/L}$, $C_{2,\text{atrazine}} = 15 \text{ } \mu\text{g/L}$, $C_c = 3.0 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	16.6	1.00
3	11.1	0.67
7	8.88	0.54
11.5	7.34	0.44
20	5.63	0.34
30	4.73	0.29
47	3.97	0.24
60	3.47	0.21
90	3.18	0.19
120	3.03	0.18
150	2.80	0.17
180	2.76	0.17
210	2.74	0.17
240	2.75	0.17

PAC = SA UF; Water = DDI; Atrazine Batch = V; $C_{1,\text{atrazine}} = 15 \text{ } \mu\text{g/L}$, $C_{2,\text{atrazine}} = 50 \text{ } \mu\text{g/L}$, $C_c = 1.9 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	50.0	1.00
3	30.5	0.61
10	18.0	0.36
20	10.9	0.22
30	7.87	0.16
46	5.46	0.11
60	4.29	0.086
98	2.98	0.060
121	2.62	0.052
154	2.32	0.046
180	2.13	0.043
210	1.95	0.039
240	1.79	0.036

PAC = SA UF; Water = DDI; Atrazine Batch = V; $C_{1,\text{atrazine}} = 15 \mu\text{g/L}$, $C_{2,\text{atrazine}} = 50 \mu\text{g/L}$, $C_c = 2.7 \text{ mg/L}$

Time (min)	$C (\mu\text{g/L})$	C/C_0
0	50.0	1.00
3	30.4	0.61
9	18.6	0.37
19	11.0	0.22
29	7.74	0.15
45	5.36	0.11
59	4.53	0.090
97	3.13	0.063
120	2.75	0.055
150	2.40	0.048
180	2.21	0.044
210	2.06	0.041
240	1.91	0.038

PAC = SA UF; Water = DDI; Atrazine Batch = V; $C_{1,\text{atrazine}} = 30 \mu\text{g/L}$, $C_{2,\text{atrazine}} = 100 \mu\text{g/L}$, $C_c = 3.0 \text{ mg/L}$

Time (min)	$C (\mu\text{g/L})$	C/C_0
0	100	1.00
3	74.2	0.74
9	42.3	0.42
18	27.5	0.28
28	20.2	0.20
44	14.8	0.15
58	12.5	0.12
96	9.15	0.091
120	8.39	0.084
150	7.52	0.075
180	7.01	0.070
210	6.50	0.065
240	6.07	0.061

PAC = SA UF; Water = DDI; Atrazine Batch = X; $C_{1,\text{atrazine}} = 213 \text{ } \mu\text{g/L}$, $C_{2,\text{atrazine}} = 50 \text{ } \mu\text{g/L}$, $C_c = 3.7 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	54.8	1.00
2	28.9	0.53
10	17.4	0.32
20	14.0	0.26
30	12.8	0.23
46	11.7	0.21
60	11.2	0.20
98	10.4	0.19
121	10.1	0.18
154	10.2	0.19
180	10.0	0.18
210	9.84	0.18
240	9.73	0.18

PAC = SA UF; Water = DDI; Atrazine Batch = X; $C_{1,\text{atrazine}} = 213 \text{ } \mu\text{g/L}$, $C_{2,\text{atrazine}} = 30 \text{ } \mu\text{g/L}$, $C_c = 2.9 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	58.0	1.00
2	36.6	0.63
10	26.9	0.46
20	22.6	0.39
30	20.7	0.36
46	19.6	0.34
60	18.4	0.32
98	17.3	0.30
121	16.7	0.29
154	16.4	0.28
180	16.2	0.28
210	15.8	0.27
240	16.0	0.28

PAC = SA UF; Water = DDI; Atrazine Batch = Z; $C_{1,\text{atrazine}} = 162 \mu\text{g/L}$, $C_{2,\text{atrazine}} = 40.5 \mu\text{g/L}$, $C_c = 1.6 \text{ mg/L}$

Time (min)	$C (\mu\text{g/L})$	C/C_0
0	54.2	1.00
4	46.4	0.86
10	42.5	0.78
20	39.8	0.73
30	38.5	0.71
45	36.8	0.68
60	36.0	0.66
90	35.2	0.65
120	34.8	0.64
150	34.3	0.63
180	34.1	0.63
210	33.7	0.62
240	33.7	0.62

PAC = SA UF; Water = DDI; Atrazine Batch = Z; $C_{1,\text{atrazine}} = 162 \mu\text{g/L}$, $C_{2,\text{atrazine}} = 40.5 \mu\text{g/L}$, $C_c = 2.2 \text{ mg/L}$

Time (min)	$C (\mu\text{g/L})$	C/C_0
0	47.0	1.00
4	33.4	0.71
10	27.7	0.59
20	24.3	0.52
30	22.4	0.48
45	21.3	0.45
60	19.9	0.42
90	19.3	0.41
120	18.7	0.40
150	18.2	0.39
180	17.8	0.38
210	17.5	0.37
240	17.6	0.37

PAC = SA UF; Water = DDI; Atrazine Batch = Z; $C_{1,\text{atrazine}} = 162 \text{ } \mu\text{g/L}$, $C_{2,\text{atrazine}} = 40.5 \text{ } \mu\text{g/L}$, $C_c = 4.2 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	41.7	1.00
4	13.5	0.32
10	7.3	0.17
20	5.0	0.12
30	4.2	0.10
45	3.8	0.090
60	3.5	0.084
90	3.3	0.080
120	3.2	0.076
150	3.0	0.072
180	3.0	0.072
210	3.0	0.073
240	3.0	0.072

PAC = SA UF; Water = DDI; Atrazine Batch = Z; $C_{1,\text{atrazine}} = 162 \text{ } \mu\text{g/L}$, $C_{2,\text{atrazine}} = 40.5 \text{ } \mu\text{g/L}$, $C_c = 6.5 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	41.3	1.00
4	7.4	0.18
10	3.7	0.089
20	2.5	0.061
30	2.2	0.054
45	2.0	0.047
60	1.8	0.043
90	1.9	0.045
120	1.6	0.040
150	1.6	0.039
180	1.6	0.039
210	1.5	0.037
240	1.5	0.037

PAC = W35; Water = DDI; Atrazine Batch = Z; $C_{1,\text{atrazine}} = 50 \mu\text{g/L}$, $C_{2,\text{atrazine}} = 50 \mu\text{g/L}$, $C_c = 4.2 \text{ mg/L}$

Time (min)	$C (\mu\text{g/L})$	C/C_0
0	50.3	1.00
5	25.6	0.51
15	11.1	0.22
30	6.79	0.13
60	4.35	0.086
98	3.36	0.067
121	3.09	0.061
154	2.70	0.054
180	2.65	0.053
210	2.28	0.045
240	2.20	0.044

PAC = W35; Water = DDI; Atrazine Batch = Z; $C_{1,\text{atrazine}} = 50 \mu\text{g/L}$, $C_{2,\text{atrazine}} = 50 \mu\text{g/L}$, $C_c = 3.2 \text{ mg/L}$

Time (min)	$C (\mu\text{g/L})$	C/C_0
0	50.4	1.00
5	29.6	0.59
15	14.7	0.29
30	9.06	0.18
60	5.59	0.11
98	4.44	0.088
121	3.81	0.076
154	3.46	0.069
180	3.14	0.062
210	2.96	0.059
240	2.81	0.056

PAC = W35; Water = DDI; Atrazine Batch = Z; $C_{1,\text{atrazine}} = 50 \text{ } \mu\text{g/L}$, $C_{2,\text{atrazine}} = 50 \text{ } \mu\text{g/L}$,
 $C_c = 2.0 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	50.9	1.00
5	39.5	0.78
15	27.1	0.53
30	20.6	0.41
60	15.2	0.30
98	12.5	0.25
121	11.2	0.22
154	10.2	0.20
180	9.57	0.19
210	9.05	0.18
240	8.86	0.17

Atrazine Adsorption Kinetics on PAC preloaded with Atrazine and NOM

PAC = SA UF; Water = CWW; Atrazine Batch = V; $C_{1,\text{atrazine}} = 21.5 \text{ } \mu\text{g/L}$, $C_{2,\text{atrazine}} = 15 \text{ } \mu\text{g/L}$, $C_c = 7.0 \text{ mg/L}$

Time (min)	$C \text{ (}\mu\text{g/L)}$	C/C_0
0	15.5	1.00
3	14.9	0.96
8	14.3	0.92
15	13.9	0.89
20	13.4	0.86
30	12.7	0.82
45	12.0	0.77
59	11.4	0.73
90	10.5	0.68
120	9.7	0.62
150	8.9	0.58
180	8.5	0.55
210	7.9	0.51
270	7.2	0.46

PAC = SA UF; Water = CWW; Atrazine Batch = V; $C_{1,\text{atrazine}} = 21.5 \mu\text{g/L}$, $C_{2,\text{atrazine}} = 15 \mu\text{g/L}$, $C_c = 5.2 \text{ mg/L}$

Time (min)	$C (\mu\text{g/L})$	C/C_0
0	16.3	1.00
3	15.8	0.97
8	15.5	0.95
15	15.3	0.94
20	15.0	0.92
30	14.7	0.90
45	14.3	0.88
59	14.0	0.86
90	13.5	0.83
120	13.0	0.80
150	12.6	0.77
180	12.3	0.76
210	11.8	0.73
270	11.4	0.70

PAC = SA UF; Water = CWW; Atrazine Batch = V; $C_{1,\text{atrazine}} = 21.5 \mu\text{g/L}$, $C_{2,\text{atrazine}} = 15 \mu\text{g/L}$, $C_c = 3.0 \text{ mg/L}$

Time (min)	$C (\mu\text{g/L})$	C/C_0
0	20.4	1.0000
3.5	20.3	0.99
8.5	20.2	0.99
15	20.4	1.00
20	20.1	0.99
30	20.1	0.99
45	20.0	0.98
59	19.9	0.98
90	19.7	0.97
120	19.6	0.96
150	19.5	0.95
180	19.4	0.95
210	19.1	0.94
270	19.0	0.93

ATRAZINE ADSORPTION IN FLOW-THROUGH ADSORPTION/MEMBRANE FILTRATION SYSTEMS

PAC = SA UF; Water = CWW; Atrazine Batch = VIII; $C_{0, \text{atrazine}} = 9.2 \mu\text{g/L}$; $m_{\text{PAC}} = 14.4 \text{ mg}$ (pulse dose); Flow rate = 10 mL/min; Backwash cycle = 360 min

Time (min)	Concentration ($\mu\text{g/L}$)	C/C_0
0	9.2	1
1	8.6	0.94
3	5.3	0.58
5	1.9	0.20
10	1.5	0.16
15	1.3	0.14
20	1.3	0.14
25	1.4	0.16
30	1.6	0.17
40	1.7	0.19
50	2.2	0.23
60	2.6	0.28
80	2.9	0.32
100	3.8	0.42
120	4.5	0.49
150	5.0	0.54
180	5.8	0.63
210	6.6	0.71
240	7.2	0.78
270	7.8	0.85
300	8.2	0.90
330	8.5	0.92
360	8.9	0.96

PAC = SA UF; Water = CWW; Atrazine Batch = VIII; $C_{0, \text{atrazine}} = 10.6 \mu\text{g/L}$; $m_{\text{PAC}} = 7.2 \text{ mg}$ (pulse dose); Flow rate = 10 mL/min; Backwash cycle = 360 min

Time (min)	Concentration ($\mu\text{g/L}$)	C/C_0
0	10.6	1.00
1	9.7	0.91
2	8.4	0.79
5	5.5	0.52
10	4.8	0.45
15	4.5	0.43
20	4.5	0.43
25	4.5	0.43
30	4.5	0.43
40	4.7	0.45
50	5.0	0.47
60	5.1	0.49
80	5.6	0.53
100	6.3	0.60
120	7.0	0.66
150	7.9	0.75
180	8.8	0.83
210	9.3	0.88
240	9.7	0.92
270	9.9	0.94
300	10.4	0.98
330	10.6	1.00
360	10.6	1.00

PAC = W35; Water = CWW; Atrazine Batch = V; $C_{0, \text{ atrazine }} = 9.8 \mu\text{g/L}$; $m_{\text{PAC}} = 14.4 \text{ mg}$ (pulse dose); Flow rate = 10 mL/min; Backwash cycle = 300 min

Time (min)	Concentration ($\mu\text{g/L}$)	C/C_0
0	9.8	1.00
4	0.9	0.09
10	0.5	0.05
20	0.6	0.06
30	0.9	0.09
46	1.7	0.18
60	2.5	0.26
90	4.1	0.42
120	5.1	0.52
150	5.9	0.61
180	6.7	0.68
210	7.0	0.72
240	7.4	0.76
270	7.8	0.80
300	10.2	1.0

PAC = W20; Water = CWW; Atrazine Batch = V; $C_{0, \text{ atrazine }} = 10.0 \mu\text{g/L}$; $m_{\text{PAC}} = 14.6 \text{ mg}$ (pulse dose); Flow rate = 10 mL/min; Backwash cycle = 270 min

Time (min)	Concentration ($\mu\text{g/L}$)	C/C_0
0	10.0	1.000
2	8.0	0.80
5	7.3	0.73
10	6.8	0.68
20	6.8	0.68
30	7.5	0.75
45	8.0	0.80
60	8.5	0.85
90	9.1	0.91
120	9.4	0.93
150	9.6	0.96
180	9.6	0.96
210	9.7	0.97
240	9.8	0.98
270	9.8	0.98

PAC = Pellet II; Water = CWW; Atrazine Batch = V; $C_{0, \text{atrazine}} = 9.5 \mu\text{g/L}$; $m_{\text{PAC}} = 14.4 \text{ mg}$ (pulse dose); Flow rate = 10 mL/min; Backwash cycle = 360 min

Time (min)	Concentration ($\mu\text{g/L}$)	C/C_0
0	9.5	1.00
2	2.0	0.21
5	0.6	0.07
10	0.4	0.04
20	0.4	0.04
30	0.4	0.04
45	0.4	0.04
60	0.6	0.06
90	0.7	0.08
120	1.2	0.12
150	1.7	0.18
180	2.4	0.25
210	2.9	0.31
240	3.6	0.38
270	4.2	0.44
300	4.7	0.50
330	5.1	0.54
360	5.6	0.59

PORE SIZE DISTRIBUTION

SA UF

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
8.6	9.36E-02	2.93E+02	2.58E-02	5.99E+01
9.0	1.03E-01	3.15E+02	2.49E-02	5.54E+01
9.4	1.15E-01	3.40E+02	2.76E-02	5.87E+01
9.8	1.29E-01	3.68E+02	3.25E-02	6.60E+01
10.3	1.45E-01	4.00E+02	3.60E-02	6.99E+01
10.8	1.63E-01	4.32E+02	3.70E-02	6.87E+01
11.3	1.81E-01	4.65E+02	3.65E-02	6.48E+01
11.8	1.98E-01	4.93E+02	3.24E-02	5.50E+01
12.3	2.13E-01	5.18E+02	2.81E-02	4.57E+01
12.9	2.27E-01	5.40E+02	2.55E-02	3.97E+01
13.5	2.42E-01	5.62E+02	2.48E-02	3.67E+01
14.1	2.58E-01	5.84E+02	2.51E-02	3.57E+01
14.7	2.71E-01	6.03E+02	2.12E-02	2.88E+01
15.4	2.84E-01	6.19E+02	1.81E-02	2.34E+01
16.1	2.94E-01	6.32E+02	1.53E-02	1.89E+01
16.9	3.05E-01	6.45E+02	1.45E-02	1.72E+01
17.7	3.16E-01	6.57E+02	1.40E-02	1.59E+01
18.5	3.26E-01	6.68E+02	1.19E-02	1.28E+01
19.3	3.32E-01	6.75E+02	7.90E-03	8.17E+00
20.2	3.37E-01	6.79E+02	5.00E-03	4.95E+00
21.1	3.37E-01	6.79E+02	0.00E+00	0.00E+00
22.1	3.37E-01	6.79E+02	0.00E+00	0.00E+00
23.1	3.40E-01	6.81E+02	2.70E-03	2.34E+00
24.2	3.46E-01	6.87E+02	5.76E-03	4.76E+00
25.3	3.55E-01	6.94E+02	7.99E-03	6.31E+00
26.5	3.66E-01	7.02E+02	9.73E-03	7.35E+00
27.7	3.79E-01	7.11E+02	1.06E-02	7.62E+00
29.0	3.92E-01	7.21E+02	1.05E-02	7.22E+00
30.3	4.04E-01	7.28E+02	8.48E-03	5.60E+00
31.7	4.14E-01	7.35E+02	7.33E-03	4.63E+00
33.2	4.26E-01	7.42E+02	8.27E-03	4.99E+00
34.7	4.38E-01	7.49E+02	7.88E-03	4.55E+00

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
36.3	4.50E-01	7.56E+02	7.84E-03	4.32E+00
37.9	4.62E-01	7.62E+02	7.03E-03	3.70E+00
39.7	4.72E-01	7.67E+02	5.77E-03	2.91E+00
41.5	4.84E-01	7.72E+02	6.24E-03	3.01E+00
43.4	4.93E-01	7.77E+02	4.82E-03	2.22E+00
45.4	5.02E-01	7.81E+02	4.48E-03	1.97E+00
47.5	5.14E-01	7.86E+02	5.72E-03	2.41E+00
49.7	5.25E-01	7.90E+02	5.22E-03	2.10E+00
52.0	5.36E-01	7.94E+02	4.67E-03	1.80E+00
54.4	5.45E-01	7.98E+02	3.72E-03	1.37E+00
56.9	5.55E-01	8.01E+02	4.09E-03	1.44E+00
59.5	5.64E-01	8.04E+02	3.51E-03	1.18E+00
62.2	5.74E-01	8.07E+02	3.51E-03	1.13E+00
65.1	5.81E-01	8.09E+02	2.38E-03	7.32E-01
68.1	5.88E-01	8.12E+02	2.35E-03	6.91E-01
71.2	5.96E-01	8.14E+02	2.74E-03	7.70E-01
74.5	6.06E-01	8.16E+02	2.89E-03	7.77E-01
78.0	6.19E-01	8.20E+02	3.87E-03	9.92E-01
81.5	6.31E-01	8.23E+02	3.27E-03	8.01E-01
85.3	6.40E-01	8.25E+02	2.56E-03	6.01E-01
89.2	6.50E-01	8.27E+02	2.44E-03	5.46E-01
93.3	6.60E-01	8.29E+02	2.44E-03	5.23E-01
97.6	6.67E-01	8.31E+02	1.78E-03	3.65E-01
102.1	6.75E-01	8.32E+02	1.66E-03	3.25E-01
106.8	6.86E-01	8.34E+02	2.31E-03	4.33E-01
111.7	6.96E-01	8.36E+02	2.05E-03	3.68E-01
116.9	7.05E-01	8.38E+02	1.75E-03	3.00E-01
122.3	7.14E-01	8.39E+02	1.68E-03	2.74E-01
127.9	7.23E-01	8.41E+02	1.59E-03	2.49E-01
133.8	7.32E-01	8.42E+02	1.52E-03	2.27E-01
139.9	7.41E-01	8.43E+02	1.44E-03	2.07E-01
146.4	7.50E-01	8.44E+02	1.40E-03	1.91E-01
153.1	7.59E-01	8.46E+02	1.42E-03	1.85E-01
160.1	7.69E-01	8.47E+02	1.33E-03	1.67E-01
167.5	7.78E-01	8.48E+02	1.26E-03	1.51E-01
175.2	7.87E-01	8.49E+02	1.19E-03	1.36E-01
183.3	7.96E-01	8.50E+02	1.11E-03	1.21E-01

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
191.7	8.06E-01	8.51E+02	1.12E-03	1.16E-01
200.6	8.17E-01	8.52E+02	1.25E-03	1.25E-01
209.8	8.26E-01	8.53E+02	9.90E-04	9.44E-02
219.4	8.35E-01	8.54E+02	9.40E-04	8.57E-02
229.5	8.44E-01	8.55E+02	9.00E-04	7.84E-02
240.1	8.53E-01	8.55E+02	8.52E-04	7.09E-02
251.2	8.60E-01	8.56E+02	6.11E-04	4.86E-02
262.7	8.64E-01	8.56E+02	3.88E-04	2.95E-02
274.8	8.71E-01	8.57E+02	5.47E-04	3.98E-02
287.5	8.83E-01	8.58E+02	9.78E-04	6.80E-02
300.7	8.94E-01	8.58E+02	8.41E-04	5.59E-02
314.5	9.02E-01	8.59E+02	5.35E-04	3.40E-02
329.0	9.09E-01	8.59E+02	5.09E-04	3.10E-02
344.2	9.16E-01	8.60E+02	4.85E-04	2.82E-02
360.0	9.31E-01	8.60E+02	9.25E-04	5.14E-02

SA Super

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
8.6	1.20E-01	3.80E+02	2.97E-02	6.92E+01
9.0	1.29E-01	3.99E+02	2.25E-02	4.99E+01
9.4	1.38E-01	4.18E+02	2.14E-02	4.56E+01
9.8	1.48E-01	4.40E+02	2.46E-02	5.01E+01
10.3	1.60E-01	4.63E+02	2.61E-02	5.07E+01
10.8	1.73E-01	4.86E+02	2.62E-02	4.88E+01
11.3	1.87E-01	5.12E+02	2.91E-02	5.17E+01
11.8	2.01E-01	5.36E+02	2.74E-02	4.65E+01
12.3	2.14E-01	5.56E+02	2.29E-02	3.71E+01
12.9	2.25E-01	5.74E+02	2.02E-02	3.13E+01
13.5	2.37E-01	5.91E+02	1.98E-02	2.94E+01
14.1	2.50E-01	6.10E+02	2.13E-02	3.02E+01
14.7	2.61E-01	6.24E+02	1.65E-02	2.24E+01
15.4	2.70E-01	6.36E+02	1.34E-02	1.74E+01
16.1	2.77E-01	6.45E+02	1.06E-02	1.31E+01
16.9	2.85E-01	6.55E+02	1.07E-02	1.27E+01
17.7	2.94E-01	6.64E+02	1.09E-02	1.23E+01
18.5	3.00E-01	6.71E+02	7.89E-03	8.54E+00
19.3	3.02E-01	6.73E+02	1.80E-03	1.86E+00
20.2	3.02E-01	6.73E+02	0.00E+00	0.00E+00
21.1	3.02E-01	6.73E+02	0.00E+00	0.00E+00
22.1	3.02E-01	6.73E+02	0.00E+00	0.00E+00
23.1	3.02E-01	6.73E+02	0.00E+00	0.00E+00
24.2	3.02E-01	6.73E+02	6.10E-04	5.04E-01
25.3	3.08E-01	6.78E+02	5.44E-03	4.30E+00
26.5	3.19E-01	6.86E+02	8.71E-03	6.58E+00
27.7	3.30E-01	6.94E+02	9.41E-03	6.80E+00
29.0	3.41E-01	7.02E+02	8.33E-03	5.75E+00
30.3	3.49E-01	7.07E+02	6.47E-03	4.27E+00
31.7	3.59E-01	7.13E+02	6.83E-03	4.31E+00
33.2	3.70E-01	7.20E+02	7.66E-03	4.62E+00
34.7	3.81E-01	7.26E+02	7.24E-03	4.18E+00

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
36.3	3.94E-01	7.33E+02	7.92E-03	4.36E+00
37.9	4.07E-01	7.40E+02	7.79E-03	4.11E+00
39.7	4.16E-01	7.45E+02	5.05E-03	2.54E+00
41.5	4.24E-01	7.49E+02	4.65E-03	2.24E+00
43.4	4.34E-01	7.53E+02	5.08E-03	2.34E+00
45.4	4.45E-01	7.58E+02	5.62E-03	2.48E+00
47.5	4.56E-01	7.63E+02	5.40E-03	2.27E+00
49.7	4.65E-01	7.67E+02	4.16E-03	1.68E+00
52.0	4.73E-01	7.70E+02	3.40E-03	1.31E+00
54.4	4.83E-01	7.73E+02	4.31E-03	1.59E+00
56.9	4.95E-01	7.77E+02	4.49E-03	1.58E+00
59.5	5.03E-01	7.80E+02	3.16E-03	1.06E+00
62.2	5.12E-01	7.83E+02	3.31E-03	1.06E+00
65.1	5.18E-01	7.85E+02	2.17E-03	6.66E-01
68.1	5.26E-01	7.87E+02	2.66E-03	7.80E-01
71.2	5.37E-01	7.90E+02	3.55E-03	9.98E-01
74.5	5.50E-01	7.94E+02	3.71E-03	9.95E-01
78.0	5.62E-01	7.97E+02	3.77E-03	9.68E-01
81.5	5.73E-01	8.00E+02	3.03E-03	7.43E-01
85.3	5.82E-01	8.02E+02	2.35E-03	5.51E-01
89.2	5.91E-01	8.04E+02	2.22E-03	4.97E-01
93.3	6.01E-01	8.06E+02	2.56E-03	5.50E-01
97.6	6.10E-01	8.08E+02	1.98E-03	4.05E-01
102.1	6.18E-01	8.09E+02	1.87E-03	3.66E-01
106.8	6.29E-01	8.11E+02	2.36E-03	4.43E-01
111.7	6.39E-01	8.13E+02	2.01E-03	3.60E-01
116.9	6.48E-01	8.15E+02	1.72E-03	2.94E-01
122.3	6.58E-01	8.16E+02	1.92E-03	3.15E-01
127.9	6.70E-01	8.18E+02	2.09E-03	3.27E-01
133.8	6.82E-01	8.20E+02	1.99E-03	2.98E-01
139.9	6.94E-01	8.22E+02	1.89E-03	2.70E-01
146.4	7.02E-01	8.23E+02	1.38E-03	1.89E-01
153.1	7.10E-01	8.24E+02	1.18E-03	1.54E-01
160.1	7.18E-01	8.25E+02	1.11E-03	1.38E-01
167.5	7.26E-01	8.26E+02	1.05E-03	1.25E-01
175.2	7.34E-01	8.27E+02	9.90E-04	1.13E-01
183.3	7.42E-01	8.28E+02	1.03E-03	1.12E-01

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
191.7	7.52E-01	8.29E+02	1.23E-03	1.28E-01
200.6	7.62E-01	8.30E+02	1.11E-03	1.10E-01
209.8	7.70E-01	8.30E+02	8.71E-04	8.31E-02
219.4	7.78E-01	8.31E+02	8.28E-04	7.55E-02
229.5	7.86E-01	8.32E+02	7.92E-04	6.90E-02
240.1	7.94E-01	8.32E+02	7.50E-04	6.25E-02
251.2	8.00E-01	8.33E+02	5.36E-04	4.27E-02
262.7	8.04E-01	8.33E+02	3.40E-04	2.59E-02
274.8	8.10E-01	8.34E+02	4.83E-04	3.51E-02
287.5	8.20E-01	8.34E+02	8.11E-04	5.64E-02
300.7	8.29E-01	8.35E+02	6.63E-04	4.41E-02
314.5	8.35E-01	8.35E+02	4.22E-04	2.68E-02
329.0	8.40E-01	8.36E+02	4.02E-04	2.44E-02
344.2	8.46E-01	8.36E+02	3.82E-04	2.22E-02
360.0	8.58E-01	8.37E+02	7.23E-04	4.02E-02

W35

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
8.6	1.18E-01	3.73E+02	3.16E-02	7.36E+01
9.0	1.30E-01	3.99E+02	2.87E-02	6.39E+01
9.4	1.40E-01	4.20E+02	2.45E-02	5.22E+01
9.8	1.51E-01	4.43E+02	2.55E-02	5.18E+01
10.3	1.62E-01	4.64E+02	2.39E-02	4.64E+01
10.8	1.71E-01	4.81E+02	2.01E-02	3.73E+01
11.3	1.82E-01	5.00E+02	2.10E-02	3.74E+01
11.8	1.92E-01	5.17E+02	2.00E-02	3.40E+01
12.3	2.02E-01	5.33E+02	1.81E-02	2.93E+01
12.9	2.10E-01	5.45E+02	1.35E-02	2.10E+01
13.5	2.17E-01	5.56E+02	1.21E-02	1.79E+01
14.1	2.25E-01	5.68E+02	1.35E-02	1.91E+01
14.7	2.32E-01	5.77E+02	1.02E-02	1.38E+01
15.4	2.38E-01	5.85E+02	9.45E-03	1.23E+01
16.1	2.43E-01	5.91E+02	6.81E-03	8.44E+00
16.9	2.48E-01	5.97E+02	6.50E-03	7.70E+00
17.7	2.53E-01	6.03E+02	6.96E-03	7.88E+00
18.5	2.58E-01	6.08E+02	5.41E-03	5.86E+00
19.3	2.58E-01	6.08E+02	9.63E-04	9.97E-01
20.2	2.58E-01	6.08E+02	0.00E+00	0.00E+00
21.1	2.58E-01	6.08E+02	0.00E+00	0.00E+00
22.1	2.58E-01	6.08E+02	0.00E+00	0.00E+00
23.1	2.58E-01	6.08E+02	0.00E+00	0.00E+00
24.2	2.59E-01	6.09E+02	7.24E-04	5.98E-01
25.3	2.63E-01	6.12E+02	3.39E-03	2.68E+00
26.5	2.68E-01	6.16E+02	4.44E-03	3.35E+00
27.7	2.74E-01	6.20E+02	5.20E-03	3.76E+00
29.0	2.81E-01	6.25E+02	4.89E-03	3.37E+00
30.3	2.86E-01	6.28E+02	3.98E-03	2.62E+00
31.7	2.91E-01	6.32E+02	3.71E-03	2.34E+00
33.2	2.96E-01	6.35E+02	3.68E-03	2.22E+00
34.7	3.03E-01	6.38E+02	3.94E-03	2.27E+00

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
36.3	3.11E-01	6.43E+02	5.24E-03	2.89E+00
37.9	3.22E-01	6.49E+02	6.84E-03	3.60E+00
39.7	3.33E-01	6.54E+02	6.04E-03	3.04E+00
41.5	3.40E-01	6.58E+02	4.04E-03	1.95E+00
43.4	3.46E-01	6.60E+02	3.00E-03	1.38E+00
45.4	3.52E-01	6.63E+02	3.12E-03	1.37E+00
47.5	3.59E-01	6.66E+02	3.14E-03	1.32E+00
49.7	3.64E-01	6.68E+02	2.60E-03	1.05E+00
52.0	3.70E-01	6.70E+02	2.48E-03	9.55E-01
54.4	3.75E-01	6.72E+02	2.19E-03	8.04E-01
56.9	3.80E-01	6.74E+02	1.83E-03	6.42E-01
59.5	3.83E-01	6.75E+02	1.20E-03	4.04E-01
62.2	3.88E-01	6.76E+02	1.75E-03	5.64E-01
65.1	3.92E-01	6.78E+02	1.29E-03	3.97E-01
68.1	3.96E-01	6.79E+02	1.45E-03	4.26E-01
71.2	4.01E-01	6.80E+02	1.73E-03	4.84E-01
74.5	4.07E-01	6.82E+02	1.70E-03	4.56E-01
78.0	4.12E-01	6.83E+02	1.62E-03	4.15E-01
81.5	4.17E-01	6.84E+02	1.17E-03	2.87E-01
85.3	4.19E-01	6.85E+02	7.62E-04	1.79E-01
89.2	4.22E-01	6.86E+02	7.41E-04	1.66E-01
93.3	4.26E-01	6.87E+02	9.46E-04	2.03E-01
97.6	4.29E-01	6.87E+02	7.14E-04	1.46E-01
102.1	4.32E-01	6.88E+02	6.76E-04	1.32E-01
106.8	4.36E-01	6.88E+02	7.92E-04	1.48E-01
111.7	4.39E-01	6.89E+02	6.67E-04	1.19E-01
116.9	4.42E-01	6.90E+02	5.53E-04	9.47E-02
122.3	4.45E-01	6.90E+02	5.70E-04	9.32E-02
127.9	4.48E-01	6.91E+02	5.59E-04	8.75E-02
133.8	4.52E-01	6.91E+02	5.32E-04	7.96E-02
139.9	4.55E-01	6.91E+02	5.08E-04	7.27E-02
146.4	4.57E-01	6.92E+02	3.56E-04	4.86E-02
153.1	4.59E-01	6.92E+02	2.97E-04	3.88E-02
160.1	4.61E-01	6.92E+02	2.79E-04	3.49E-02
167.5	4.63E-01	6.92E+02	2.65E-04	3.16E-02
175.2	4.65E-01	6.93E+02	2.50E-04	2.85E-02
183.3	4.67E-01	6.93E+02	2.34E-04	2.55E-02

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
191.7	4.69E-01	6.93E+02	2.17E-04	2.26E-02
200.6	4.70E-01	6.93E+02	1.95E-04	1.95E-02
209.8	4.72E-01	6.93E+02	1.54E-04	1.47E-02
219.4	4.73E-01	6.94E+02	1.46E-04	1.33E-02
229.5	4.75E-01	6.94E+02	1.40E-04	1.22E-02
240.1	4.76E-01	6.94E+02	1.33E-04	1.11E-02
251.2	4.77E-01	6.94E+02	9.47E-05	7.54E-03
262.7	4.78E-01	6.94E+02	6.00E-05	4.57E-03
274.8	4.79E-01	6.94E+02	9.63E-05	7.01E-03
287.5	4.81E-01	6.94E+02	1.76E-04	1.22E-02
300.7	4.83E-01	6.94E+02	1.31E-04	8.72E-03
314.5	4.84E-01	6.94E+02	8.35E-05	5.31E-03
329.0	4.85E-01	6.94E+02	7.98E-05	4.85E-03
344.2	4.86E-01	6.94E+02	7.56E-05	4.40E-03
360.0	4.89E-01	6.95E+02	1.42E-04	7.89E-03

W20

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
8.6	9.47E-02	3.01E+02	2.12E-02	4.93E+01
9.0	1.00E-01	3.13E+02	1.38E-02	3.07E+01
9.4	1.05E-01	3.23E+02	1.15E-02	2.45E+01
9.8	1.10E-01	3.34E+02	1.21E-02	2.46E+01
10.3	1.16E-01	3.44E+02	1.21E-02	2.35E+01
10.8	1.22E-01	3.56E+02	1.28E-02	2.38E+01
11.3	1.31E-01	3.72E+02	1.89E-02	3.35E+01
11.8	1.41E-01	3.89E+02	1.86E-02	3.17E+01
12.3	1.47E-01	3.99E+02	1.13E-02	1.84E+01
12.9	1.51E-01	4.06E+02	8.06E-03	1.25E+01
13.5	1.56E-01	4.12E+02	7.59E-03	1.13E+01
14.1	1.61E-01	4.20E+02	8.07E-03	1.14E+01
14.7	1.64E-01	4.24E+02	5.17E-03	7.01E+00
15.4	1.66E-01	4.27E+02	3.30E-03	4.28E+00
16.1	1.68E-01	4.29E+02	2.61E-03	3.23E+00
16.9	1.71E-01	4.32E+02	3.27E-03	3.88E+00
17.7	1.74E-01	4.35E+02	3.50E-03	3.97E+00
18.5	1.75E-01	4.37E+02	2.05E-03	2.22E+00
19.3	1.75E-01	4.37E+02	0.00E+00	0.00E+00
20.2	1.75E-01	4.37E+02	0.00E+00	0.00E+00
21.1	1.75E-01	4.37E+02	0.00E+00	0.00E+00
22.1	1.75E-01	4.37E+02	0.00E+00	0.00E+00
23.1	1.75E-01	4.37E+02	0.00E+00	0.00E+00
24.2	1.75E-01	4.37E+02	3.32E-05	2.75E-02
25.3	1.78E-01	4.39E+02	2.22E-03	1.75E+00
26.5	1.82E-01	4.42E+02	3.31E-03	2.50E+00
27.7	1.86E-01	4.45E+02	3.53E-03	2.55E+00
29.0	1.90E-01	4.48E+02	3.09E-03	2.14E+00
30.3	1.93E-01	4.50E+02	2.26E-03	1.49E+00
31.7	1.96E-01	4.52E+02	2.62E-03	1.65E+00
33.2	2.01E-01	4.55E+02	3.02E-03	1.82E+00
34.7	2.06E-01	4.57E+02	3.10E-03	1.79E+00

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
36.3	2.12E-01	4.61E+02	3.91E-03	2.15E+00
37.9	2.20E-01	4.65E+02	5.05E-03	2.66E+00
39.7	2.30E-01	4.70E+02	5.52E-03	2.78E+00
41.5	2.38E-01	4.74E+02	4.20E-03	2.02E+00
43.4	2.41E-01	4.76E+02	2.00E-03	9.20E-01
45.4	2.45E-01	4.77E+02	1.66E-03	7.32E-01
47.5	2.49E-01	4.79E+02	1.98E-03	8.34E-01
49.7	2.53E-01	4.80E+02	1.72E-03	6.94E-01
52.0	2.56E-01	4.82E+02	1.65E-03	6.34E-01
54.4	2.60E-01	4.83E+02	1.57E-03	5.78E-01
56.9	2.64E-01	4.85E+02	1.47E-03	5.17E-01
59.5	2.66E-01	4.85E+02	1.01E-03	3.39E-01
62.2	2.69E-01	4.86E+02	9.81E-04	3.15E-01
65.1	2.71E-01	4.87E+02	6.68E-04	2.05E-01
68.1	2.73E-01	4.87E+02	7.07E-04	2.08E-01
71.2	2.75E-01	4.88E+02	5.61E-04	1.57E-01
74.5	2.77E-01	4.88E+02	5.69E-04	1.53E-01
78.0	2.80E-01	4.89E+02	8.89E-04	2.28E-01
81.5	2.82E-01	4.90E+02	7.27E-04	1.78E-01
85.3	2.85E-01	4.90E+02	5.58E-04	1.31E-01
89.2	2.87E-01	4.91E+02	5.30E-04	1.19E-01
93.3	2.89E-01	4.91E+02	5.45E-04	1.17E-01
97.6	2.91E-01	4.92E+02	3.93E-04	8.05E-02
102.1	2.92E-01	4.92E+02	3.78E-04	7.40E-02
106.8	2.94E-01	4.92E+02	4.17E-04	7.82E-02
111.7	2.96E-01	4.93E+02	3.40E-04	6.08E-02
116.9	2.97E-01	4.93E+02	2.88E-04	4.93E-02
122.3	2.99E-01	4.93E+02	3.25E-04	5.32E-02
127.9	3.01E-01	4.93E+02	3.24E-04	5.06E-02
133.8	3.03E-01	4.94E+02	3.08E-04	4.61E-02
139.9	3.05E-01	4.94E+02	2.98E-04	4.26E-02
146.4	3.06E-01	4.94E+02	2.13E-04	2.91E-02
153.1	3.07E-01	4.94E+02	1.76E-04	2.30E-02
160.1	3.08E-01	4.95E+02	1.66E-04	2.07E-02
167.5	3.09E-01	4.95E+02	1.57E-04	1.87E-02
175.2	3.11E-01	4.95E+02	1.48E-04	1.69E-02
183.3	3.12E-01	4.95E+02	1.38E-04	1.51E-02

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
191.7	3.13E-01	4.95E+02	1.34E-04	1.39E-02
200.6	3.14E-01	4.95E+02	1.24E-04	1.23E-02
209.8	3.15E-01	4.95E+02	9.79E-05	9.34E-03
219.4	3.16E-01	4.95E+02	9.30E-05	8.47E-03
229.5	3.17E-01	4.95E+02	8.90E-05	7.75E-03
240.1	3.18E-01	4.95E+02	8.43E-05	7.02E-03
251.2	3.18E-01	4.96E+02	5.98E-05	4.77E-03
262.7	3.19E-01	4.96E+02	3.82E-05	2.91E-03
274.8	3.19E-01	4.96E+02	6.59E-05	4.80E-03
287.5	3.21E-01	4.96E+02	1.30E-04	9.04E-03
300.7	3.22E-01	4.96E+02	9.65E-05	6.42E-03
314.5	3.23E-01	4.96E+02	6.16E-05	3.91E-03
329.0	3.24E-01	4.96E+02	5.88E-05	3.57E-03
344.2	3.25E-01	4.96E+02	5.58E-05	3.24E-03
360.0	3.27E-01	4.96E+02	1.03E-04	5.75E-03

Pellet II

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
8.6	7.20E-02	2.24E+02	2.93E-02	6.82E+01
9.0	8.38E-02	2.50E+02	2.99E-02	6.66E+01
9.4	9.57E-02	2.75E+02	2.88E-02	6.12E+01
9.8	1.17E-01	3.01E+02	5.57E-02	1.13E+02
10.3	1.44E-01	3.53E+02	5.95E-02	1.16E+02
10.8	1.72E-01	4.06E+02	5.99E-02	1.11E+02
11.3	2.07E-01	4.66E+02	6.88E-02	1.22E+02
11.8	2.44E-01	5.30E+02	7.24E-02	1.23E+02
12.3	2.73E-01	5.77E+02	5.41E-02	8.78E+01
12.9	2.96E-01	6.13E+02	4.02E-02	6.23E+01
13.5	3.15E-01	6.41E+02	3.19E-02	4.74E+01
14.1	3.33E-01	6.66E+02	2.89E-02	4.10E+01
14.7	3.50E-01	6.90E+02	2.67E-02	3.62E+01
15.4	3.68E-01	7.13E+02	2.66E-02	3.45E+01
16.1	3.84E-01	7.32E+02	2.18E-02	2.70E+01
16.9	3.97E-01	7.48E+02	1.77E-02	2.10E+01
17.7	4.10E-01	7.63E+02	1.71E-02	1.94E+01
18.5	4.24E-01	7.78E+02	1.70E-02	1.84E+01
19.3	4.31E-01	7.85E+02	7.77E-03	8.04E+00
20.2	4.31E-01	7.85E+02	0.00E+00	0.00E+00
21.1	4.31E-01	7.85E+02	0.00E+00	0.00E+00
22.1	4.31E-01	7.85E+02	0.00E+00	0.00E+00
23.1	4.31E-01	7.85E+02	0.00E+00	0.00E+00
24.2	4.37E-01	7.90E+02	5.69E-03	4.70E+00
25.3	4.51E-01	8.01E+02	1.29E-02	1.02E+01
26.5	4.73E-01	8.18E+02	1.91E-02	1.44E+01
27.7	4.97E-01	8.35E+02	1.94E-02	1.40E+01
29.0	5.20E-01	8.51E+02	1.78E-02	1.23E+01
30.3	5.39E-01	8.63E+02	1.43E-02	9.45E+00
31.7	5.57E-01	8.75E+02	1.29E-02	8.14E+00
33.2	5.76E-01	8.86E+02	1.28E-02	7.74E+00
34.7	5.91E-01	8.95E+02	1.03E-02	5.94E+00

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
36.3	6.09E-01	9.05E+02	1.13E-02	6.22E+00
37.9	6.20E-01	9.10E+02	6.21E-03	3.28E+00
39.7	6.20E-01	9.10E+02	0.00E+00	0.00E+00
41.5	6.26E-01	9.13E+02	3.39E-03	1.63E+00
43.4	6.38E-01	9.19E+02	6.50E-03	2.99E+00
45.4	6.51E-01	9.25E+02	6.64E-03	2.93E+00
47.5	6.65E-01	9.31E+02	6.53E-03	2.75E+00
49.7	6.81E-01	9.37E+02	7.37E-03	2.96E+00
52.0	6.99E-01	9.44E+02	7.59E-03	2.92E+00
54.4	7.15E-01	9.50E+02	6.95E-03	2.56E+00
56.9	7.31E-01	9.56E+02	6.39E-03	2.25E+00
59.5	7.43E-01	9.60E+02	4.37E-03	1.47E+00
62.2	7.52E-01	9.63E+02	3.43E-03	1.10E+00
65.1	7.53E-01	9.63E+02	3.40E-04	1.05E-01
68.1	7.54E-01	9.63E+02	2.84E-04	8.34E-02
71.2	7.65E-01	9.66E+02	3.54E-03	9.93E-01
74.5	7.80E-01	9.70E+02	4.70E-03	1.26E+00
78.0	7.99E-01	9.75E+02	5.28E-03	1.35E+00
81.5	8.15E-01	9.79E+02	4.46E-03	1.09E+00
85.3	8.29E-01	9.82E+02	3.93E-03	9.21E-01
89.2	8.44E-01	9.86E+02	3.69E-03	8.28E-01
93.3	8.61E-01	9.89E+02	4.13E-03	8.86E-01
97.6	8.74E-01	9.92E+02	3.17E-03	6.49E-01
102.1	8.87E-01	9.95E+02	2.92E-03	5.73E-01
106.8	9.12E-01	9.99E+02	5.28E-03	9.89E-01
111.7	9.35E-01	1.00E+03	4.66E-03	8.34E-01
116.9	9.58E-01	1.01E+03	4.37E-03	7.47E-01
122.3	1.01E+00	1.02E+03	9.07E-03	1.48E+00
127.9	1.06E+00	1.02E+03	1.04E-02	1.62E+00
133.8	1.12E+00	1.03E+03	9.88E-03	1.48E+00
139.9	1.18E+00	1.04E+03	9.91E-03	1.42E+00
146.4	1.26E+00	1.05E+03	1.15E-02	1.58E+00
153.1	1.33E+00	1.06E+03	1.12E-02	1.46E+00
160.1	1.41E+00	1.07E+03	1.06E-02	1.32E+00
167.5	1.48E+00	1.08E+03	1.00E-02	1.20E+00
175.2	1.56E+00	1.09E+03	9.50E-03	1.08E+00
183.3	1.63E+00	1.10E+03	8.99E-03	9.81E-01

Pore Width (Å)	Cumulative Pore Volume (cm ³ /g)	Cumulative Surface Area (m ² /g)	Differential Pore Volume (cm ³ /Å/g)	Differential surface area (m ² /Å/g)
191.7	1.68E+00	1.10E+03	6.13E-03	6.40E-01
200.6	1.70E+00	1.10E+03	2.13E-03	2.12E-01
209.8	1.71E+00	1.10E+03	1.65E-03	1.57E-01
219.4	1.73E+00	1.11E+03	1.57E-03	1.43E-01
229.5	1.74E+00	1.11E+03	1.50E-03	1.30E-01
240.1	1.76E+00	1.11E+03	1.42E-03	1.18E-01
251.2	1.77E+00	1.11E+03	1.02E-03	8.09E-02
262.7	1.78E+00	1.11E+03	6.41E-04	4.88E-02
274.8	1.79E+00	1.11E+03	8.17E-04	5.95E-02
287.5	1.79E+00	1.11E+03	2.69E-04	1.87E-02
300.7	1.79E+00	1.11E+03	6.14E-05	4.08E-03
314.5	1.79E+00	1.11E+03	3.83E-05	2.43E-03
329.0	1.79E+00	1.11E+03	4.00E-05	2.43E-03
344.2	1.79E+00	1.11E+03	3.49E-05	2.03E-03
360.0	1.79E+00	1.11E+03	7.46E-05	4.15E-03