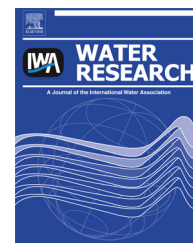


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The effect of dichlorophen binding to silica nanoparticles on its photosensitized degradation in water

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ABSTRACT

The production of dichlorophen (2,2'-methylenebis(4-chlorophenol), DCP) and its use as an anthelmintic and in pesticide products result in its direct release to the environment. To the purpose of modelling the possible photodegradation routes of DCP sorbed on sediments or suspended particles, the synthesis and characterization of silica nanoparticles modified with DCP (NP–DCP) is reported.

The reactivity of NP–DCP with the excited states of riboflavin, a sensitizer usually present in natural waters, and with singlet oxygen were investigated. Comparison of the kinetic results obtained here to those previously reported for irradiated aqueous solutions of DCP allowed the discussion of the effect of adsorption of the pesticide on its photodegradation.

We show with the aid of computer simulations that in natural waters the relevance of the different photodegradation routes dichlorophen is very much affected by attachment to sediments.

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1. Introduction

The production of dichlorophen (2,2'-methylenebis(4-chlorophenol), DCP) and its use as an anthelmintic and in pesticide products result in its direct release to the environment. DCP has been recognized as very toxic to aquatic organisms and may cause long-term effects in the aquatic environment (EC Directive 2001/58/EC). Once released to the environment, its hydrophobicity allows it to bioconcentrate in

marine organisms, bioaccumulate, and eventually biomagnify. Previous studies have reported that DCP can be accumulated in fish exposed to wastewater treatment works effluents and this compound was also detected in wastewater effluents at concentrations of 10–450 ngL⁻¹, a fact which indicates that its presence is mainly due to its widespread use also as a bactericide and fungicide in a variety personal care product formulations (Hill et al., 2010; Rostkowski et al., 2011).

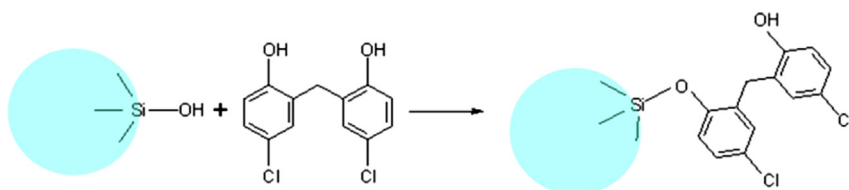
The degradation of a pesticide in an aquatic natural environment can be carried out by direct photolysis or through its

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reaction with reactive oxygen species (ROS) if another light-absorbing compound – a photosensitizer – is present in the medium. Among the sensitizers usually present in water courses, lakes and seas are humic acids (HA) (Carlos et al., 2011) and the pigment riboflavin (Rf) (Escalada et al., 2006).

Based on the estimated Koc value it can be predicted that if released to water, DCP adsorbs strongly to suspended solids and sediment in the water column (Toxicology Data Network). The adsorption of dissolved DCP to suspended silica particles in natural waters motivated us to synthesize silica nanoparticles functionalized with DCP (NP–DCP) by employing the condensation reaction 1.



(1)

Note that reaction 1 depicts the anchoring of DCP to the silica nanoparticles but does not mean the existence of only one bonded molecule of DCP per nanoparticle.

The photodegradation of DCP mediated by Rf, a sensitizer usually present along with HA in water courses, lakes and seas (Escalada et al., 2006; Zeng et al., 2003; Benassi et al., 1967), was recently investigated (Escalada et al., 2011). Upon visible light irradiation and in the absence of interacting compounds, the contribution of HA to the generation of reactive oxygen species (ROS) is very small, if compared to that of Rf (Carlos et al., 2011; Leech et al., 2009). For this reason, the sensitizer Rf was recently employed as proxy of chromophore dissolved organic matter (DOM) (Vione et al., 2011).

With this background we set out to investigate the kinetics of the possible routes leading to the photosensitized degradation of the silica particles modified with DCP suspended in aqueous solutions of Rf. Comparison of the kinetic results obtained here to those previously reported for irradiated aqueous solutions of the phenolic pesticide (Escalada et al., 2011) allows the discussion of the effect of adsorption of the pesticide on its photodegradation.

2. Materials and methods

2.1. Reagents

Fumed silica (Sigma, specific surface area; SSA = (390 ± 40) m²/g, particle diameter estimated from the SSA = 7 nm) was dried in a crucible for 15 h at 120 °C and then in a muffle for 3 h at 250 °C and stored in desiccators. The solvent *o*-xylene (Aldrich) was distilled onto molecular sieves, which had been dried at 250 °C for 4 h. Superoxide dismutase (SOD), DCP, furfuryl alcohol (FFA), deuterium oxide (D₂O), deuterated

methanol (MeOD) and CaCl₂, all from Sigma–Aldrich, rose bengal (RB) and sodium azide from Anedra, CaH₂ (Fluka), 2-propanol and methanol (MeOH) from Sintorgan, ethyl acetate (Cicarelli, p.a.), and K₂HPO₄ and KH₂PO₄ (Merck) were used without further purification.

2.2. Synthesis of the nanoparticles

A modification of the condensation method reported for the synthesis of nanoparticles functionalized with alcohols (Ruiz et al., 2007; Arce et al., 2011) was employed here (see reaction 1). Briefly, 0.5 g of DCP and 180 mL of *o*-xylene were

added to 1.0 g of silica nanoparticles. The mixtures were placed in a Soxhlet extractor containing CaH₂ equipped with a condenser with anhydrous CaCl₂, and refluxed during 24 h. The products were filtered with 20 nm- nylon filters, washed with 50 mL hot *o*-xylene and finally with 50 mL ethyl acetate. The resulting gel was first dried at 0.1 Torr and at room temperature for 3 h and then at 120 °C for 5 h. White powders were obtained.

To reduce colloidal aggregation the aqueous suspensions of NP–DCP were buffered with a mixture of K₂HPO₄ and KH₂PO₄ (pH = 6.4) (Ruiz et al., 2007).

2.3. Characterization of the nanoparticles

The particles were characterized by Fourier transform infrared spectroscopy (FTIR), Brunauer–Emmett–Teller (BET) analysis, thermogravimetry (TG), dynamic light scattering (DLS), and UV–vis spectroscopy. The experimental details are given in the Supplementary data.

2.4. Fluorescence spectroscopy

Fluorescence lifetimes were evaluated with a time-correlated single photon counting technique (SPC) on an Edinburgh FL-9000CD instrument provided with a PicoQuant subnanosecond pulsed LED emitting at 450 nm. The emission wavelength for Rf was 515 nm. The measurements were performed with solutions of Rf ($A^{450} = 0.23$) in aqueous phosphate buffer of pH = 6.4 and with (0–2.5 gL^{−1}) NP–DCP suspensions in this solution.

Steady state fluorescence anisotropy measurements $\langle r \rangle$ were obtained from eq. (2) using a Hitachi 2500 spectrofluorometer.

$$\langle r \rangle = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \quad (2)$$

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