

# Effect of humic acid on the photolysis of the pesticide atrazine in a surfactant-aided soil-washing system in acidic condition

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## Abstract

The photolytic destruction of Atrazine (ATZ) following a surfactant-aided soil-washing process was investigated in the presence of humic acid (HA). A non-ionic surfactant, Brij 35, was found to be a good solvating agent, extracting ATZ without causing any retardation effect on the photolysis process. However, the HA that was co-extracted from the surfactant-aided soil-washing system was found to be capable of improving the photolysis of ATZ at low concentrations, while quenching the photodegradation of ATZ at higher concentrations. By considering the light attenuation effect due to surfactant and HA, the quantum yields of the system with respect to the proposed reaction mechanisms of the associated excited states of ATZ were investigated and modeled. The relative kinetic rates of the dominant reaction mechanisms (i.e., deactivation of triplet, direct photolysis of triplet, product formation, and quenching of triplet) were then compared.

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*Keywords:* Atrazine; Humic acid; Model; Surfactant; Quantum yield

## 1. Introduction

The contamination of hazardous organic pollutants in soils or sediments is an environmental concern. Organic compounds, such as aromatic compounds, polyaromatic hydrocarbons (PAHs), herbicides, and pesticides, are of special interest because they are commonly detected in the environment and may be strongly adsorbed onto soil or be retained in a saturated zone underground. The surfactant-aided remediation of ground water and washing of soil are technologies used to enhance the removal of organic contaminants (Abdul et al., 1992; Yeom et al., 1996), and cleaning of hydrophobic organic compounds (HOCs) from contaminated soil or sediment

(Jafvert et al., 1995; Chu et al., 1998; Chu and Chan, 2003). They are pretreatments to further degrade the surfactant/HOCs mixtures that are extracted from soils and sediments (Chu and Jafvert, 1994; Chu, 1999). Surfactants are particularly attractive for this process as they potentially have low toxicity and favorable biodegradability; thus, they can be more environmentally friendly than many systems based on organic solvents. However, guidance in selecting the surfactants to be evaluated in the ex situ washing of soil is important for the soil remediation industry (Deshpande et al., 1999).

Surfactants are amphiphilic molecules that can dissolve in solvents, sorb at interfaces and form micelles, which have the ability to solubilize compounds whose water solubility is limited. The solubilization of compounds is generally initiated at the critical micelle

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Nomenclature	
$A$	absorbance
$\alpha$	intersystem crossing efficiency
ATZ	atrazine, 2-chloro-4-(ethylamino)-6-(isopropylamino)-s- triazine
[ATZ]	concentration of atrazine, M
CMC	critical micelle concentration, M
DDW	distilled-deionized water
$1/\delta$	maximum ratio of $k_q/k_d$ , $M^{-1}$
$\epsilon_{p,\lambda}$	molar absorptivity of the probe p at wavelength $\lambda$ , $L\ mol^{-1}\ cm^{-1}$
$F$	fraction of photons available for the probe photodecay
$\Phi$	quantum yield
$\Phi_0$	initial quantum yield
$\Phi_{max}$	maximum quantum yield
$1/\gamma$	marginal effect of changing $k_q/k_d$
HA	humic acid
[HA]	concentration of humic acid, M
[HA] <sub>opt</sub>	optimum concentration of humic acid, M
HOC	hydrophobic organic compound
HPLC	high-pressure liquid chromatography
$\bar{I}$	attenuated light intensity, <i>Einstein</i> $L^{-1}\ s^{-1}$
$I_0$	incident light, <i>Einstein</i> $L^{-1}\ s^{-1}$
$I_e$	emerging beam, <i>Einstein</i> $L^{-1}\ s^{-1}$
$k_{d1}$	rate of deactivation of singlet excited state, $s^{-1}$
$k_{d3}$	rate of deactivation of triplet excited state, $s^{-1}$
$k_f$	rate of fluorescence, $s^{-1}$
$k_{HA}$	rate of photochemical reaction due to humic acid, $M^{-1}\ s^{-1}$
$k_{isc}$	rate of intersystem crossing, $s^{-1}$
$k_p$	rate of phosphorescence, $s^{-1}$
$k_q$	rate of quenching of triplet excited state, $M^{-1}\ s^{-1}$
$k_r$	rate of direct photolysis, $s^{-1}$
LC	liquid chromatography
$\ell$	cell path length, cm
$\lambda$	wavelength, nm
MW	molecular weight, $g\ mol^{-1}$
$R$	size (radius) of the cuvette, cm
[S]	surfactant concentrations, M
$\Psi$	a term for solving the $k_{HA}/k_d$ (Eq. (17))

concentration (CMC) and is proportional to the concentration of surfactants above the CMC (Edwards et al., 1991). The magnitude of the solubilization of HOCs by surfactant micelles was observed in the order of non-ionic, cationic, and anionic for similar non-polar chain lengths. In this work, a non-ionic surfactant, Brij 35 ( $C_{12}H_{25}-O-(CH_2CH_2O)_{23}-H$ ), was selected in order to obtain a higher solubilization capacity for dissolving the target compound and a lower surfactant loss to the soil.

On the other hand, other researchers have suggested that there was no enhancement of organic solute solubility at surfactant concentrations below the CMC (Tokiwa and Tsujii, 1973; Moroi et al., 1983; Moroi et al., 1982). Zheng and Obbard (2002) found that the maximum sorption of a surfactant onto soil can be used to estimate the effective CMC of the surfactant in the soil/aqueous system, and that this provides valuable information for the application of in situ surfactant-enhanced soil bioremediation and ex situ surfactant soil washing.

Humic materials, a complex mixture of polymeric phenolic macromolecules, can also be extracted from soils by a surfactant soil-washing process. These materials have the property of complex formation to increase the solubilities, reactivities, and mobilities of environmental chemicals. They also have the ability of photosensitization to absorb solar energy and generate radical species that may attack chemicals in the environment and initiate their degradation (Zepp et

al., 1981; Frimmel et al., 1987). Humic acid (HA) is the major extractable component of soil humic substances. It flocculates under acidic conditions and contains free and bound phenolic OH groups, quinone structures, nitrogen, and oxygen as bridge units; and COOH groups variously placed on aromatic rings (Stevenson, 1982). Frimmel and Hessler (1994) found that the humic substances are sensitizers that produce reactive intermediates such as singlet oxygen ( $^1O_2$ ), superoxide anion ( $^{\bullet}O_2^-$ ), hydrogen peroxide ( $H_2O_2$ ), solvated electrons ( $e_{aq}^-$ ), and peroxyradicals ( $ROO^{\bullet}$ ) in the water. Sanlaville et al. (1996) suggested that the acceleration of the rate of photolysis in the presence of humic substances could be due to a radical mechanism rather than to a triplet-triplet energy transfer. In addition, HA has been shown to facilitate various advanced oxidation processes including ozone/UV treatments (Beschkov et al., 1997) and  $TiO_2$ /UV (Schmelling et al., 1997). It is believed that ozonation of HA carbon-carbon double bonds promote the formation of  $H_2O_2$ , which enhances the transformation of triethylene glycol dimethyl ether through the formation of more  $HO^{\bullet}$  radicals (Beschkov et al., 1997). On the other hand, Zepp et al. (1975) reported that the phenolic humic substances present in most inland waters could inhibit the chain reactions of free radicals. Thus, quantum yields for direct photolysis of chlorinated compounds in the aquatic environment are not likely to exceed unity. Besides being a scavenger of radicals, HA may act as a light filter and consume most of the photon during the photolysis process (Hawari et al., 1992).

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