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EFFECTS OF NATURAL ORGANIC MATTER ON ADSORPTION CAPACITY FOR ATRAZINE BY ACTIVATED CARBON

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Key Words **:** Atrazine, adsorption, activated carbon, adsorption capacity

ABSTRACT

Adsorption capacities for atrazine on granular activated carbon (GAC) were determined in batch contactors. Conditions in the batch contactors were chosen to determine the reduction in atrazine capacity resulting from competitive adsorption with dissolved organic carbon (DOC), or due to the preadsorbed DOC on the GAC before exposure to atrazine. For aqueous atrazine at 7 μg/L, adsorption capacities in the batch contactors were generally greater than 10 mg/g, and competition with DOC was found to decrease atrazine capacities almost twice as much as preadsorbed DOC. Batch contactor experiments which resulted in low adsorption capacities for atrazine (1-2 mg/g) are considered kinetically limited or by the effects of competitive adsorption with DOC.

INTRODUCTION

Adsorption is defined as the increase in concentration of a particular component at the surface or interface between two phases. The high adsorbability of activated carbon comes from its high surface area (~1000 m^2/g) which results from a porous structure of macropores ($r_p \approx$ 25-1000 nm) subdivided into meso-pores ($r_p \approx$ 2-50 nm) and micropores ($r_p <$ 2 nm). Generally it is believed that the mesopores and micropores provide the internal surface area for adsorption of synthetic organics ($r \approx$ 0.3-0.4 nm), whereas the macropores control the rate of diffusion of an organic from water to the adsorptive surface [1]. Thermodynamic properties of the solute, water and adsorbent surface determine an adsorbent's capacity. Both the capacity and the rate of adsorption need to be understood when a given adsorbent is used for a specific solute.

Activated carbon adsorption remains an important process for drinking water purification. Two mechanisms involving background natural organic matter (NOM) are believed to limit adsorption capacities for hydrophobic synthetic organic contaminants (SOCs) at trace levels: competition and preadsorption. This paper presents experimental results for the effect of background NOM on adsorption of atrazine as a model compound. Atrazine is of interest as a mode-rately hydrophobic synthetic organic (log K_{ow} 2.75; solubility 30 mg/L); atrazine is also a widely used herbicide, commonly found in surface and ground waters receiving agricultural runoff [2]. Since atrazine is only used seasonally, it is not yet clear whether it is best removed by short-term or permanent modifications to the treatment process. Possibilities that have been examined include an elevated dose of powdered activated carbon (PAC; <45 μm) in contact basins [3], PAC applied to a contact basin with membrane filtration [4], and GAC in fixed-bed adsorbers or filter-adsorbers [5]. Atrazine adsorption by PAC or GAC is subject to competition from background NOM. Atrazine adsorption by GAC is also subject to pre-adsorption of background NOM, for the time that a contactor is in service before it receives an input of atrazine. The effects of both competition and pre-adsorbed background NOM are considered in this paper, in an effort to determine if the two processes are related in their ability to limit adsorption capacities for atrazine. Adsorption experiments were conducted in batch contactors, and their effect on the results is also considered.

At present, granular activated carbon is recognized as a best available technology for removal of SOCs from drinking water, including atrazine [6-7]. This designation was largely based on the measurement of adsorption isotherms under single-solute conditions, although it was understood that adsorption capacities would be diminished for individual compounds in a mixture. Mathematical solutions to this problem were developed by Crittenden

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et al. [8], using adsorption isotherms that were determined under single-solute conditions, for all of the compounds known to be present in a mixture. Competition from NOM is regarded as a somewhat more complex problem than competition from other SOCs, primarily because NOM is a mixture of substances with different adsorption properties that are not well characterized by existing methods of analysis. Several mathematical me-thods have been proposed to describe the dependence of a synthetic compound's adsorption isotherm on the concentration of background organic matter [1, 9]. The easiest way is treat the background as a single compound; its adsorption parameters are obtained from the overall isotherms where the organic concentration is measured as dissolved organic carbon (DOC).

The semi-empirical Freundlich equation is perhaps the most widely used nonlinear mathematical description of single solute adsorption equilibrium between aqueous phase (C_e) and solid phase (Q_e):

$$Q_e = K_F \times C_e^{\frac{1}{n}} \quad (1)$$

where K_F and 1/n are Freundlich constants.

For competitive adsorption between atrazine and NOM, Ideal Adsorbed Solution Theory (IAST) can be used to describe the competitive adsorption between DOC and synthetic organic(s) such as atrazine [9-13]. Partitioning of the surface between two solutes can be described by:

$$F_i(Q_1, Q_2) = C_{i0} - \frac{M}{V}Q_i - \frac{Q_i}{\sum_{j=1}^{2} Q_j}\left[\frac{\sum_{j=1}^{2} n_j Q_j}{n_i K_{Fi}}\right]^{n_i} \quad (2)$$

The equilibrium state is described by values of aqueous phase concentration (C_i) and solid phase concentration (Q_i) for which F_i is equal to zero. This equation can be solved using the constants of the single-solute Freundlich isotherms K_{Fi} , $1/n_i$, the initial concentration C_{i0} and the carbon dosage M/V. For atrazine and DOC as solutes, there are two nonlinear simultaneous equations to be solved for the two unknown Q_i values. There should be an unique solution to these simultaneous equations. However, it has been shown that IAST is sensitive to low solute concentrations and problems arise when the numerical calculations require extrapolation beyond the range of the single-solute isotherms.

Crittenden *et al*. [9] investigated the possibility of describing the adsorption of NOM in terms of fictive components, which could be used in calculations of competitive adsorption with synthetic organic contaminants. As an alternative, Najm and Snoeyink developed a procedure which used adsorption isotherms for a synthetic organic compound, measured at several different initial concentrations in the presence of NOM, to deduce the effect of background organic matter [10]. All of these methods involve the use of adsorption isotherms which are determined in batch contactors, and which are most similar to the use of PAC in full-scale systems. Previous study showed that atrazine adsorption isotherms were not found to be strongly temperature dependent and the effect of competition with background DOC was found to be similar at temperatures ranging from 5 to 35 °C [14]. However, the rates of adsorption decrease as the temperature decrease. Atrazine adsorption capacities measured in minicolumns are noted to avoid some of the external diffusion limitations of batch contactors [15]. The results obtained show that capacities for atrazine decrease with increasing particle size and seem in reasonable agreement with concentrations of atrazine found at the top of a filter-adsorber and post-contactor previously operated for 30 weeks at Waterford Water Works [15]. However, more work is needed to establish correct scaling relationships for atrazine adsorption in minicolumns and pilot columns with different GAC particle sizes and contact times.

The effects of preadsorbed NOM on SOC capacities are primarily of concern when granular activated carbon (GAC; 0.42-2.38 mm) is used in fixed beds. Not only are these contactors typically in service for a relatively long time, on the order of one year, but individual contaminants advance through the bed at different rates, because of significant differences in their influent concentrations and affinity for the adsorbent. Results from pilot and full-scale systems have indicated that NOM moves through a fixed bed relatively rapidly, on a time scale of 100 days. In contrast, hydrophobia and weakly soluble SOCs are slow to move through a fixed bed, and generally reach saturation and breakthrough after NOM, if at all. In fixed beds, therefore, NOM and SOCs are chromatographically separated, and the NOM is in effect preadsorbed on GAC at deep bed depths in advance of SOCs. A number of studies have demonstrated that adsorption capacities for trichloroethylene are reduced approximately two-fold by NOM that has been preadsorbed on activated carbon [16-17]. Li *et al*. [18] reported that when the PAC was preloaded with NOM, the pore blockage effect of the NOM caused a reduction of up to two folds of magnitude in the surface diffusion rate of atrazine compared to simultaneous adsorption of atrazine and NOM with fresh PAC. A PAC with relatively large fraction of large micropores and mesopores was shown to suffer much less from the pore blockage effect. The NOM with molecular size between 200 and 700 Dalton appeared to be responsible for the pore blockage effect. However, Knappe et al. [19] showed that preloading NOM had the greatest effect on GAC capacity and the adsorption kinetics was not severely affected.

EXPERIMENTAL METHODS

I. Water Supply

Bench-scale experiments were conducted using two different waters to study atrazine adsorption, a GAC-processed laboratory water with a low background of organic matter, and finished water from Waterford Water Works, Waterford, NY, with a mo-derate background of organic matter.

The laboratory water was the tap water from Albany Water Works, Albany, NY, a surface water supply from the Alcove Reservoir in upstate New York. At the time of this project, this water was further treated by passage through a fixed bed of GAC (15 cm id × 1 m long; 0.42 × 1.68 mm Calgon F400), which removed residual chlorine and reduced background organic matter to below 0.1 mg/L DOC. In the discussion of results, this water is designated organic-free.

Finished water from Waterford Water Works, Waterford, NY, is pumped from the Hudson River and treated by aeration, coagulation, flocculation, sedimentation; pre- and post-chlorination [5]. The concentration of background organic matter averages 2.4 mg/L DOC in this Waterford water [20].

II. Activated Carbon

Stocks of two different activated carbons were used to study atrazine adsorption, fresh Calgon F300 (initially 0.60-2.38 mm), and Calgon F300 collected from a control pilot column that received background organic matter for 30 weeks at Waterford Water Works [5]. Properties of the F300 activated carbon can be seen elsewhere [15]. All samples of GAC were ground in a rotary disc mill (Spex Shatterbox) for two to five minutes, and the resulting powder was sieved to obtain a 53 to 149 μm fraction (100 by 270 mesh), designated 100-μm GAC. Samples of pilot-column GAC were dried at room temperature, first in air, and then in a vacuum overnight, before grinding and sieving to collect a nominal 100-μm fraction.

For adsorption isotherm experiments in the laboratory, GAC from this pilot column was collected at bed depths of 23, 43 and 84 cm, after 21, 48, 76 and 141 days in operation: amounts of preadsorbed DOC on these samples have been calculated from breakthrough data and range from 2.1 to 31.6 mg DOC/g GAC [5, 16].

III. Adsorption Isotherm Experiments

A batch contactor procedure was used to determine Freundlich isotherms for GAC adsorption of atrazine. A desired amount of atrazine was weighed and transferred to a large glass bottle (~19 L), half-filled with the water to be studied: additional water was added to 17 L, and the mixture was stirred overnight to reach an initial concentration C_0, between 1000 and 3 μg/L. The stock solution was used to fill small batch contactors to a fixed volume (V, 0.9 L). Each batch contactor contained a known amount (M) of 100-μm GAC, preweighed on an analytical balance and typically between 1 and 40 mg. Different amounts of GAC were used in the batch contactors, so that final concentrations of atrazine in the aqueous and adsorbed phase, C_e (μg/L) and Q_e (mg/g), respectively, would be distributed over a range of values. The amounts of GAC were also chosen according to the value of C_0, in order to have detectable concentrations of atrazine remaining in the water after contact with the GAC.

Contact times of seven days were allowed for atrazine adsorption onto activated carbon. During this time, the contents of the batch contactors were continuously agitated on a plat form shaker (Eberbach Model 6010), and occasionally the contactors were inverted to resuspend settled GAC. Experiments were conducted in a temperature-controlled Environmental Hotpack at 12 °C , since this was the average temperature of the pilot-column study of atrazine adsorption at Waterford, NY [5]. At the end of the 7-day contact time, water samples were filtered (0.45 μm) to remove the GAC and then extracted to determine the aqueous-phase atrazine concentration C_e. The concentration of atrazine in the adsorbed-phase, Q_e, was calculated by assuming a mass balance with atrazine in the aqueous phase:

$$Q_e = \frac{(C_0 - C_e) \times V}{M} \tag{3}$$

Linear regression analysis was used to find the coefficients K_F and l/n of the Freundlich isotherm which fit the experimental data:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

IV. Analysis for Atrazine

The concentration of atrazine ($C_8H_{14}N_5Cl$) in water was determined by solvent extraction and analysis using capillary-column gas chromatography with nitrogen-phosphorus detection, similar to a procedure developed by Graves [21]. Atrazine was first extracted from water samples (800 mL) in methylene chloride, which was exchanged for methyl t-butyl ether (MtBE) and concentrated to 1 mL using a Kuderna-Danish evaporator attached to a Snyder column. Compounds of interest were analyzed using a Hewlett Packard 5880 gas chromatograph: extracts were injected (2 μL) on a capillary column (30 m by 0.25 mm id, 0.31 μm DB5), which was temperature-programmed from 60 °C to 275 °C at 4 °C/min, with a

1-min hold at the initial and final temperatures. The injector and detector temperatures were 250 and 300 °C, respectively. Ametryn ($C_9H_{17}N_5S$) and tripropyl phosphate ($(C_3H_7O)_3PO_4$) were added to sample extracts and calibration mixtures as internal standards at 500 µg/L.

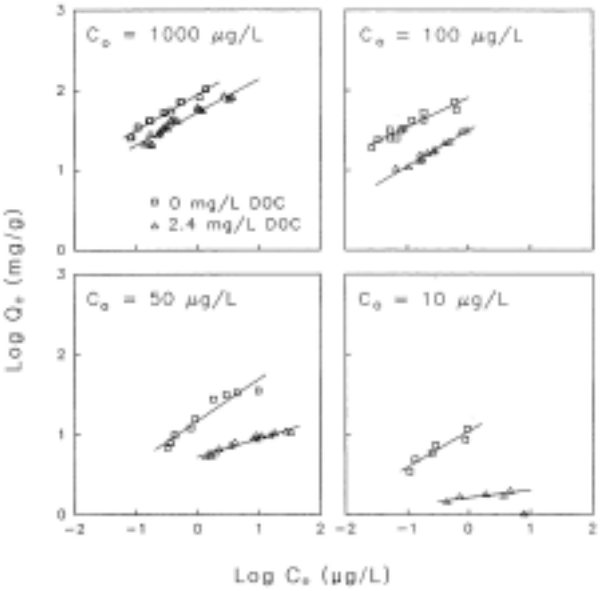

Fig. 1. Isotherms for adsorption of atrazine to 100 µm GAC at 12 °C, with and without competition from background DOC.

RESULTS AND DISCUSSION

I. Effect of Background DOC

A reduction in the GAC capacity for atrazine is expected in systems where atrazine is competitively adsorbed with DOC. As shown in Fig. 1, Freundlich isotherms for adsorption of atrazine in the presence of DOC generally lies below those obtained in organic-free water. However Fig. 1 also reveals a more subtle tendency for adsorption capacities to decrease as the initial concentration C_0 of atrazine decreases, even when atrazine is adsorbed from organic-free water.

This effect is seen more clearly by calculating the concentration of atrazine on the GAC, Q_e, at a specific aqueous phase concentration C_e, for the isotherm coefficients specific to each C_0. In Fig. 2, GAC capacities are calculated at an aqueous phase concentration of 7 µg/L (the average influent concentration in pilot column studies [5]). As expected for competitive adsorption, GAC capacities in the presence of 2.4 mg/L DOC are consistently below capacities predicted from isotherms in organic-free water. However, both sets of data show a dramatic decrease in the isotherm capacity as the value of C_0 decreases to below 200 µg/L. In this region, adsorption is labeled particle-limited, for reasons discussed in a later section.

Freundlich coefficients for GAC adsorption of atrazine, without and with background DOC, are given in Tables 1 and 2, respectively. In both cases, values for the Freundlich K_F generally decrease as the initial atrazine concentration decreases. A similar trend is evident in values for the Freundlich l/n, but only with DOC present. From results in Tables 1 and 2, it can also be seen that experiments at low initial concentrations C_0 were conducted using a lower dose (M/V) of GAC. By decreasing the GAC dose at low C_0, it was found possible to allow the system to equilibrate and still have final concentrations C_e in the range established for quantitation of atrazine. In the presence of DOC, adsorption capacities at 7 µg/L could be determined using GAC doses on the order of 20, 4 and 1 mg/L for initial concentrations C_0 of 1000, 100 and 10 µg/L, respectively. However, in the absence of DOC, GAC doses on the order of 10, 1 and 0.1 mg/L were required for initial concentrations C_0 of 1000, 100 and 10 µg/L.

II. Effect of Preadsorbed DOC

GAC samples from a pilot column operated at Waterford Water Works, NY, were used to determine the effect of preloaded background organics of atrazine adsorption [5]. Detail description on the effects of preadsorbed DOC on atrazine adsorption and coefficients of Freundlich isotherms obtained with preloaded GAC are presented elsewhere [16].

Figure 3 attempts to make a more direct analysis of the atrazine capacity, calculated at an aqueous phase concentration of 7 µg/L: at each initial concentration C_0, capacities are fitted to a linear function of preadsorbed DOC. Negative slopes are obtained, consistently indicating a decrease in adsorption capacity with increased preloading; however, the correlation coefficients are weak, decreasing from R^2 of 0.54 at C_0 of 1000 µg/L to an R^2 of 0.46 at C_0 of 10 µg/L. The maximum loss in atrazine capacity is 40 percent, based on experiments at an initial concentration of 1000 µg/L atrazine, using GAC with 31.6 mg/g pre-adsorbed DOC. In other work, the same GAC samples have been used to determine adsorption capacities for trichloroethylene: decreasing capacities for adsorption of trichloroethylene were strongly correlated with increased preloading of DOC, as indicated by an R^2 value of 0.78; the decrease in the adsorption capacity for trichloroethylene reached a maximum of 60 percent at 31.6 mg/g preadsorbed DOC [5].

Figure 4 analyzes capacities from the preloading experiments as a function of initial concentration C_0: as expected from Fig. 2, the data show a dramatic decrease in the isotherm capacity as the value of C_0 decreases to below 200 µg/L. In Fig. 4, it can also be seen that capacities for atrazine on GAC with 8 mg DOC/g GAC are essentially the same as on GAC with

no DOC. At 16.8, 24.1 and 31.6 mg DOC/g GAC, capacities for atrazine are significantly below those on GAC with no preadsorbed DOC: the inability to relate capacities to the precise amount of preadsorbed DOC is the reason that weak correlation coefficients were obtained for the interpretations in Fig. 3. A difference in adsorption capacity for atrazine can only be resolved for GAC with a low versus high amount of

Table 1. Experimental conditions and coefficients of Freundich isotherms for adsorption of atrazine by 100-μm GAC in organic-free laboratory water.

Atrazine initial concentration	GAC dosage	Freundich coefficients		Sample number	Correlation coefficient	Theoretical values at C_e = 7 μg/L	
C_0	M/V	K_F	1/n	N	R^2	Q_e	M/V
(μg/L)	(mg/L)	(mg/g)(L/μg)$^{1/n}$	-	-	-	(mg/g)	(mg/L)
1000	11-44	30.97	0.449	14	0.975	74.2	13.4
500	6-27	33.19	0.448	14	0.990	79.3	6.2
100	2-6	34.36	0.370	12	0.901	70.6	1.3
50	1-4	14.93	0.519	9	0.914	41.0	1.0
10	0.5-1.7	10.89	0.447	6	0.893	26.0[a]	0.1
3	0.3-1.7	5.64	0.510	6	0.849	15.2[a]	-

[a] The value of Q_e is extrapolated. For a C_0 of 10 μg/L, the experimental isotherm only goes to C_e 1 μg/L, rather than 7 μg/L, and the dose M/V is below the experimental range. A C_0 of 3 μg/L is less than 7 μg/L; a value can be calculated for Q_e, but the dose M/V is mathematically undefined.

Table 2. Experimental conditions and coefficient of Freundich isotherms for adsorption of atrazine by 100-μm GAC in Waterford water with 2.4±0.8 mg/L DOC.

Atrazine initial concentration	GAC dosage	Freundich coefficients		Sample number	Correlation coefficient	Theoretical values at C_e = 7 μg/L	
C_0	M/V	K_F	1/n	N	R^2	Q_e	M/V
(μg/L)	(mg/L)	(mg/g)(L/μg)$^{1/n}$	-	-	-	(mg/g)	(mg/L)
1000	10-40	20.37	0.412	24	0.938	45.4	21.8
800	11-44	18.25	0.324	11	0.885	34.3	23.1
600	6-33	17.03	0.277	10	0.958	29.2	20.3
500	5-20	16.32	0.428	12	0.981	37.5	13.1
400	6-22	14.55	0.318	12	0.924	27.1	14.4
200	2-17	10.38	0.293	11	0.925	18.4	10.5
100	2-10	11.14	0.453	12	0.971	26.8	3.5
70	2-10	8.00	0.362	10	0.988	14.6	4.3
50	2-5	5.25	0.230	15	0.945	8.45	5.1
40	2-6	7.41	0.287	10	0.899	14.9	2.2
10	1-3	1.62	0.098	5	0.770	1.96	1.5
3	1-3	0.68	0.120	4	0.849	0.86[a]	-

[a] The value of Q_e is extrapolated. Since C_0 < 7 μg/L, the dose M/V is mathematically undefined.

preadsorbed DOC.

III. Reduction in Adsorption Capacities from Competition and Preadsorbed DOC

The interpretations in Figs. 2 and 4 provide a basis for comparing the loss in atrazine capacity from competitive adsorption of DOC to the loss in atrazine capacity when DOC is preadsorbed on the GAC. As shown in Fig. 5, the greatest loss in capacity is observed when atrazine is adsorbed competitively with DOC: the loss in capacity increases from 51 percent at C_0 of 1000 μg/L to 92 percent at C_0 of 10 μg/L, with a mean standard deviation of 14 percent. For preadsorbed DOC, maximum losses are calculated from results obtained for 16.8 to 31.6 mg DOC/g GAC: the loss in capacity increases from 26 percent at C_0 of 1000 μg/L to 41 percent at C_0 of 10 μg/L, with a mean relative standard deviation of 8 percent. In the batch contactors, therefore, competition with DOC decreases atrazine capacities almost twice as much as preadsorbed DOC.

Additional isotherm experiments were conducted in Waterford water using GAC with preadsorbed DOC: coefficients of the adsorption isotherms are given in Table 3. Results of these experiments do not simply represent the combined effects of competition and preadsorbed DOC, since the use of GAC with preadsorbed DOC should inhibit adsorption of additional DOC and its ability to actively compete

with atrazine. Similar to the experiments already described, the results can be evaluated quantitatively for the case that atrazine decreases from an initial concentration of 1000 μg/L to an equilibrium concentration of 7 μg/L. Based on a comparison of results in Table 3 to those in Table 2, the reduction in capacity that can be attributed to preadsorption alone is found to be 24 percent. A comparison of results in Table 3 to those in Table 1 indicates a total reduction in capacity of 54 percent. Therefore, the net reduction in capacity that can be attributed to competition is 30 percent: this is still a surprising amount of the 51 percent reduction expected from the competitive adsorption experiment using clean GAC (Table 2). By implication, preadsorbed DOC does not entirely inhibit adsorption of additional DOC.

Table 3. Experimental conditions and coefficients of Freundich isotherms for atrazine adsorption from Waterford water (2.4±0.8 mg/L DOC) by 100-μm GAC perloaded with organic matters.

Preloaded DOC	Atrazine initial concentration	GAC dosage	Freundich coefficients		Sample number	Correlation coefficient	Theoretical values at C_e = 7 μg/L	
	C_0	M/V	K_F	1/n	N	R^2	Q_e	M/V
(mg/g)	(μg/L)	(mg/L)	(mg/g)(L/μg)$^{1/n}$	-	-	-	(mg/g)	(mg/L)
4.3	1000	11-44	25.53	0.308	10	0.956	46.5	21.3
6.8	1000	11-44	26.00	0.322	11	0.960	48.6	20.4
8.3	1000	11-44	23.17	0.357	12	0.943	46.3	21.4
16.8	1000	11-44	16.93	0.352	11	0.940	33.5	29.7
24.1	1000	11-44	18.71	0.328	12	0.965	35.4	28.0
24.1	10	1-3	1.46	0.216	7	0.915	2.22	1.4
31.6	1000	11-44	19.50	0.296	10	0.985	34.7	28.7
31.6	10	1-3	1.26	0.132	8	0.669	1.62	1.9

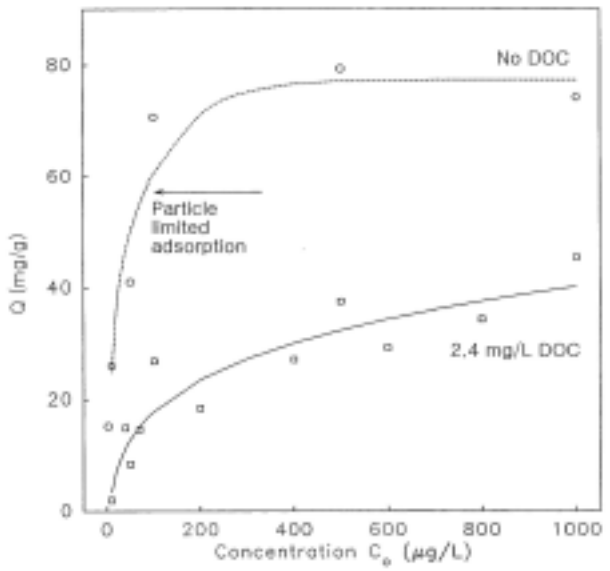

Fig. 2. Effect of competition from background DOC on the GAC capacity for atrazine, at an equilibrium concentration C_e of 7 μg/L, and as a function of the initial concentration C_o.

It should be noted that the ability to compare the effects of competition and preadsorbed DOC is limited by the precision of experimentally-determined capacities for adsorption of atrazine. For unused Calgon F300 in organic-free water and Waterford water with 2.4 mg/L DOC, the relative deviation of experimental capacities from the Freundlich isotherm is found to be 13.4 and 31.4 percent, respectively. Similarly, using Calgon F300 with 16.8, 24.1 and 31.6 mg DOC/g GAC (in organic-free water), the relative deviation is found to be 14.3, 20.8, and 23.8 percent, respectively.

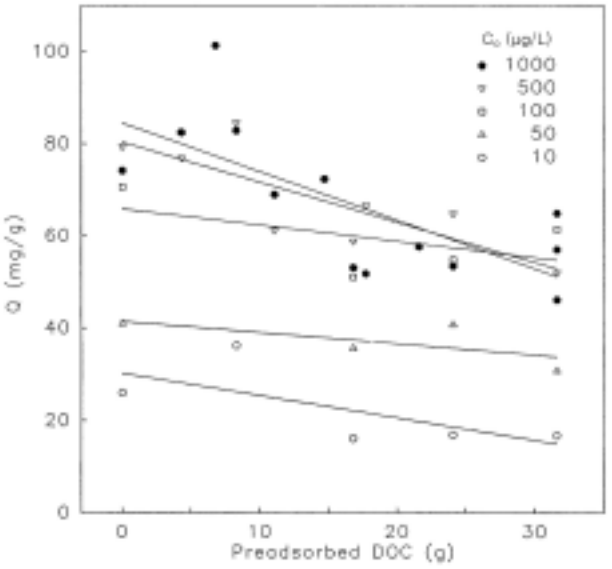

Fig. 3. Effect of preadsorbed DOC on GAC capacity for atrazine at an equilibrium concentration C_e of 7 μg/L.

IV. Kinetic Limitations in Batch Isotherm Experiments

Conditions in the batch contactors also affect the ability to observe the effect of competition and preadsorption. It is generally assumed that experiments in batch contactors are designed to avoid limitations

from bulk diffusion processes or the frequency of collisions between particles. In some cases, however, these processes are thought to have limited atrazine adsorption: for example, in experiments where the capacity for atrazine decreased sharply as the initial concentration of atrazine was lowered, even in organic-free water (Figs. 2 and 4). As the initial concentration of atrazine was lower down, the molecular
numbers of atrazine were reduced; in the mean time, the number of activated carbon particles were also lower than normal (Tables 1 and 2). Since the concentrations of the background organic matter was not changed, we can expect that DOC should have a significant competitive advantage relative to atrazine. At low doses of GAC, used with initial atrazine concentrations of 100 µg/L or less, there is reason to believe that adsorption of both atrazine and DOC is dominated by the limited frequency of their collisions with GAC particles. The relatively low temperature (12 °C) used for batch adsorption experiments also limits the kinetics of the adsorption processes [14, 22]. For atrazine, and compounds which are even more hydrophobic, there remains a need for bench-scale methods that can be reliably used to determine adsorption isotherms, and support the development of predictive models for pilot and full-scale GAC contactors [15].

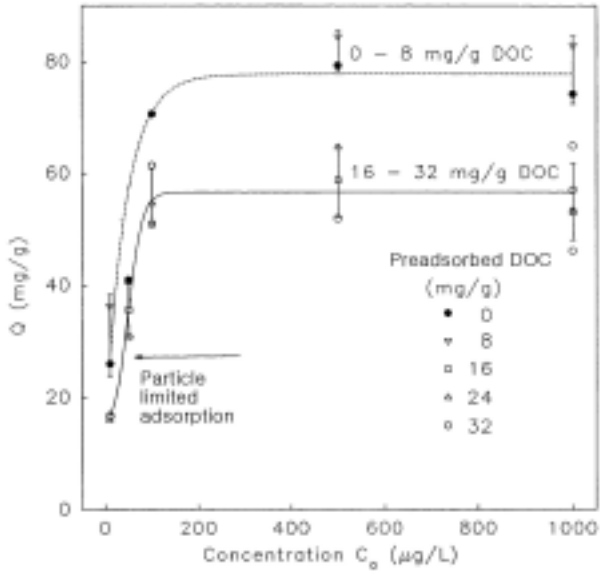

Fig. 4. Effect of preadsorbed DOC on GAC capacity for atrazine at an equilibrium concentration C_e of 7 µg/L, as a function of initial concentration C_o.

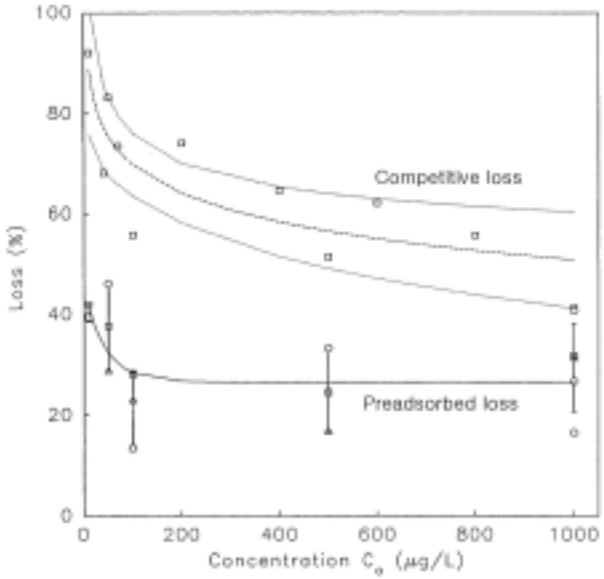

Fig. 5. Comparison of the loss in GAC capacity for atrazine (C_e 7 µg/L), due to competition with 2.4 mg/L DOC and due to preadsorbed DOC. For competitive loss, the dash line shows the regression of the data and the dotted lines indicate the upper and lower 95% confidence intervals of the regression. For preadsorbed loss, see Figure 4 for symbol descriptions.

CONCLUSIONS

Adsorption isotherm capacities were found to decrease strongly with a decrease in initial concentration of atrazine. The decrease in adsorption capacity for atrazine due to competition with background DOC is quantified by comparing isotherms obtained with different concentrations of DOC but the same initial concentration of atrazine and the same contact time. The effect of competition with background organics is determined by comparing adsorption capacities for atrazine in organic-free water (<0.1 mg/L DOC) to those in Waterford water (2.4 mg/L DOC). At an initial atrazine concentration of 10 µg/L, competition with background organics in Waterford water results in a 90 percent decrease in adsorption capacity. Similar results are obtained for the effect of competition, regardless of whether the activated carbon used in adsorption isotherm experiments is fresh or preloaded with background DOC: competition with background DOC results in an 84 percent decrease in adsorption capacities for atrazine on GAC preloaded with 32 mg DOC/g GAC, compared to the 90 percent decrease observed using fresh GAC.

Several results suggest that the bulk of DOC in treated natural water is not responsible for competitive reductions in GAC capacity for atrazine. Regardless of whether the activated carbon used in adsorption isotherm experiments is fresh or preloaded with background DOC, similar results are obtained for the effect of competition: an 84 percent reduction in adsorption capacities for atrazine is obtained in experiments using GAC preloaded with 32 mg DOC/g GAC, compared to a 90 percent reduction using fresh

GAC. At low initial atrazine concentrations, adsorption of both atrazine and DOC is dominated by the limited frequency of their collisions with GAC particles. Therefore analytical attention needs to be focused on identifying a specific fraction or component of background organics in treated natural waters, which has transport and adsorption properties similar to atrazine.

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水中天然有機物對活性碳吸附 ATRAZINE 吸附容量之影響

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關鍵詞：草除盡（Atrazine）、吸附、活性碳、吸附容量

摘　　要

本研究使用批次等溫吸附方法決定粒狀活性碳對 atrazine 之吸附容量。批次反應條件之設定主要在探討水中溶解性有機物所造成之競爭性吸附及其在活性碳表層之預吸附對 atrazine 吸附容量之影響。在水中 atrazine 平衡濃度為 7 μg/L 之條件下，由批次等溫吸附實驗所決定之 atrazine 吸附容量一般可達 10 mg/L 以上；水中溶解性有機物所造成之競爭性吸附及其在活性碳表層之預吸附對 atrazine 吸附容量均有影響，且競爭性吸附所造成之吸附容量降低程度為預吸附效應之兩倍以上。反應時間不足或競爭吸附之影響均會影響批次等溫吸附試驗所決定之吸附容量（可低至 1-2 mg/g）。