

ADSORPTION OF ATRAZINE IN PACKED BEDS

I.D. KOVAIOS^{1, 2}
C.A. PARASKEVA^{1, 2, *}
P.G. KOUTSOUKOS^{1, 2}

¹University of Patras, Department of Chemical Engineering
Rion, Patras, GR-26504, Greece

²Institute of Chemical Engineering and High Temperature
ICE-HT/FORTH, Patras, 26 500, Greece

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*to whom all correspondence should be addressed:
e-mail: takis@chemeng.upatras.gr

ABSTRACT

The adsorption of the herbicide atrazine in packed beds filled with solids modelling soil components, (silica and humic acid), was studied at conditions simulating the adsorption of atrazine in cultivated soils. The choice of only two constituents of soil in the experimental study was based on the assumption that these two compounds contribute significantly to the adsorption of herbicides in soil relative to others, like alumina, calcium carbonate, etc. Packed beds were filled with inorganic material (silica gel grains) and solid organic compounds (humic acid). Adsorption data were fitted to the Freundlich isotherm. The presence of humic acid, even in small quantities, increases considerably the amount of adsorbed atrazine. Increasing humic acid content in the packed beds, the amount of adsorbed atrazine increased. Reversibility tests showed that the adsorption of atrazine was reversible. Two steps for adsorption and desorption were observed. The first fast step is attributed to the physical adsorption on the free adsorption sites of the substrates washed by the solution, while the second slow step is attributed to the diffusion of the molecules of atrazine within the structure of the silica and of the humic acid. Study of the hydrodynamics of atrazine containing solutions flow in the packed beds filled with silica and humic acid showed that the morphology of insoluble humic acid upon hydration changed its shape resulting in its transport through the bed and clogging of the narrow pores of the medium. As a result the packed bed permeability was reduced by 99%.

KEYWORDS: atrazine, herbicide, humic acid, silica, adsorption isotherms, packed beds.

INTRODUCTION

Atrazine, despite limitations in availability, is among the widely used herbicides for the control of annual weeds which grow together with cultivated plants as sorghum, corn and sugarcane crops (Vencill, 2002; Chen *et al.*, 2009). The European Union (Sass and Colangelo, 2006) has characterised atrazine as a non-environmental friendly herbicide causing hazardous effects on animal and human health (Alvarez and Fuiman, 2005). However, in developing countries atrazine is still in use, while in USA the use of atrazine is still under negotiation (Chen *et al.*, 2009).

A considerable amount of work has been done focusing on atrazine sorption in different types of soils (Wang *et al.*, 1992; Moorman *et al.*, 2001; Huang *et al.*, 2003), in soil organic matter (SOM) or in humic acid (Wang *et al.*, 1991; Martin-Neto *et al.*, 1992; Kulikova and Perminova, 2002) and on clay minerals (Clausen *et al.* 2001; Chappell *et al.*, 2005). Significant research effort has been done towards the elucidation of the mechanisms of interaction of atrazine with SOM or with humic acid through investigations of the competition of atrazine for the available sorption sites (Xing *et al.*, 1996). Relevant studies have concentrated on the effect of humic acid hydration on sorption (Graber and Borisover, 1998; Borisover and Graber, 2002) or on the use of various spectroscopic techniques (Martin-Neto *et al.*, 1994; Davis and Jabeen, 2003). Batch and column techniques have been used for kinetic and non-equilibrium sorption studies (Sposito *et al.*, 1996; Beltran *et al.*, 1998).

In the present work experimental results on the uptake of atrazine by inorganic substrates (silica gel grains) and different mixtures of humic acid with silica are presented. Recent work by the authors

(Kovaios *et al.*, 2006; Kovaios, 2007) showed that among the main constituents of soil, i.e. aluminosilicate and calcium carbonate minerals it was only on silica that significant uptake of atrazine was measured. Atrazine was not adsorbed (within the limits of experimental error) on the surface of γ -alumina and calcite even at low solid-to-liquid ratio of 0.5 g ml^{-1} , over a pH range between 7.7 and 11.7 for calcite and 3.8 to 12.1 for γ -alumina. Similar results have been presented by Clausen *et al.* (2001) where the results of adsorption measurements of some pesticides on quartz, calcite, kaolinite and α -alumina were presented. As a result, it was only silica with a relatively high porosity that was selected as the only inorganic sorbent to be used as packing main material. Indeed, packed bed experiments filled only with silica gel showed significant adsorption of atrazine. Recent work in batch experiments by Kovaios (2007) in which model organic constituents were used, has demonstrated that the presence of soil organic matter is of primary importance in the sorption processes of non polar organic substances (Beck and Jones, 1996; Seol and Lee, 2000; Ben-Hur *et al.*, 2003). The results of Kovaios *et al.* (2006) and Kovaios (2007) obtained in batch experiments were in good agreement with literature reports (Chiou *et al.*, 1979). In the present work, where experiments in packed beds are presented, the presence of low concentrations of humic acid (1.2 % w/w, maximum organic content in topsoil is 5%) has shown a significant increase in the retention of atrazine within the beds. As humic acid concentration increased, atrazine sorption increased significantly. The experiments in packed beds showed that the sorption of atrazine is a reversible process for the experimental period used. Finally, the changes of the morphology of the substrates (mainly of the humic acid) were monitored in order to investigate the effect of plasticity of the humic acid on the porous medium permeability. Measurements of the column permeability as a function of time, and SEM observation of the morphology of the column filling material past adsorption, suggested that humic acid is not a rigid inflexible substance. It is rather a soft material, the grains of which may form aggregates because of intra- and inter- molecular interactions. Under the influence of water movement, the aggregates moved to downward pores changing their mechanical structure and conformation, and clogged the free volume between the column rigid grains.

MATERIAL AND METHODS

Materials

The column was filled with Silica-gel (silica gel 60, mean particle diameter 40-63 μm , Merck) and humic acid (Cat. No. 53680, Fluka). Different amounts of silica-gel grains and humic acid were used, in order to investigate the effect of the main soil sorbents. The silica gel powder used as sorbent, was porous with an internal porosity of 0.41. The porosity between grains, estimated by laboratory techniques, was 0.37, close to the porosity values encountered in cultivated surface soils. Only the insoluble fraction of humic acid was used as sorbent. 1 g of humic acid was suspended in 1 l of triply distilled water stirred magnetically for 24 hours, followed by treatment in an ultrasonic bath for 10 minutes. Next, the suspension was filtered through 0.22 μm membrane (Millipore, type GS). The solid on the filter was washed several times with triply distilled water for the removal of any residual soluble fraction of humic acid. The solid was dried at 60 $^{\circ}\text{C}$ for 24 hours. The dried insoluble fraction of humic acid was used in the adsorption experiments. Atrazine (99.2% pestanal analytical standard, Sigma-Aldrich) was chosen as the prototype herbicide. Alachlor (99.9% pestanal analytical standard, Sigma-Aldrich) was used as internal standard for GC analysis. Dichloromethane (99.9% for GC, Fluka) and ethyl acetate (99.5% for GC, Fluka) were used for extraction of atrazine from water samples and as solvent for GC analysis respectively. In pH deviation experiments, pH was adjusted using HCl, or NaOH solutions of proper concentration. Ionic strength was adjusted to the desired value (0.1 M) by adding NaCl (GR for analysis, Merck). The water used in experiments was distilled once and deionized (18.2 $\text{m}\Omega \text{ cm}$) by Millipore's Milli-Q plus deionization system. Atrazine was analyzed by gas chromatography (GC 17-A, Shimadzu) with NPD detector. The specific surface area of sorbents ($\text{SSA}_{\text{humic acid}} = 0.73 \text{ m}^2 \text{ g}^{-1}$, $\text{SSA}_{\text{SiO}_2} = 405 \text{ m}^2 \text{ g}^{-1}$) was determined by N_2 adsorption using BET method (Micromeritics, Gemini). The particle size distribution of sorbents (Size distribution: 100-500 μm for insoluble humic acid and 30-90 μm for silica-gel) were measured using laser light scattering technique (Mastersizer S, Malvern Instruments Ltd).

Column Experiments

Stainless steel columns of 2.5 cm internal diameter and 2.5 cm high were packed with a mixture of silica-gel and humic acid, so that the humic acid material was uniformly distributed within the silica-

gel grains: The columns were filled with water in order to exclude the air from the material pores and pre-weighted amounts of silica and humic acid, suspended in water and allowed to equilibrate, was added alternately to form thin layers. Every addition was done so that sufficient time was allowed for the sedimentation of the packing material. The columns were closed air tight and were fed with an electrolyte solution at constant flow with the help of a pump for 24 hours in order to equilibrate. Past the equilibration period, the columns were fed at constant flow with atrazine solutions of the desired concentration and samples were taken at the outlet of the column at different time intervals. When the concentration of atrazine at the outlet was the same with the feed concentration, atrazine solution was replaced by an electrolyte solution for the desorption experiments. Samples were taken at the outlet of the column until no detectable atrazine concentration change was observed. All samples were analyzed by GC-NPD according to a procedure described above.

RESULTS AND DISCUSSION

The experimental breakthrough curves of sorption and desorption of atrazine in columns filled only with silica are shown in Figures 1a and 1b, for two different solution concentrations of atrazine, $C_{in}=5 \text{ mg L}^{-1}$ and 20 mg L^{-1} , respectively (the dashed lines represents fitting of the experimental results and do not refer to any mathematical model that take into account advective and dispersive terms). Normalized values for the concentration of atrazine and the number of pore volumes instead of time were chosen for the sake of comparison of the results at different conditions. Comparison of Figures 1a and 1b showed that there is no detectable time difference in atrazine adsorption and desorption on silica for different concentrations of atrazine (C_{in}) in the feed solution. Sorption reached plateau after ~ 7 pore volumes (N); (1 N corresponds to 8.61 ml of solution that flows through the bed, at time intervals about 2.18 hours), while the desorption step was completed after about 18 N. Figures 2a, b, c and d show the breakthrough curves of atrazine sorption on mixtures of 1.2 % w/w humic acid and 98.8 % w/w silica for $C_{in} = 5, 10, 15$ and 20 mg L^{-1} , respectively. As may be seen, the increase of humic acid even by low amounts, resulted in slower kinetics of sorption and desorption: Sorption reached a plateau value after about 9 N for $C_{in}=20 \text{ mg L}^{-1}$, 16 N for $C_{in}=15 \text{ mg L}^{-1}$, 18 N for $C_{in}=10 \text{ mg L}^{-1}$ and 20 N for $C_{in}=5 \text{ mg L}^{-1}$. The desorption step lasted for more than ~ 35 N, for all cases, approximately twice the cycle number when the columns were filled with only silica grains. Comparison of Figures 1 and Figures 2 shows that the presence of small quantities of humic acid enhanced the adsorption of atrazine and this is an important conclusion for the adsorption of herbicides in soil where humic acid varies from 1 to 5 %.

The differences in atrazine sorption in the presence of humic acid are more pronounced in Figure 3. As may be seen, the breakthrough curves of normalized concentration of atrazine at the outlet of the column presented for different compositions of the packed beds, in terms of the quantity of used humic acid (0 %, 1.2 % and 3.4 %) and at $C_{in}=20 \text{ mg L}^{-1}$. With increasing humic acid content in the packed column, the amount of the adsorbed atrazine increased as well. The normalized atrazine concentration reached a plateau at $N=7$ for 0 %, $N=11$ for 1.2 % and $N=16$ for 3.4 % humic acid within the packed bed. Moreover, the desorption curves showed that the highest amount of atrazine desorbed quickly after almost 6 N - 12 N for all three compositions tested, while it continued to desorb slowly over a long period of time ($N = 36$). This is due to the desorption of atrazine entrapped in the humic acid pore network which diffused into the bulk solution.

In all cases of adsorption / desorption of atrazine in mixtures of humic acid / silica grains, a two stage kinetics was found. The first step of adsorption was very fast and 90 % of the initial atrazine is being adsorbed in this stage and was retained on the solid substrates during the flow of the first 7-9 injected pore volumes of the solution. The second stage of adsorption, much longer in total duration, was rather slow. During this step the remaining 10 % of atrazine was adsorbed. Similar behaviour was exhibited in the desorption process, during which most of atrazine was rapidly desorbed past 7 N, the remaining adsorbed amount required more than 36 N for the complete release from the solid substrates. The first fast step was attributed to the adsorption of atrazine molecules at surface sites of the solid, which are readily accessible for the atrazine containing solution. During the second stage, either the molecules of atrazine stereochemically restricted were adsorbed or the remaining adsorption sites were of higher energy. Such sites (positions for adsorption) might be present in the internal structure of the humic acid. Molecules of atrazine may also be trapped in the voids, formed because of the complex conformation of the humic acid molecules. Similar events take place during desorption, where molecules of atrazine adsorbed on the outer surface of the substrates were

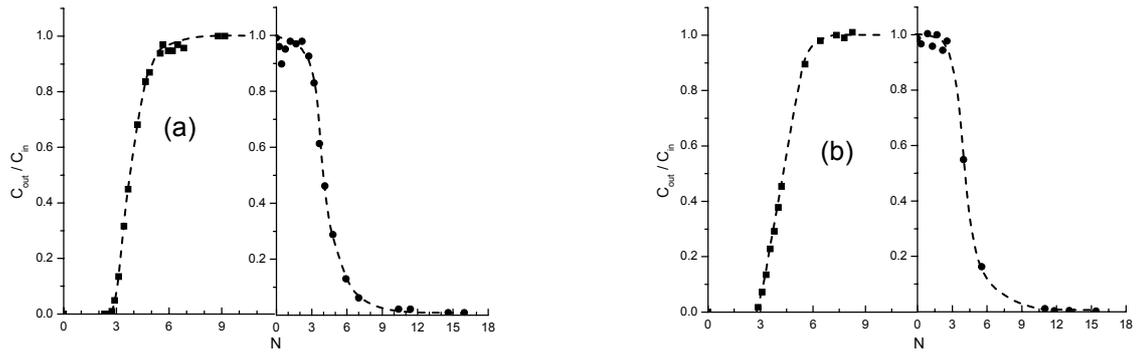


Figure 1. Normalized concentration of atrazine at the outlet of the column packed with silica-gel during a sorption and a desorption experiment.

$C_{in} = 5 \text{ mg L}^{-1}$ in (a) and 20 mg L^{-1} in (b), (■ sorption points; ● desorption points).

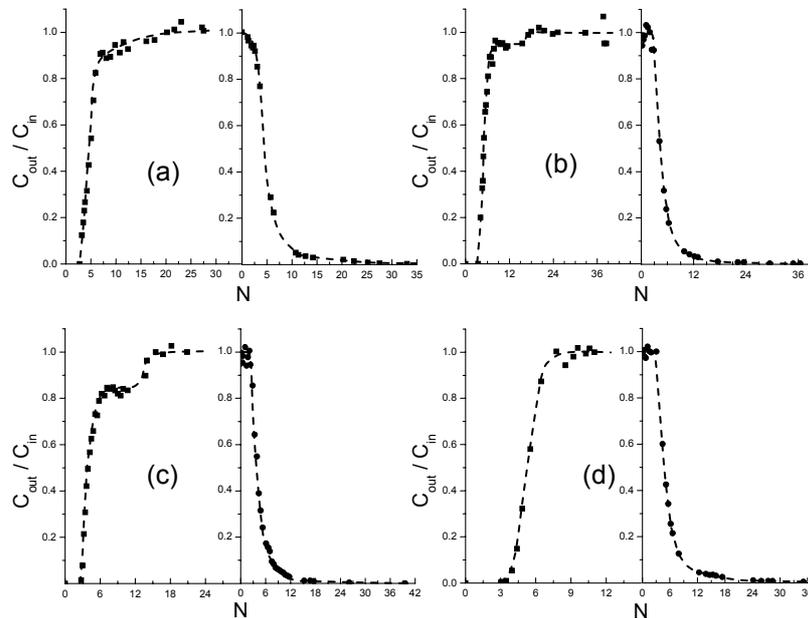


Figure 2. Normalized concentration of atrazine at the outlet of the column packed with 1.2% w/w humic acid in silica-gel during a sorption and a desorption experiment. The initial concentration of atrazine is a) 5 mg L^{-1} , b) 10 mg L^{-1} , c) 15 mg L^{-1} , d) 20 mg L^{-1} (■ sorption points; ● desorption points)

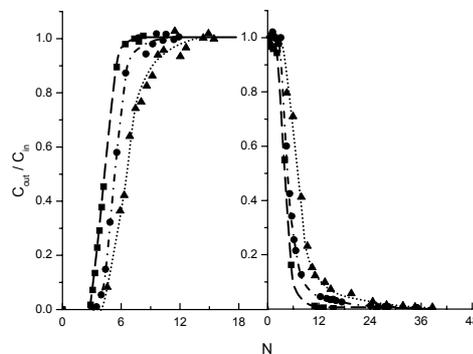


Figure 3. Normalized concentration of atrazine at the outlet of the column packed with different % w/w amount of humic acid in silica-gel during a sorption and a desorption experiment at constant temperature $T = 25 \text{ °C}$, $C_{init} = 20 \text{ mg L}^{-1}$, ionic strength $IS = 0.1$ and $pH = 5.5$ (■ 0% ; ● 1.2%, ▲ 3.4% w/w humic acid in silica-gel)

released first. The entrapped molecules, within the porous structure of silica or humic acid, were released at a lower rate as suggested by the 'tail' on the respective curves, shown in Figures 1-3. This type of asymmetric curves has been presented by a number of investigators for the adsorption of atrazine or other herbicides in soils (Bouchard, 1999, Chen *et al.*, 1997, Pang *et al.*, 2005). It is important to note that in the case of mixtures of humic acids and silica, a characteristic step was observed (Figure 2b and 2c) before reaching equilibrium. Curves in Figure 2b and 2c reveal the presence of a time step during which the concentration of the atrazine taken up by the sorbent remained constant or in other words the rate of sorption was temporarily increased. It may be suggested that at the beginning and for some pore volumes before the step shown in Figures 2b and 2c, molecules of atrazine did not adsorb at high rate on the sorbent grains, because of the fast flow of atrazine containing solutions through narrow channels. Otherwise, it is possible that the atrazine molecules could not reach the adsorption sites hidden within group of aggregates of the substrates. However, past the lapse of sufficient time the solid humic acid was hydrated and became plastic that is deformable and in some cases broke into smaller aggregates, exposing new adsorption sites. Similar 'steps' in experiments in soil packed beds have also been observed by Beltran *et al.* (1998) and Bouchard (1999).

Quantitative evaluation of absorption – desorption on packed beds

The quantitative evaluation of absorption – desorption on packed beds is based on simple mass balances. The concentration of adsorbed atrazine C_s (mg g^{-1}) is calculated using Eqs. (1)-(11) (Kovačios, 2007).

$$m_{in} - m_{out} = m_s + m_d \tag{1}$$

where m_{in} (μg) is the total mass of the atrazine entering the bed, m_{out} (μg) is the total mass of atrazine exiting the bed, m_s (μg) is the mass of atrazine sorbed on the packing material and m_d (μg) is the mass of atrazine remaining in the bulk space between the sorbent grains. Each term in Eq. (1) may be calculated from equations (2)-(4):

$$m_{in} = C_{in} N_{eq} \tag{2}$$

$$m_{out} = \int \frac{C_{out}}{C_{in}} dN_{eq} \tag{3}$$

$$m_d = C_{in} V_d \tag{4}$$

where C_{in} and C_{out} are the inlet and outlet concentrations of atrazine ($\mu\text{g L}^{-1}$), respectively, N_{eq} is the number of pore volumes of the solution that was injected up to the equilibrium, V_d is the total void space (l), and the integral in Eq. 2 it is equal to the area under the sorption curve up to N_{eq} . Thus, from Eqs 1-4 the total mass of sorbed atrazine may be calculated as:

$$m_s = C_{in} N_{eq} - \int \frac{C_{out}}{C_{in}} dN_{eq} - C_{in} V_d \tag{5}$$

The corresponding adsorbed surface concentration of atrazine, C_s , ($\mu\text{g m}^{-2}$) that is the concentration divided by the SSA of the substrates, for each of the tested values of C_{in} (adsorption isotherm) is given by:

$$C_s = \frac{m_s}{m(x_{sil}SSA_{sil} + x_{ha}SSA_{ha})} = \frac{C_{in} N_{eq} - \int \frac{C_{out}}{C_{in}} dN_{eq} - C_{in} V_d}{m(x_{sil}SSA_{sil} + x_{ha}SSA_{ha})} \tag{6}$$

where x_{sil} and x_{ha} are the fractions of silica and humic acid, respectively, and SSA_{sil} and SSA_{ha} ($\text{m}^2 \text{g}^{-2}$) are the specific areas of the silica and humic acid respectively. The porosity was taken as $\epsilon = 0.78$, and the pore volume $N = 8.61$ ml, in the calculations listed in Table 1. All experiments were performed under steady state flowrate, $Q = 4$ ml hr^{-1} , which corresponded to a superficial velocity of $v_o = 0.48$ m d^{-1} . The experiments were conducted at constant temperature, $\theta = 25 \pm 2$ °C, in a thermostated chamber.

The surface concentration of atrazine desorbed from the substrates was also calculated from mass balance as:

$$m'_{out} = m'_s + m'_d \tag{7}$$

where m'_{out} (μg) is the total mass of atrazine released from the bed during desorption, m'_s (μg) the mass of atrazine that was desorbed from the substrates, and m'_d is the mass of atrazine suspended in the bulk space of the bed and finally was released from the bed. The terms in Eq. 7 may be calculated from the system of equations [8] – (9):

$$m'_{out} = \int \frac{C_{out}}{C_{in}} dN'_{eq} \quad (8)$$

$$m'_d = C_{in} N'_{eq} \quad (9)$$

where N'_{eq} (ml) is the volume that corresponds to the pore volumes needed for the completion of the

desorption and the integral $\int \frac{C_{out}}{C_{in}} dN'_{eq}$ is the surface area below the curve of desorption. From eqs.

(7), (8) and (9) m'_s is calculated by eq. (10):

$$m'_s = \int \frac{C_{out}}{C_{in}} dN'_{eq} - C_{in} N'_{eq} \quad (10)$$

The corresponding desorbed surface concentration of atrazine, C'_s , ($\mu\text{g m}^{-2}$) for each one of the tested values of C_{in} (desorption isotherm) is given by:

$$C'_s = \frac{m'_s}{m(x_{sil}SSA_{sil} + x_{ha}SSA_{ha})} = \frac{\int \frac{C_{out}}{C_{in}} dN'_{eq} - C_{in} N'_{eq}}{m(x_{sil}SSA_{sil} + x_{ha}SSA_{ha})} \quad (11)$$

Based on Eq. (6) and (11), the adsorbed and desorbed amount of atrazine was calculated for the cases presented above, that is pure silica and two different mixtures with humic acid (1.2 % and 2.4 %). In

Table 1 the experimental values of C_s and C'_s for the sorption and desorption respectively and the relative deviation (%) of the experimental values of sorption and desorption, are presented. Negative values (observed only for 1.2 % of humic acid and $C_{in}=15 \text{ mg l}^{-1}$), were probably due to experimental error. All positive values in the difference between sorption and desorption suggested that a small amount of atrazine might have remained within the bed, trapped in the porous structure of the substrates. The reversibility of the process depends on the duration of the process and on system parameters (soil composition, atrazine concentration, ionic strength, porosity, etc.) as reported elsewhere (Clay *et al.*, 1990; Ma, *et al.*, 1993; Roy *et al.*, 1994). A number of researchers have suggested that the desorption process in natural soils presents a hysteresis and that all adsorbed atrazine cannot be recovered with aqueous extraction. In our work (Kovaios, 2007), it has been observed that in long term experiments there is a quantity of atrazine that remained bound to the bed. The residual amount may be attributed to the atrazine penetrating in the micropores of the substrate from where release is difficult. On the contrary, in short term experiments, it has been observed that most of the atrazine was released from the packed bed. However, according to Table 1 and the small deviations between the sorbed-desorbed concentrations of the atrazine (in the limits of the experimental errors) it may be suggested that in the results shown, the phenomenon of sorption was reversible. Based on the values of Table 1, the experimental isotherm for the case of a mixture of 1.2 % of humic acid in silica is presented in Figure 4. The data gave an excellent fit to the Freundlich model. The values of the respective parameters calculated from the Freundlich model are given in Table 2.

Table 1. Sorbed atrazine concentration in solid phase C_s and desorbed atrazine concentration, $C_{s'}$ measured in packed beds. Deviations of the measured concentrations are given as, %Dev(ad-des)

% humic acid	C_{in} (ng l ⁻¹)	C_s (ng m ⁻²)	$C_{s'}$ (ng m ⁻²)	%Dev(ad-des)
0.0	5000	59.3	66.7	+12
0.0	2000	252	272	+7.9
1.2	5000	95.0	95	0.0
1.2	10000	187	190	+1.6
1.2	15000	270	257	-4.8
1.2	20000	352	395	+12
3.4	20000	445	567	+27

Table 2. Experimental values of the parameters in Freundlich model for the adsorption of atrazine in a mixture 1.2% of humic acid in silica

Parameter	Estimated values
K_f (ng ⁽¹⁻ⁿ⁾ m ⁻² mL ⁿ)	20.93
n	0.945
R	0.998

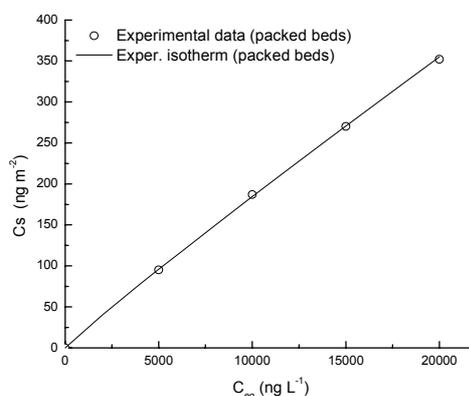


Figure 4. Adsorption isotherm of atrazine on humic acid, 1.2%, at constant temperature $\theta = 25$ °C, ionic strength, IS = 0.1 M KNO₃ and pH = 5.5. The experimental data were fitted to the Freundlich model

The mechanistic behavior of silica / humic acid mixtures

It has been observed that the addition of even a small amount of humic acid in a column filled with silica resulted in a drop of pressure along the column over the time. To quantify this observation, the permeability K of a column filled with silica was measured at different time intervals and the results were used as reference. K is given by Eq. (12):

$$K = \frac{\mu L}{A} \frac{Q}{\Delta P} \tag{12}$$

where μ (Pa s) is the viscosity of water, L (m) the length of the column, Q (m³ s⁻¹) the volumetric flow rate, A (m²) is the cross-sectional area of the column and ΔP (Pa) the pressure drop along the column. The permeability of pure silica filled column was found equal to ca 1.0 Darcy. This value was compared with the theoretically calculated value using the Blake-Kozeny Equation (13). This equation is valid when porosity of the material $\epsilon < 0.5$ and the flow is laminar ($\frac{Re}{1-\epsilon} < 10$). Here,

$$\epsilon = 0.39 \text{ and } \frac{Re}{1-\epsilon} = 0.015$$

$$U_0 = \frac{\Delta P \epsilon^3 D_p^2 \psi^2}{\mu L 150 (1-\epsilon)^2} \tag{13}$$

where D_p is the mean diameter of the particles, ψ (dimensionless) is the sphericity of the particles and ε (dimensionless) is the porosity of the material. Sphericity ψ of silica was taken 0.65, a value for crushed glass. For $\varepsilon = 0.35$, $K = 0.9$ Darcy, while for $\varepsilon = 0.39$, $K = 1.4$ Darcy. These values are in a good agreement with the experimentally found value of 1.0 Darcy. Next, a column was filled with 2% humic acid in silica and the permeability was monitored for several days. The drop of the permeability of the column as a function of time is shown in Figure 5. It is interesting that the permeability reached almost a zero value past a month. Two processes simultaneously occurring inside the column may explain the observations. First, as humic acid is hydrated the intramolecular bonds break down and the corresponding three dimensional structure is expanded. The material becomes “softer” and can more readily change the conformation upon stress. At the same time, humic acid aggregated grains are transferred by the downflow water and infiltrate silica grains. Humic acid aggregated grains seal the pores between the silica grains taking the shape of the void space. Photographs of the column material taken by SEM after the completion of the experiment supported this hypothesis (Figure 6). Humic acid present even at very low concentrations in the bed packing material may clog effectively key paths of the water stream, lowering drastically the permeability of the respective column.

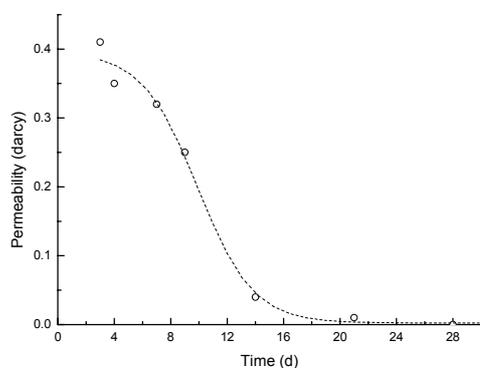


Figure 5. Decrease of the permeability of a column packed with a mixture of silica-gel and humic acid during a continuous flow of an electrolyte solution

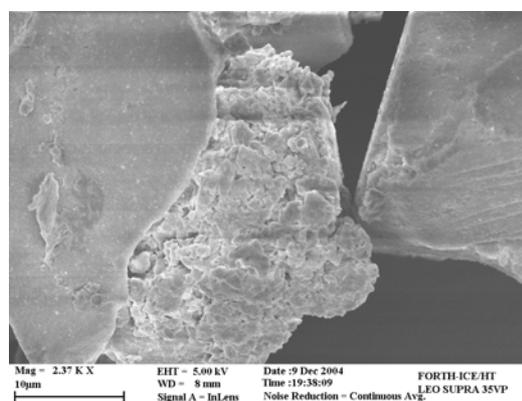


Figure 6. SEM photograph of humic acid material between silica-gel grains. The humic acid can take the shape of the free space clogging the pores

CONCLUSIONS

Kinetic measurements of the adsorption of atrazine in packed beds consisting of silica gel and humic acid, have shown that nearly 90 % of the atrazine in aqueous solutions was adsorbed on the surface of materials during the first hours. A slower adsorption step followed lasting for days. Desorption presented tailing and mass recovery of the adsorbed atrazine. The adsorption data gave an excellent fit to the Freundlich isotherm. Adsorption experiments with mixtures of silica / humic acid showed that atrazine adsorbed to a considerably larger extent on humic acid rather than on silica, however the adsorption rate is lower. Column experiments showed that the process was reversible, with respect to the time scale of the experiments. The permeability of the columns was reduced during the experiments, reaching almost zero values past one month. This finding was attributed to the clogging of critical fluid pathways by the leaching downwards humic acid with time. SEM photographs have confirmed the deformation of humic acid aggregates resulted in clogging of the empty pore space between silica grains.

DEDICATION

The present work is dedicated with gratitude to our advisor Professor Alkis Payatakes who passed away November 28th, 2009. We have had the good fortune to be students or colleagues of him. His presence though the years has been a great asset for all of us.

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