Parameters Explaining Removal of PAHs from Sewage Sludge by Ozonation

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This study aimed at explaining the differences in the removal efficiencies of 12 polycyclic aromatic hydrocarbons (PAHs, from low to high molecular weight) stated during the ozonation of contaminated sewage sludge. Correlation between PAH removal efficiency at fixed ozone doses and the characteristics of PAHs (molecular weight, number of aromatic rings, number of 5-carbon rings, solubility in water, octanol–water partitioning coefficient) was established through partial least-squares (PLS) regression. PAHs removal efficiency was primarily determined by the solubility of PAHs in water and the number of 5-carbon rings. Considering six ozone doses (from 0.5 to 4 g/L), the impact of added ozone on PAH removal efficiency decreased. PLS analysis suggested that 77% of the ozone efficiency variability was a result of the sludge soluble chemical oxygen demand (SCOD) concentration in sludge. The competition between SCOD and PAHs was confirmed by ozonation experiments in the presence of surfactants. The use of surfactants actually led to higher gas–liquid transfer coefficients and to higher PAH removal efficiencies, which shows that ozone concentration was the limiting factor. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3612–3620, 2006

Keywords: partial least-squares (PLS) regression, polycyclic aromatic hydrocarbons (PAHs), persistent pollutants, solubility, mass transfer

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are xenobiotics particularly monitored because of their carcinogenic properties and their ubiquity in the environment. They are generated during partial combustion of organic compounds and originate from motor vehicle exhausts, industrial combustion, and domestic heating. They are thus carried by runoff waters and converge to wastewater treatment facilities. They are known to be persistent to conventional wastewater biological treatment and, because of their hydrophobicity, they strongly adsorb on sludge where they concentrate. Their presence in municipal sewage sludge is a major problem arising from the environmental risks associated with the sludge spreading on agricultural soils. French regulation has set three PAHs as the maximum concentration for sludge spreading: fluoranthene, benzo[*b*]fluoranthene, and benzo[*a*]pyrene with level limits of 5, 2.5, and 2 $\text{mg/kg}_{\text{Total Solids}}$ (kg_{TS}), respectively. Lower levels are anticipated in the framework of current European policies. Indeed, a limit value of 6 mg/kg_{TS} for the sum of 11 PAHs from acenaphthene to indeno[123cd]pyrene is under discussion.

High reactivity between ozone and PAHs has been shown in liquid media.[1,2] The direct attack of dissolved molecular ozone is often emphasized as the main mechanism. Indeed, Legube et al.[1] carried out reactions in acid media; addition of radical initiators (hydrogen peroxide or UV irradiation) did not accelerate the reaction of PAHs–ozone[3,4] and radical inhibitors (*tert*-butyl alcohol) had no significant effect on PAH ozonation.[3] According to other authors,[5] both mechanisms (direct ozone molecular attack and hydroxyl radical oxidation) take place simultaneously, irrespective of the pH, ranging from 2 to

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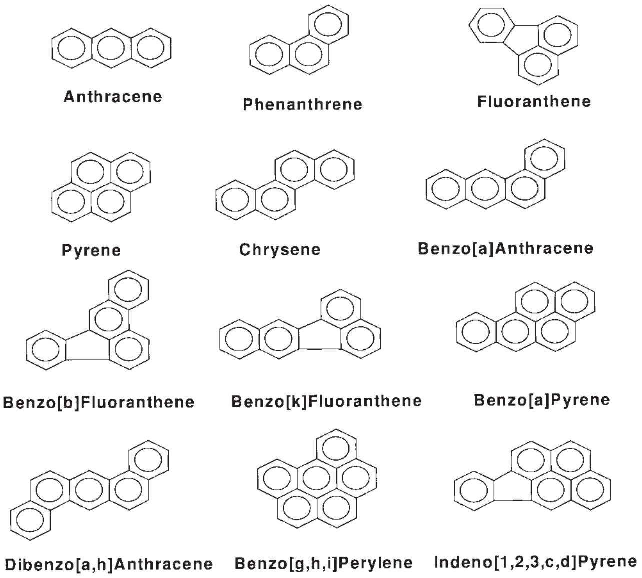

Figure 1. Molecular structure of PAHs considered in this study.

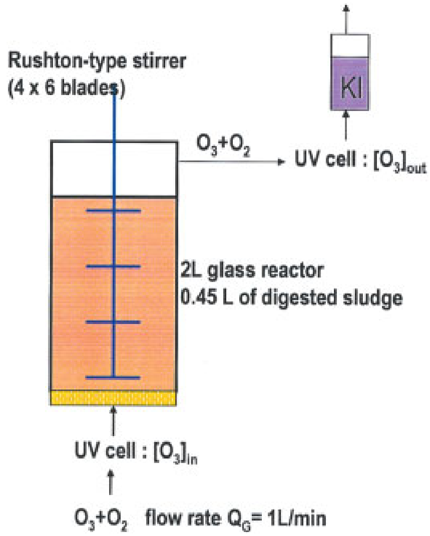

Figure 2. Diagram of ozone reactor.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

12. Contribution of either the one or the other mechanism depended on the molecular structure of the PAH. For example, direct attack represented more of 75% of chrysene degradation for pH $\leq$ 9, whereas it represented only 25% of benzo-[*a*]pyrene degradation at pH = 9. In the same way, fluorene was shown to be degraded by both direct and hydroxyl radical reactions, whereas phenanthrene and acenaphthene developed direct reactions only with ozone.[2]

The ozonation of PAHs was also investigated in dodecane/water emulsions,[6] which showed that PAHs–ozone reactions took place in dodecane droplets and was a result of the direct mechanism. Moreover, ozonation of PAHs was selective given that no dodecane oxidation occurred. This selectivity of ozone toward PAHs among aliphatic compounds was also observed in kerosene films.[7]

Few published studies concern sediment[8] or soil[9,10] remediation by ozonation. They show the reversed effect of soil organic carbon content on the efficiency of ozone treatment. To our knowledge, ozonation of PAHs in sewage sludge has not yet been investigated. However, sludge ozonation is primarily studied with the aim of reducing sludge production. Sludge is thus partially oxidized and recycled into aerobic wastewater biological reactors[11] or into anaerobic sludge digestors,[12] although no data are available with respect to the impact of ozone on PAHs or persistent organic pollutants. In a previous work,[13] we showed that low ozone doses (up to 1.5 g/L) were efficient enough to remove PAHs naturally present in sewage sludge. The objective of this work was to explain the differences in the removal efficiencies of 12 PAHs (from low to high molecular weight; Figure 1) observed during ozonation of contaminated sludge.

Experimental

Sludge

The sewage sludge samples were collected in a wastewater plant in an industrial area. They were recurrently and naturally contaminated with PAHs. The samples were a mixture of primary sludge and excess waste activated sludge. Samples were stored at −20°C. Sludge samples were digested in a 20-L completely mixed continuous anaerobic reactor where the sludge hydraulic retention time was 40 days and temperature was 35°C. Characteristics of the digested sludge used for ozonation experiments are shown in Table 1.

Ozonation conditions

The digested sludge was ozonated in a 2-L batch reactor (Figure 2). Sludge (0.45 L) was introduced in the reactor and ozone was fed continuously. The ozone was generated from pure oxygen by an Ozat CFSI generator and injected into the bottom of the reactor through a thin bubble diffuser. The ozone concentrations in the gas phase (before and after the reaction with sludge) were determined every 30 s using UV BMT 963 analyzers. The gas flow rate was 1 L/min and the O_3 inlet concentration in oxygen varied between 50 and 60 mg/L. Ozone that had not reacted was destroyed by an iodide potassium solution.

Table 1. Characteristics of the Digested Sludge Used for Ozonation Experiments

pH	Total Solids (g/L)	Organic Solids (g/L)	Total COD (g/L)	Soluble COD* (g/L)	PAHs** μmol/L	PAHs** μg/L	PAHs** $\mu g/g_{TS}$
7.8	12.9	6.7	12.7	0.5	0.930	209	16.2

* Soluble chemical oxygen demand, or SCOD.
**Total of 12 PAHs.

Ozone consumption or ozone dose was calculated by the following equation:

$$dose = \sum_{i=1}^{end} Q_G \frac{([O_3]_{in(i)} - [O_3]_{out(i)})}{V} \Delta t$$

where Q_G is the gas flow rate, $[O_3]_{in}$ and $[O_3]_{out}$ are the ozone concentrations in the gas phase at the inlet and outlet of the reactor, V is the sludge sample volume, and $\Delta t = 30$ s.

Ozone doses ranged from 0.5 to 4 g /L. Each ozonation experiment was duplicated.

When surfactants (Tergitol NP10 from Sigma, Tyloxapol and Brij35 from Acros Organics with 99% purity) were used, they were mixed with the sludge in the reactor for 30 min before the start of ozonation. Surfactant concentrations in the sludge were 1 g/L.

Analyses of PAHs

Analytical methods were previously tested and validated in the laboratory by the use of certified matrices.[14] The minimum volume of sample for analysis of PAHs was 350 mL. Total solids were determined twice by drying 20 mL of the sludge sample in an oven at 110°C for 24 h. The remaining 300 mL of the sludge sample was first centrifuged (20,000*g*, 25 min). Liquid phases were stored at -20°C for further solid-phase extraction on a PAH–affinity column (Supelco ENVI-18™) according to recommendations of the manufacturer. Solid pellets were ground with glass beads (diameter 4 mm) and were dried in a ventilated oven (60 h, -40°C). Dry samples were sieved by grid (diameter 2 mm) and were stored at -20°C for further accelerated solvent extraction with an ASE-200 system (Dionex™). The extracting conditions are as reported in Trably et al.[14] The diverse extracts were then softly evaporated under nitrogen flow to dryness. Residues were dissolved in acetonitrile and analyzed by reverse phase–high-performance liquid chromatography.[14] Measurement errors were $<2\%$. A standard solution of PAHs (PAH-mix 9) was purchased from Cluzeau Info Labo.

Other analyses

Chemical oxygen demand (COD) and solids (total and organic) were measured in accordance with standard methods.[15] Total COD was measured in total sludge samples and soluble COD (SCOD) in supernatant after centrifugation (20,000*g*, for 25 min at 5°C).

Mass-transfer coefficient

The oxygen mass-transfer coefficient (K_La) was measured under the same conditions as ozonation runs (sludge volume and mixing, 20°C) using the unsteady method with an oxygen probe CellOx 325 and an Oxy340 oxygen analyzer. The oxygen concentration in sludge was initially reduced to zero by nitrogen bubbling. Then oxygen concentration increased by the introduction of air into the reactor and the mass-transfer coefficient was given by the following equation:

$$\frac{dC}{dt} = K_La(C^* - C)$$

where C is the dissolved oxygen concentration in sludge and C^* is the dissolved oxygen concentration at the equilibrium.

PLS regression

The partial least-squares (PLS) regression technique is based on constructing PLS factors (also called principal components) by minimizing the covariance between the dependent variables (*Y block*) and the explicative variables (*X block*). Then, the prediction of the Y block was calculated with a multivariable linear regression on the X block through PLS1 models using the software R version 1.2.2© for Windows and by using PLS functions developed by Durand et al.[16] The algorithm constructs orthogonal PLS factors in each block by minimizing the covariance between the X and Y blocks. The first PLS factor contains the highest percentage of variance and the following factors account for decreasing amounts of variance. The number of PLS factors [also called *dimensions* (dim)] of the models was determined by minimizing the mean squared prediction error [predicted residual sum of squares (PRESS)] through a cross-validation procedure. One of the advantages of this technique is the possibility of considering linked explicative variables.

In a first part, PLS regression was applied for each ozone dose. The Y block consisted of the removal efficiencies of PAHs and the X block contained PAH properties (molecular weight, number of aromatic rings, number of 5-carbon rings, solubility in water logarithm, K_{ow} logarithm). In a second part, all experimental data (six ozone doses) were computed by a PLS regression; the Y block contained ratios of the removal efficiencies of PAHs divided by ozone dose and the X block contained the properties of PAHs and sludge SCOD.

Results and Discussion

Previous work[13] showed that $<0.6\%$ of the 12 PAHs was lost by stripping during ozonation with 1.5 g O_3/L. Moreover, $<0.4\%$ of total PAHs were found in the liquid phase of sludge. Thus, in the following discussion, only concentrations of PAHs adsorbed on sludge are considered.

Experimental results

Figure 3 shows the variation of the removal efficiency of each PAH as a function of ozone doses. Removal efficiencies are equal to the difference between PAH concentrations before and after ozonation divided by initial concentration of the PAH. Variations in removal efficiencies according to the nature of various PAHs can be observed for each ozone dose. The first part of this study proposed an explanation for the variability of removal efficiencies of PAHs as a function of their structure and physical properties.

Figure 3 shows the increase of removal efficiencies of PAHs with ozone dose. However, removal of PAHs was more sensitive with low ozone doses, suggesting higher efficiencies of PAH ozonation at low ozone doses. This effect can be clearly observed in Figure 4 where differential ratios of removal efficiencies of PAHs divided by ozone dose are plotted. Figure 4

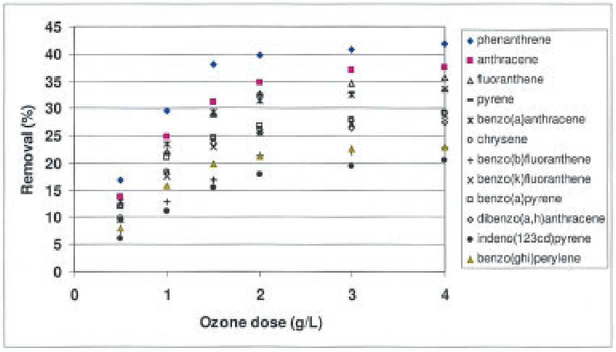

Figure 3. Removal efficiencies of each PAH as a function of ozone dose.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

is in fact the derivative of Figure 3. Thus, for ozone doses > 2 g O_3/L, removals of PAHs are almost constant and independent of ozone dose. Ozone was primarily oxidizing sludge. In the second part of this work, we will consider the impact of ozone dose and competition between PAHs and sludge.

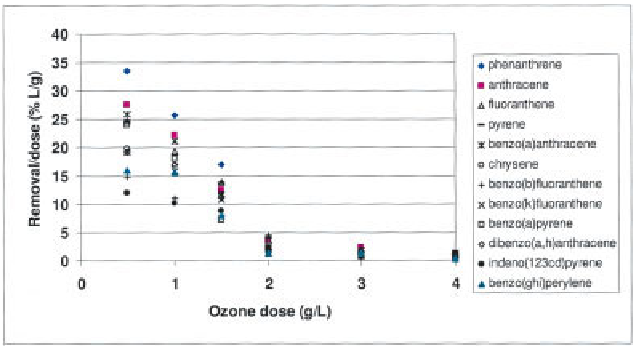

Figure 4. Ratios of differential removal efficiencies of PAHs divided by differential ozone doses.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

Impact of structure and properties of PAHs at fixed ozone doses

The objective of this section is to propose a model to calculate the removal efficiencies of PAHs in sludge as a function of PAH properties. Parameters that were considered are:

- Molecular weight (*M*) and the number of aromatic rings (N_{aro}). These parameters were already used to explain ozonation of PAHs in soils[9] and to study Fenton process oxidation of PAHs in soils.[17]
- The number of 5-carbon rings (N_{5C}), which was taken into account to explain degradation of PAHs adsorbed on sludge with Fenton system.[18]
- The water-solubility logarithm (log *s*) used to explain ozonation of PAHs in oil/water emulsions.[6]
- The octanol–water partitioning coefficient logarithm (log K_{ow}), which was considered to interpret anaerobic biodegradation of PAHs in sludge.[19]

All these parameters are shown in Table 2.

For all ozone doses, the highest removal efficiencies of PAHs (Figure 3) were observed for phenanthrene and anthracene, the smallest molecules among the studied compounds. Moreover, the most degraded compound (phenanthrene) was the most soluble in water but also presented the lowest octanol–water partitioning coefficient K_{ow}. The lowest PAH removal efficiency was obtained for indeno[123cd]pyrene, which has the lowest solubility in water and has one of the highest molecular weights and nearly highest K_{ow} coefficient.

However, if we consider benzo[b]fluoranthene and benzo[a]pyrene, which have the same molecular weight and almost the same solubilities in water, and K_{ow} coefficients, we can observe that the removal efficiency of benzo[a]pyrene is higher than that of benzo[b]fluoranthene removal (24.6 vs. 16.9% at 1.5 g O_3/L). Thus any difference in removal efficiencies of PAHs cannot be explained solely by solubility and molecular weight; structures of the PAHs may be considered. Indeed, among these two PAHs, benzo[b]fluoranthene has a 5-carbon ring, whereas benzo[a]pyrene has only aromatic rings and presents the higher reactivity with ozone.

For each ozone dose, PLS regression was applied to model the removal efficiency of PAHs as a function of PAH molecular weight (*M*), number of aromatic rings (N_{aro}), number of 5-carbon rings (N_{5C}), solubility logarithm (log *s*), and octanol–water partitioning coefficient logarithm (log K_{ow}).

The minimum squared prediction errors (PRESS) were obtained when the number of PLS factors (or dimension of the model) was equal to 3. Correlations between explicative parameters (X block) are shown in Figure 5. Molecular weight, aromatic ring number, and octanol–water partitioning coeffi-

Table 2. Properties of PAHs and Initial Concentration in Sludge Solid Phase

PAH	*M* (g/mol)	N_{aro}	N_{5C}	Solubility in Water (25°C) (μmol L^{-1})	log (K_{ow})	Initial Concentration (μmol L^{-1})
Phenanthrene	178	3	0	5.62	4.46	8.43×10^{-2}
Anthracene	178	3	0	0.25	4.5	1.46×10^{-2}
Fluorenthene	202	3	1	1.02	4.9	15.3×10^{-2}
Pyrene	202	4	0	0.65	4.88	20.5×10^{-2}
Benzo[a]anthracene	228	4	0	0.041	5.63	6.10×10^{-2}
Chrysene	228	4	0	0.0079	5.63	6.75×10^{-2}
Benzo[b]fluoranthene	252	4	1	0.0059	6.04	7.70×10^{-2}
Benzo[k]fluorenthene	252	4	1	0.032	6.21	4.44×10^{-2}
Benzo[a]pyrene	252	5	0	0.0063	6.06	9.64×10^{-2}
Dibenzo[a,h]anthracene	278	5	0	0.018	6.86	0.98×10^{-2}
Indeno[123cd]pyrene	276	5	1	0.00072	6.78	7.28×10^{-2}
Benzo[ghi]perylene	276	6	0	0.0025	6.58	4.42×10^{-2}

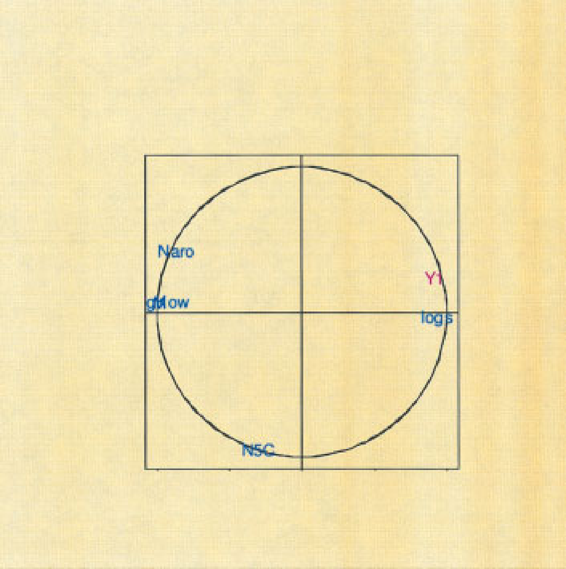

Figure 5. Correlation circle of explicative parameters (M, N_{aro}, N_{5C}, log K_{ow}, log s) according to the two first axes of the PLS model.

Log K_{ow} and M are plotted in the same place. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

cient are correlated and negatively correlated with solubility in water, which seems consistent because all four of these parameters are linked to the affinity of PAHs to the organic phase of sludge and their availability in the aqueous phase. The number of 5-carbon rings is independent of other parameters.

Values of parameters of multilinear models, for each ozone dose, are shown in Table 3. In all cases, the coefficient of solubility of PAHs in water was positive, which shows the favorable effect of high solubilities of PAHs in the aqueous phase and the importance of their availability to ozone in water. On the contrary, coefficients of molecular weight and numbers of aromatic and 5-carbon rings were always negative, indicating a lower reactivity of heavy PAHs. Finally, the partitioning octanol–water coefficient was either negative or positive and generally of less magnitude than coefficients for log s.

To assess the relative influence of each parameter, coefficients of multilinear models were also determined on centered and normalized data. These results are shown in Table 4. Even if their relative importance varied with the ozone dose, the two most influential parameters for removal efficiency of PAHs were the solubility of PAHs in water and the number of 5-carbon rings.

The high importance of solubility of PAHs in water may indicate that the limiting step of PAH ozonation is the desorption and transfer of PAHs from sludge solid phase to the liquid phase. This is in agreement with the results of Goi and Trapido[9] and of Nam and Kukor,[10] who investigated ozonation of PAHs adsorbed onto soils. Reactivity efficiencies were higher for PAHs of two or three aromatic rings than for heaviest compounds, which have lower water solubilities than those of the smallest compounds. These authors[9,10] indicated desorption of PAHs from soils as the limiting phenomenon. On the other hand, Kornmuller et al.,[6] who worked on ozonation of PAHs in oil/water emulsions, did not notice any dependency of PAH reactivity on the solubility of PAHs in water nor on the number of condensed rings. They concluded, in contrast to the results of this work, that reaction efficiencies were primarily affected by the molecular structure of each PAH.

The other important parameter is the number of 5-carbon rings (N_{5C}), which always appears in the correlation with a negative coefficient. This means that ozone reactivity is higher for totally aromatic PAHs than for compounds with a 5-carbon ring. This effect may be explained by the high reactivity of

Table 3. Coefficients of Different Parameters for Multilinear Models (Three-Dimensional PLS Models) to Describe Removal Efficiencies for Each Ozone Dose

	Ozone Dose (g/L)					
Parameter	0.5	1	1.5	2	3	4
Constant	0.212971	0.3634179	0.3734499	0.4479859	0.4778594	0.4394947
log s*	0.00623827	0.01149493	0.03801843	0.03249284	0.0310616	0.03242565
N_{5C}	−0.02037664	−0.04505195	−0.04692208	−0.03586515	−0.03313748	−0.03760144
N_{aro}	−0.00311962	−0.00419346	−0.0099006	−0.01131001	−0.01281712	−0.01996766
M**	−0.00016381	−0.00029821	−0.00010897	−0.00017958	−0.00023432	−0.0000986
log K_{ow}	−0.00683079	−0.0113383	0.0027528	−0.00393493	−0.00392637	0.00449768
PRESS	0.18	0.18	0.09	0.05	0.12	0.11

* In μmol L^{-1}.
**In g mol^{-1}.

Table 4. Relative Influence of Each Parameter in Three-Dimensional PLS Models Describing Removal Efficiencies for PAHs for Different Ozone Doses

	Ozone Dose (g/L)					
Parameter	0.5	1	1.5	2	3	4
log s	0.23	0.22	0.53	0.50	0.44	0.46
N_{5C}	0.31	0.37	0.28	0.23	0.24	0.22
N_{aro}	0.09	0.07	0.11	0.14	0.16	0.23
M	0.19	0.18	0.05	0.09	0.11	0.04
log K_{ow}	0.18	0.16	0.03	0.04	0.04	0.05

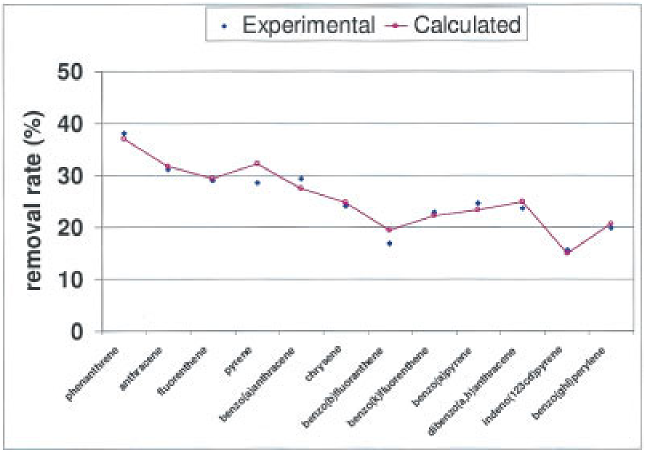

Figure 6. Experimental and calculated (three-dimensional PLS model) removal efficiencies for each PAH.

Ozone dose = 1.5 g/L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

ozone toward unsaturated bonds and aromatic molecules. Moreover, this was already observed for the oxidation of PAHs by the Fenton process.[18]

Another parameter of importance is the number of aromatic rings. Its influence is less than that of the number of 5-carbon rings and it also always appears with a negative coefficient. This shows higher reactivities of molecules with low number of aromatic rings. This is once again in agreement with the results obtained during ozonation of PAHs adsorbed on soils.[9,10]

Finally, molecular weight and K_{ow} coefficient were found to be the less influential parameters. Indeed, coefficients of K_{ow} in the models were either positive or negative, which can be explained by the fact that this parameter was not significant. The K_{ow} coefficient is often used as an assessment of the hydrophobicity of organic compounds, although it does not correctly represent the affinity of PAHs for organic sludge as previously reported by Mastrup et al.,[20] who studied the interactions of sludge and another organic pollutant (contraceptive pill).

Results of this present work are different from results concerning ozonation of PAHs in aqueous solutions. Indeed, reactivities of PAHs with ozone decreased as the molecular weight (or number of aromatic rings) decreased.[2-4] Phenomena limiting PAH reactivity with ozone are thus different in aqueous media or if PAHs are adsorbed on sludge or soils. In aqueous solutions, there is no problem of PAH accessibility and reactions are controlled by chemistry. If PAHs are adsorbed on sludge or soils, reaction with ozone is mainly limited by the accessibility of PAHs. PAHs have to be desorbed from sludge and then they can react with ozone.

As an example, modeled data for 1.5 g/L ozone dose are plotted together with experimental ones in Figure 6. Except for pyrene and benzo[b]fluoranthene for which calculated removal efficiency is slightly higher than the experimental data, predicted values are in very good agreement with the experimental values. Besides, given that solubility in water and the number of 5-carbon rings were shown to be the two most important parameters to represent the removal rate of PAHs, Figure 7 shows removal efficiencies of PAHs for 1.5 g/L ozone dose as a function of both of these parameters. Except for pyrene for which experimental removal efficiency is low, removal efficiencies could be classified as a function of the number of 5-carbon rings. In each class, removal efficiency could be correlated to PAH solubility in water by a semilogarithmic function and coefficients were almost equal in both classes.

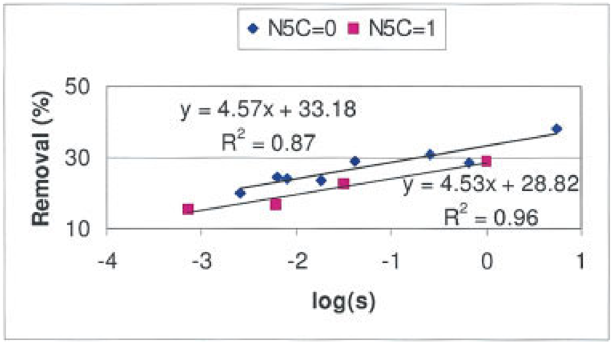

Figure 7. Experimental (points) and calculated (solid lines) removal efficiencies for each PAH vs. solubility in water and number of 5-carbon rings.

Ozone dose = 1.5 g/L. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

Impact of ozone dose and competition between PAHs and sludge

Figure 4 shows that ozone efficiency to remove PAHs from sludge decreased as the dose increased. Considering total concentration of PAHs, we assumed that this decrease was the result of sludge solubilization during ozonation and high concentrations in SCOD were in competition with PAHs for reaction with ozone.[13] Table 5 shows the concentrations in total and SCOD obtained after sludge ozonation at different doses. For low ozone doses (≤1.5 g/L), total COD remained constant, whereas SCOD increased: ozonation led to sludge solubilization. For higher ozone doses (≥2 g/L), total COD decreased slightly and SCOD remained almost constant and equal to 4 g/L: organic matter was solubilized and then oxidized by ozone, whereas additional removal of PAHs was low. To assess the influence of competition between SCOD and PAH for ozone attack, we carried out a PLS analysis where the Y block was differential ratios of removal efficiencies divided by ozone doses (as defined in Figure 4) of the 12 PAHs for the six tested ozone doses (72 points). The X block consisted of the proper-

Table 5. Total and Soluble COD in Sludge before and after Ozonation at Different Ozone Doses

Ozone Dose (g/L)	0	0.5	1	1.5	2	3	4
Total COD (g/L)	12.7	12.5	12.7	12.7	12.3	12.0	11.1
Soluble COD (g/L)	0.52	1.91	2.62	3.57	3.83	3.88	4.01

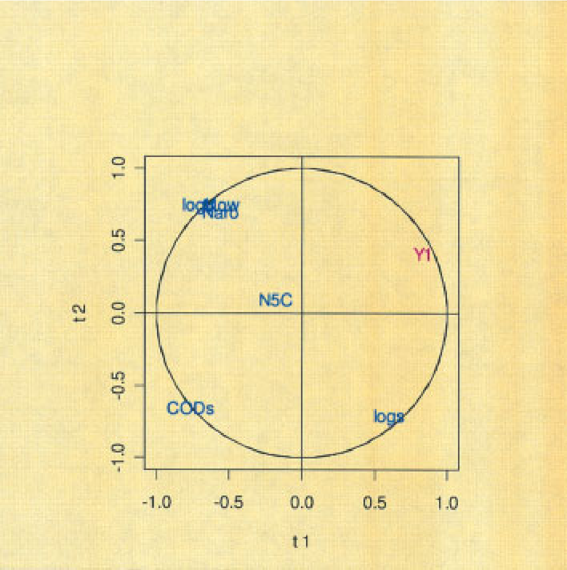

Figure 8. Correlation circle of explicative parameters (M, N_{aro}, N_{5C}, log K_{ow}, log s, DCOs) according to the two first axes of the PLS model.

Log K_{ow}, M, and N_{aro} are plotted in the same place. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

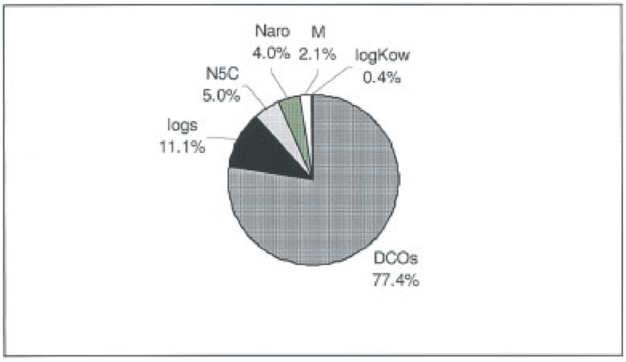

Figure 9. Relative influence of parameters in a three-dimensional PLS model to represent differential ratios removal/dose.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

ties of PAHs (as in a previous section) and SCOD. Correlations between these parameters are shown in Figure 8. We can again observe correlations between M, N_{aro}, and log K_{ow}, which are negatively correlated with the solubility of PAHs in water. N_{5C} and SCOD are independent parameters. PLS analysis led to a three-dimensional model with a minimum squared prediction error PRESS equal to 14%. Coefficients of the multilinear model are shown in Table 6. The same remarks as in models of removal efficiencies of PAHs at fixed ozone doses can be made: the solubility of PAHs had a positive coefficient, whereas M, N_{aro}, N_{5C}, and log K_{ow} had negative ones. Moreover, SCOD had a negative coefficient showing the competition between oxidation of SCOD and PAHs.

An analysis on centered and normalized data allowed us to determine the relative influence of different parameters (Figure 9). SCOD proved to be by far the most important parameter and represented 77% of ratios removal/dose variability. Thus, removal of PAHs absorbed on sludge depended more on competition between SCOD than on properties of PAHs (notably solubility of PAHs in water and the number of 5-carbon rings, which remain the most influencing parameters).

This competition between soluble and particulate matter was previously shown by Cesbron et al.,[21] who pointed out that for certain conditions, ozone can react first with the soluble fraction of sludge and after attacks and solubilizes the particulate fraction. Although mass-transfer film thickness (which increases when ozone absorption enhancement decreases) is lower than the sludge particle diameter, the soluble fraction has a screening effect on the particulate matter attack by ozone.[21] In the present case, SCOD was relatively low when low doses were used; ozone could then reach the particulate fraction of sludge and partially solubilized sludge COD and some PAHs, which reacted with ozone (concentration of PAHs in the ozonated sludge aqueous phase was always very low). As ozone dose increased, SCOD concentration increased, reducing the mass-transfer film thickness and the probability of reaction between particulate fraction of sludge and PAHs. Thus, for the highest doses, ozone was mainly used to oxidize SCOD.

This assumption of limitation of PAH removal by competition with SCOD implies that reactions are limited by ozone concentration in the aqueous phase, which results from gas–liquid mass transfer. We attempted to increase ozone gas–liquid transfer by adding surfactants in sludge before ozonation. Surfactants were assumed to increase the interfacial area (a) thanks to the inhibition of bubble coalescence.[22] This was confirmed by measuring oxygen mass-transfer coefficients (K_La) in the ozone reactor. These measures led to higher values in the mixture of sludge and surfactants ($K_La = 0.06\ s^{-1}$ whatever the surfactant used) than in the sludge alone ($K_La = 0.03\ s^{-1}$), thus implying a more efficient ozone transfer by a factor of two. Moreover, removal efficiencies of PAHs with surfactant addition were, on average, 2.4 times higher than removal efficiencies obtained with simple ozonation (Figure 10), which confirms the assumption of limitation of the reac-

Table 6. Coefficients of Different Parameters for Three-Dimensional PLS Model to Describe Differential Ratios Removal/Dose*

Constant	Log s**	N_{5C}	N_{aro}	$M^{\dagger}$	log K_{ow}	DCOs††
0.3943642	0.01054198	−0.01105452	−0.00476482	−0.00006242	−0.00052781	−0.0816073

* All ozone doses are taken into account.
**In μmol L^{-1}.
† In g mol^{-1}.
††In g O$_2$ L^{-1}.

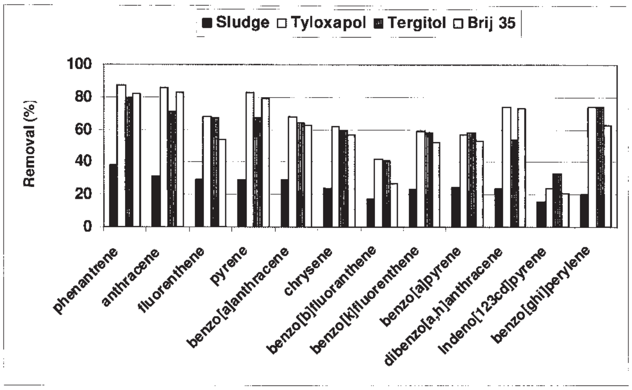

Figure 10. Removal efficiencies of PAHs after ozonation with 1.5 g O_3/L dose without and with addition of surfactant (1 g /L).

tion by ozone concentration in the liquid phase and thus competition between sludge SCOD and PAHs. Moreover, it should be noted that total concentration of PAHs represents a very low part of total or soluble COD of sludge. Indeed, if we consider the total oxidation of PAHs into CO_2 and H_2O, theoretical COD of PAHs ranges from 528 g O_2/mol (phenanthrene or anthracene) to 816 O_2/mol (dibenzo[a,h]anthracene). The initial total concentration of PAHs present in sludge was equivalent to 0.6 mg COD/L, which represents only 0.005% of total initial COD.

Surfactants may also enhance the part of PAHs in the liquid phase of sludge and thus increase their chance to react with ozone. Nevertheless, the part of PAHs in liquid phase before ozonation remained low (2% of total PAHs with tergitol, 1.7% with tyloxapol, and 0.6% with Brij 35[23]). Because the concentration of total PAHs in the liquid phase was about 0.4% of total PAHs, we can conclude that PAHs in the sludge liquid phase were not significantly increased by Brij 35 or slightly increased by the other surfactants. In all cases, the concentration of PAHs in the liquid phase was lower than their solubility in water, showing high affinity of PAHs for the sludge solid phase. Thus, surfactants had a greater impact on ozone gas–liquid mass transfer than on the solid–liquid transfer of PAHs.

Conclusions

Sludge ozonation led to partial removal of PAHs adsorbed onto sewage sludge. Ozone efficiency in removal of PAHs was higher at low ozone doses and PLS analyses showed that soluble COD (or SCOD) was the most important parameter and represented 77% of the ozone efficiency variability. Competition with SCOD and thus ozone concentration in the sludge liquid phase was the main limiting parameter for reaction between PAHs and ozone.

At fixed ozone doses and fixed SCOD concentrations, PLS regressions showed that the most important parameters to explain the removal efficiency variability of PAHs were their solubility in water and their number of 5-carbon rings. Reactivity with ozone was improved by high values of PAH solubilities, which emphasized that the limiting factor is the low accessibility of PAHs that are adsorbed onto the sludge. Ozone was less reactive toward PAHs with a 5-carbon ring than toward totally aromatic compounds.

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Literature Cited

1. Legube B, Sugimitsu H, Guyon S, Dore M. Ozonation du naphthalène en milieu aqueux. II. Etudes cinétiques de la phase initiale de la réaction. *Water Res.* 1986;20:209-214.
2. Beltran JF, Ovejero G, Encinar MJ, Rivas J. Oxidation of polynuclear aromatic hydrocarbons in water. 1. Ozonation. *Ind Eng Chem Res.* 1995;34:1596-1606.
3. Rivas JF, Beltran JF, Acedo B. Chemical and photochemical degradation of acenaphthylene. Intermediate identification. *J Hazard Mater.* 2000;75:89-98.
4. Trapido M, Veressinina Y, Munter R. Ozonation and advanced oxidation processes of polycyclic aromatic hydrocarbons in aqueous solution—A kinetic study. *Environ Technol.* 1995;16:729-740.
5. Miller SJ, Olejnik D. Ozonation of polycyclic aromatic hydrocarbons in water solution. *Ozone Sci Eng.* 2004;26:453-464.
6. Kornmüller A, Cuno M, Wiesmann U. Selective ozonation of polycyclic aromatics hydrocarbons in oil/water-emulsions. *Water Sci Technol.* 1997;35:57-64.
7. Marley AK, Larson AR, Stapleton LP, Garrison JW, Klodnyoky MC. Ozonolysis of naphthalene derivatives in water and in kerosene films. *Ozone Sci Eng.* 1987;9:23-36.
8. Zeng Y, Hong PKA. Slurry phase ozonation for remediation of sediments contaminated by polycyclic aromatic hydrocarbons. *J Air Waste Manage Assoc.* 2002;52:58-68.
9. Goi A, Trapido M. Degradation of polycyclic aromatic hydrocarbons in soil: The Fenton reagent versus ozonation. *Environ Technol.* 2004; 25:155-164.
10. Nam K, Kukor JJ. Combined ozonation and biodegradation for remediation of mixtures of polycyclic aromatic hydrocarbons in soils. *Biodegradation.* 2000;11:1-9 (Online).
11. Déléris S, Geaugey V, Camacho P, Debellefontaine H, Paul E. Minimization of sludge production in biological processes: An alternative solution for the problem of sludge disposal, *Water Sci Technol.* 2002; 46:63-70.
12. Battimelli A, Millet C, Delgenès JP, Moletta R. Anaerobic digestion of waste activated sludge combined with ozone post-treatment and recycling. *Water Sci Technol.* 2003;48:61-68.
13. Bernal-Martínez A, Carrère H, Patureau D, Delgenès JP. Combining anaerobic digestion and ozonation to remove PAHs from urban sludge. *Process Biochem.* 2005;40:3244-3250.
14. Trably E, Delgenès N, Patureau D, Delgenès JP. Optimization and validation of a highly reproducible method for polycyclic aromatic hydrocarbons (PAHs) analysis in sludge samples. *Int J Environ Anal Chem.* 2004;84:995-1008.
15. American Public Health Association (APHA). *Standard Methods for the Examination of Water and Wastewater.* 18th Edition. Washington, DC: APHA/AWWA/WPCF; 1992.
16. Durand JF. Partial least-squares regression: From linearity to nonlinear additive spline modeling. May be accessed at http://jf-durand-pls.com/
17. Nam K, Rodriguez W, Kukor JJ. Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton reaction. *Chemosphere.* 2001;45:11-20.
18. Flotron V, Delteil C, Padellec Y, Camel V. Removal of sorbed polycyclic aromatic hydrocarbons from soil, sludge and sediment samples using the Fenton's reagent process. *Chemosphere.* 2005;59: 1427-1437.
19. Trably E, Patureau D. Mass balance model for assessing trace organic compound removal in continuous bioreactors. *Biodegradation.* 2006; submitted.
20. Mastrup M, Schafer AI, Khan SJ. Predicting fate of the contraceptive pill in wastewater treatment and discharge. *Water Sci Technol.* 2005; 52:279-286.

21. Cesbron D, Déléris S, Debellefontaine H, Roustan M, Paul E. Study of competition for ozone between soluble and particulate matter during activated sludge ozonation. *Trans IChemE Part A.* 2003;81:1165-1170.
22. Gottschalk C, Libra AJ, Saupe A. *Ozonation of Water and Waste Water*. Weinheim, Germany: Wiley–VCH; 2000.
23. Trably E. *Etude et optimisation de la biodégradation d'hydrocarbures aromatiques polycycliques et de polychlorobiphényls au cours de la digestion anaérobie et aérobie de boues urbaines contaminées*. PhD thesis. Montpellier, France: University de Montpellier II; 2002.

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