

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Removal and degradation of aromatic compounds from a highly polluted site by coupling soil washing with photocatalysis

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/104388> since 2020-07-07T16:06:18Z

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier. It is posted here by agreement between Elsevier and the University of Turin. Changes resulting from the publishing process - such as editing, corrections, structural formatting, and other quality control mechanisms - may not be reflected in this version of the text. The definitive version of the text was subsequently published in CHEMOSPHERE, 71, 2008, 10.1016/j.chemosphere.2007.10.028.

You may download, copy and otherwise use the AAM for non-commercial purposes provided that your license is limited by the following restrictions:

- (1) You may use this AAM for non-commercial purposes only under the terms of the CC-BY-NC-ND license.
- (2) The integrity of the work and identification of the author, copyright owner, and publisher must be preserved in any copy.
- (3) You must attribute this AAM in the following format: Creative Commons BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/deed.en>), 10.1016/j.chemosphere.2007.10.028

When citing, please refer to the published version.

Link to this full text:

<http://hdl.handle.net/2318/104388>

1 **REMOVAL AND DEGRADATION OF AROMATIC COMPOUNDS FROM A HIGHLY**
2 **POLLUTED SITE BY COUPLING SOIL WASHING WITH PHOTOCATALYSIS.**

3

4 D. Fabbri, A. Bianco Prevot, V. Zelano, M. Ginepro and E. Pramauro*

5

6 Dipartimento di Chimica Analitica, University of Torino, 10125 – Torino – Italy

7 Tel (+039) 011/6707631 Fax (+039) 011/6707615

8 (*): Corresponding author.

9

10 **ABSTRACT**

11 The possible application of two environmental remediation technologies – soil washing and
12 photocatalysis – to remove and decompose various aromatic pollutants present in excavated soils of
13 a contaminated industrial site has been investigated. Aqueous solutions containing the non ionic
14 surfactant Brij 35 were used to extract the contaminants from the soil samples. The photocatalytic
15 treatment of the obtained washing wastes, performed in the presence of TiO₂ suspensions irradiated
16 with simulated sunlight, showed a slow abatement of the toxic compounds due to the relevant
17 concentrations of organics in the waste. A neat improvement of the process performances, obtained
18 by operating in the presence of added potassium peroxydisulfate, suggests a feasible treatment
19 route.

20

21 **KEYWORDS:** soil-washing, surfactants, photocatalysis, aromatic pollutants

22

23 **Introduction**

24 Soil washing, a treatment technology used for removing contaminants from polluted soils, is
25 largely based on the use of aqueous surfactant solutions and exploits both the solubilization
26 capabilities of micelles and the lowering of the interface tension between the washing liquid and the

27 soil particles, thus facilitating the solutes desorption and their exit from the soil pores (Edwards et
28 al., 1991; Gotlieb et al., 1993; Chu and So, 2001; Chu and Chan, 2003). Surfactant-enhanced
29 remediation (SER) has been, in particular, proposed as a suitable approach for removal of
30 hydrophobic organic pollutants and the performances of different amphiphiles have been reported
31 (Edwards et al., 1991; Desphande et al., 1999).

32 Among the proposed amphiphiles, nonionic surfactants have been often employed on the basis of
33 their high solubilization capabilities and low critical micelle concentrations, CMC (that is the
34 amphiphilic concentration at which the aggregation of monomer occurs, giving rise to the formation
35 of micelles) (Zheng and Obbard, 2002), whereas anionic surfactants have been usually selected
36 taking into account their lower adsorption on the soils. However, it is well known that ionic
37 surfactants exhibit higher CMC values and this implies the presence of higher surfactant
38 concentrations in the residual washing wastes. The use of mixtures of non-ionic and ionic
39 surfactants has been also reported in the literature (Zhu and Feng, 2003; Yang et al. 2006), as well
40 as the possible application of solvent/surfactant mixtures (Chu and Kwan, 2003).

41 However, further problems arise after the soil washing since the collected wastes must be
42 adequately disposed or treated by applying suitable microbial or chemical degradation procedures.
43 Heterogeneous photocatalysis, one of the more promising advanced oxidation processes developed
44 in the past, has been proposed for the treatment of a wide variety of washing wastes. This process
45 allows not only to perform the effective degradation of a great number of organic pollutants present
46 at moderate concentration levels in aqueous wastes (Ollis et al., 1989; Pichat et al., 1993;
47 Bahnemann et al., 1994; Hoffmann et al., 1995; Alfano et al., 2000; Malato et al., 2002), but in
48 most cases leads to the complete mineralization of such compounds.

49 The possible applications of photocatalysis to treat complex aqueous wastes, including those
50 containing surfactants, have been recently considered. In these cases it must be recalled that
51 surfactants are themselves degraded (Hidaka et al., 1990) and that a competition between these
52 molecules and the target pollutants for the active sites of the semiconductor usually occurs. In some

53 previous investigations we have, in fact, found that the degradation of various aromatic pollutants is
54 inhibited in the presence of surfactants (Pramauro et al., 1998; Bianco Prevot et al., 1999; Fabbri et
55 al., 2004), but beneficial kinetic effects due to the accumulation of hydrophobic substrates in the
56 adsorbed surfactant layers covering the TiO₂ particles have been also observed (Tada et al., 2002;
57 Fabbri et al., 2006). It is, thus, essential to study in detail the evolution of the process in order to
58 find the suitable experimental conditions under which the treatment could be effectively performed.
59 The aim of the present work was to investigate the possible application of photocatalysis to treat
60 soil washing wastes arising from a vast contaminated site located in Cengio (Savona, Italy), where a
61 former chemical plant was involved in the production of many chemicals for the synthesis of dyes.
62 The nonionic aliphatic surfactant Brij 35 has been chosen to perform the soil washing step, whereas
63 different experimental conditions have been examined in order to optimize and speed up the
64 photocatalytic treatment of the surfactant-containing wastes.

65

66 **EXPERIMENTAL SECTION**

67 **Materials and methods**

68 **Soil samples**

69 The reported mean composition of the sampled soil (previously determined in different points of
70 the site) was in the following range: sand: 50-55%; silt: 40-43%; clay: 4-5%, organic carbon:
71 around 3%. Soil samples were sieved to < 2 mm to remove the bigger particles (in particular the
72 rock pieces) and were mechanically homogenized. Various aromatic pollutants having different
73 toxicities have been found in the contaminated soil samples.

74 **Reagents**

75 Polycrystalline TiO₂ Degussa P25 (composed of c.a. 80% anatase and 20% rutile) was employed in
76 all the photodegradation experiments. In order to remove any organic impurity this oxide was
77 washed with water and irradiated with simulated solar light for about 12 h. The washed

78 semiconductor was then dried in the oven at 80 °C. The resulting powder was resuspended in water
79 by sonication immediately before use.

80 Acetonitrile (Lichrosolv, Merck) and potassium acetate (99.5%, Carlo Erba) were used to
81 prepare the eluents. Pure standards of the analytes (purchased from Aldrich, Merck, Carlo Erba)
82 were used for calibration runs and for preliminary photocatalytic experiments. Brij 35 (Aldrich) was
83 used for soil washing. Acetone (from Aldrich) and n-hexane (from Aldrich) were used for the
84 exhaustive extraction of the soil samples. Pure water was produced using a Milli-QTM system
85 (Millipore).

86 **Instruments**

87 The following instruments were used: HPLC Merck-Hitachi, equipped with L-6200 pumps and a
88 UV-VIS L-4200 detector; GC-MS: Varian 3400 gas chromatograph interfaced to a Varian Saturn
89 4D ion trap detector equipped with a Supelco MDN-5S column (30 m, 0.25 mm i.d. with 0.25 µm
90 film thickness); microwave digestion system MARSX from CEM Corporation. Surface tension
91 measurements were performed with a digital-tensiometer (K10, Krüss).

93 **Analytical procedures**

94 **Soil samples analysis**

95 The soil samples have been analyzed according to the following procedure: ca. 3 g of soil were
96 directly weighed in the teflon microwave vessel and 20 mL of solution acetone/hexane (50:50, v/v)
97 was added. Then the sample was micro-waved at 110 °C and 689 kPa for 20 min. The liners were
98 cooled to 25 °C, then the solution was filtered through 0.45 µm Millex –LCR filters (Millipore).

99 All the analytes were identified by means of GC-MS analysis and from the match of their HPLC
100 retention properties and UV spectra with those of the corresponding authentic standards.

101 The GC temperature program conditions were: 60 °C isothermal for 1 min, ramped to 160 °C in
102 15 min and then isothermal for 8 min. The mass spectrometer was operated in EI-mode at electron
103 energy of 70 eV. The ion source temperature was 200 °C.

104 The quantification of each compound has been performed by HPLC, according to two different
105 elution procedures: i- For the analysis of 2-naphthol, 3,4-dichloroaniline and 2,4-dichloroaniline
106 the employed eluent was: acetonitrile and an aqueous solution of potassium acetate 20 mM (45:55
107 v/v); a column 100 RP-C18 (Lichrospher, 4 mm i.d.×125 mm, 5 µm) was used, working in isocratic
108 condition at a flow rate of 1 mL min⁻¹; the detector wavelength was 240 nm; ii- A mixture of
109 acetonitrile and water (55:45 v/v) was employed as eluent for the analysis of all the remaining
110 analytes. A column 100 RP-C18 (Lichrospher, 4 mm i.d. × 250 mm, 10 µm) was used. The detector
111 wavelength was 200 nm.

112

113 **Soil washing experiments.**

114 Most extraction experiments were performed on 2 g of soil extracted with 25 mL of washing
115 solution, placed in stopped tubes in a rotatory mixer (rotation speed: ca. 10 rpm). The standard
116 contact time was 5 h.

117 The obtained soil dispersions were centrifuged at 5000 rpm for 10 min and aliquots of the
118 supernatant clear solutions were sampled for the analysis and filtered through a 0.45 µm Millex LCR
119 hydrophilic PTFE membranes (Millipore). The concentration of each analyte was successively
120 determined on the filtered solution by HPLC, following the previously detailed procedures.

121

122 **Preliminary degradation experiments.**

123 A series of preliminary photocatalytic runs were performed in stirred cylindrical closed cells (40
124 mm i.d. x 25 mm high, made of Pyrex glass) on 5 mL of aqueous dispersions containing 6 mg L⁻¹ of
125 each individual pollutant and 500 mg L⁻¹ of TiO₂. The concentration of Brij 35 was 2.5x10⁻² M.
126 Similar experiments were also performed on the washing extract diluted (1:2) with water to have
127 the same surfactant concentration.

128 A 1500 W Xenon lamp source (Solarbox, CO. FO. MEGRA, Milan, Italy) equipped with a 340
129 nm cut-off filter was employed to furnish simulated solar irradiation. The temperature within the

130 cells was ca. 55 °C. The dispersions were collected from the cells at the end of the programmed
131 irradiation period, then were filtered before the analysis.

132

133 **Degradation runs performed in laboratory photoreactor.**

134 Another series of experiments were performed using an annular photoreactor (from Helios-
135 Italquarz, Milan) equipped with a medium pressure mercury lamp (125 W). This light source better
136 simulates the treatment conditions of real wastes in plants. The irradiated solutions were kept
137 saturated with air during the treatment.

138 Degradations were performed on 500 mL of waste solutions containing 500 mg L⁻¹ of TiO₂ (and
139 eventually other additives). The temperature was kept at 25 °C. The starting pH of the irradiated
140 suspensions was around 7.5. Samples (1-2 mL) of irradiated dispersion were taken from the reactor
141 at different times; all the analytical determinations were performed after filtration.

142

143 **RESULTS AND DISCUSSION**

144 **Analysis of the contaminated soil samples**

145 The soil samples, analyzed following the procedures detailed in the previous section showed the
146 presence of relevant amounts of aromatic compounds (ca. 3 g kg⁻¹). The concentrations of the
147 identified main pollutants are given in Table 1. The standard deviations of the found values,
148 estimated from five replicated measurements, were in the range 4-7%.

149 It has to be noted that anthraquinone and benzanthrone, which are well known dyestuff
150 intermediates employed for the production of anthraquinonic dyes, are the more abundant
151 components found in the contaminated soil. Traces of benzene have also been detected.

152

153 **Soil washing performances**

154 The surfactant Brij 35 –poly(oxyethylene)₂₃ dodecyl ether- was chosen on the basis of its high
155 solubilization capability towards aromatic solutes and taking into account its low CMC (1.0x10⁻⁴ M,

156 see inset in Fig. 1). Moreover, due to the non-aromatic nature of this surfactant, the interferences
157 with the soil pollutants during the photocatalytic runs are expected to be less important. After the
158 established contact period (5 h) all the soil extracts showed a yellowish colour.

159 The surface tension measurements performed on the filtered soil extract and on the solutions
160 obtained after its dilutions clearly indicates (see Fig. 1) that, under the described working
161 conditions, micellar aggregates are present in the washing solutions, even in the presence of
162 surfactant adsorption on the soil. This condition is important since micellar solubilization plays a
163 crucial role in the removal of adsorbed hydrophobic pollutants from soils (Liu et al., 1992).

164 Another set of surface tension measurements was performed in order to confirm the presence of
165 micellar aggregates after the equilibration of the washing solutions with the proper amount of TiO₂.
166 The surface tension of filtered washing solutions was measured after equilibration in the dark for 30
167 min. Also in this case the presence of surfactant aggregates was evident.

168 Due to the complexity of the solid matrix and to the abundance of organic pollutants (including
169 those coming from alterations of the initially present compounds and/or from the organic soil
170 fraction), the components listed in Table 1 were chosen as reference pollutants and their evolution
171 was investigated. They have been divided into two distinct groups representing both highly
172 hydrophobic and moderately hydrophobic contaminants present in the soil samples:

173 Group 1: moderately hydrophobic compounds. Measured retention times (min): 2-naphthol = 4.2;
174 3,4-dichloroaniline = 6.1; 2,4-dichloroaniline = 8.0. Group 2: more hydrophobic compounds.
175 Retention times (min): chlorobenzene = 10.2; 9,10-anthraquinone = 11.4; 1,4-dichlorobenzene =
176 15.8; 7[H]-benz[de]-anthracen-7-one (benzanthrone) = 19.5; 1,2,4-trichlorobenzene = 25.8; 1,2,3,4-
177 tetrachlorobenzene = 37.2; 1,2,4,5-tetrachlorobenzene = 43.6.

178 The recovery yields after 5 h extraction with Brij 35 0.05 M, calculated with respect to the
179 corresponding recoveries obtained using the microwave-assisted extraction with organic solvents,
180 are reported in Table 2.

181 The standard deviations of the found values, estimated from five replicated measurements, were
182 in the range 4-8% for most pollutants. For chlorobenzene a higher uncertainty was found (ca. 15%).

183 Compounds of Group 1 are significantly extracted after 5 h, whereas for analytes pertaining to
184 Group 2 the extraction yields are generally lower and largely vary depending on the solutes
185 structures. It has to be underlined that the extraction of chlorobenzene was scarcely reproducible
186 and that, due to its higher volatility, relevant amounts of this component were detected in the gas
187 phase and lost during the soil washing runs. Also 9,10-anthraquinone exhibited modest recovery
188 yields under the examined conditions.

189

190 **Photocatalytic degradation experiments**

191 The fundamentals of photocatalysis have been abundantly reported in the literature (Ollis et al.,
192 1989; Pichat et al., 1993; Bahnemann et al., 1994; Hoffmann et al., 1995). Basically, the light-
193 induced formation of electron-hole pairs leads to the formation of reactive species (in particular the
194 oxidizing OH radicals) able to attack and degrade the organic pollutants. The contribution of
195 reductive pathways involving the electrons present in the conduction band can be also present in
196 some cases (Muneer and Bahnemann, 2002).

197 **i) Degradation of individual pollutants in Solarbox:** In order to examine and compare the
198 pollutants evolution during the photocatalytic treatment, the primary degradation of each reference
199 contaminant was investigated in the presence of Brij 35 0.025 M, corresponding to the surfactant
200 concentration of soil washing extracts after dilution 1:2 with water. The obtained data fit well a
201 pseudo-first order kinetic law, as typically found in most photocatalytic degradations of organics
202 (see Fig. 2).

203 As for most similar experiments the formation of transient intermediate species, which in turn
204 undergo degradation, has been observed. The transformation of the organic carbon of the
205 investigated substrates to CO₂ cannot be followed under the described experimental conditions due
206 to the presence of the large excess of added surfactant.

207 It can be seen that the degradation of polychlorobenzenes is much slower than that of the other
208 aromatic substrates. Moreover, a noticeable induction period ranging from ca. 2 h for 1,4-
209 dichlorobenzene up to ca. 4 h for tetrachlorobenzenes has been observed before the beginning of the
210 effective degradation process. During this induction time a negligible degradation (less than ca. 5%)
211 of the pollutants was observed, whereas after this period the substrate degradation becomes faster
212 and follows the expected kinetic behaviour. The two tetrachlorobenzene isomers, which showed the
213 same degradation rate, were reported together. For comparison purposes, the kinetic plots shown in
214 Fig. 2 do not include the induction period.

215 In order to estimate the effective pollutants persistency during the treatment, their half-life times
216 ($t_{1/2}$) have been measured. The obtained $t_{1/2}$ values (min) were: 9,10-anthraquinone: 8; 2-naphthol:
217 10; 2,4-dichloroaniline: 37; 3,4-dichloroaniline: 47; benzanthrone: 60; 1,4-dichlorobenzene: 120;
218 1,2,4-trichlorobenzene: 300; tetrachlorobenzenes: 620.

219 Although a detailed study of the factors which are at the basis of the observed slow steps in the
220 degradation of polychlorobenzenes was out of the scope of this work, the scarce tendency of these
221 pollutants to transfer from micelles to the surfactant coated TiO₂ particles (where the degradation
222 reactions can initiate) could play a significant role. In fact, it is known from micellar
223 chromatography experiments that the mass transfer of highly bound solutes from micelles to
224 adsorbed surfactant layers covering solid surfaces is a very slow process which involves a peculiar
225 direct transfer mechanism (Borgerding et al., 1988).

226 In order to verify the extent of micelle-solute binding, the binding constants (K_B) of the
227 examined polychlorobenzenes to Brij 35 micelles have been estimated starting from available
228 literature data for benzene and chlorobenzene (Marina et al., 1989), exploiting the well known
229 existing correlation between the free energy of transfer of solutes from water to micelles and their
230 corresponding binding constants (Bunton and Sepulveda, 1979):

231

$$\Delta\mu_t^\circ = \mu_{mic}^\circ - \mu_w^\circ = -RT \ln (55.5 K_B) \quad (1)$$

232

233 Since the free energy of transfer of polysubstituted molecules can be calculated from the
234 individual contributions of the substituent groups, the following equation holds for
235 polychlorobenzenes having n chlorine atoms:

$$\Delta\mu^{\circ}_{t \text{ molecule}} = \Delta\mu^{\circ}_{t \text{ benzene}} + n \Delta\mu^{\circ}_{t \text{ chlorine}} \quad (2)$$

238
239 From K_B and $\Delta\mu^{\circ}_t$ values reported for benzene ($K_B = 34 \text{ M}^{-1}$, $\Delta\mu^{\circ}_t = -18.71 \text{ kJ mol}^{-1}$) and
240 chlorobenzene ($K_B = 239 \text{ M}^{-1}$; $\Delta\mu^{\circ}_t = -23.53 \text{ kJ mol}^{-1}$), the contribution of each chlorine atom to the
241 free energy of transfer of the chlorinated molecules was estimated to be $-4.81 \text{ kJ mol}^{-1}$. The free
242 energies of transfer of the investigated polychlorobenzenes were then calculated using Eq. 2 and the
243 corresponding K_B values of polychlorobenzenes were obtained by applying Eq. 1. These values
244 ($1,670 \text{ M}^{-1}$ and $11,640 \text{ M}^{-1}$ for 1,4-dichlorobenzene and 1,2,4-trichlorobenzene, respectively)
245 largely justify the assumption that the solutes are completely bound to the micelles and, thus, their
246 slow release from the host aggregates is expected. The estimated K_B value for tetrachlorobenzenes
247 is even much higher (around $80,000 \text{ M}^{-1}$).

248 **ii) Degradation of soil-washing extracts in Solarbox:** In order to examine the degradation
249 kinetics of the pollutants mixture present in the real waste, some experiments were also performed
250 on the soil washing extracts (diluted 1:2 with water) in the presence of 500 mg L^{-1} of TiO_2 . From
251 the examination of the HPLC profiles I and II (see Figs. 3a and 3b), corresponding to the initial
252 composition and that obtained after 1 h irradiation, respectively, it can be seen that the pollutants
253 abatement is negligible for compounds belonging to Group 1, whereas for those of Group 2 only the
254 neat abatement of 9,10-anthraquinone is observed together with the formation of a transient
255 intermediate peak (*), which successively disappears.

256 In order to increase the degradation rate, the amount of TiO_2 can be increased, but it is known
257 that the maximum amount of added photocatalyst is limited by the scattering of impinging light in

258 the dispersion. The introduction of suitable additives was thus considered as a possible way to
259 improve the treatment performances.

260 Various additives capable to trap e^-_{CB} , delaying electron-hole recombination, and to favour the
261 formation of active oxidizing radicals have been proposed. Among them, peroxydisulfates can offer
262 relevant beneficial effects which can be explained taking into account both the electron scavenging
263 action of $S_2O_8^{2-}$ (Eqs. 3 and 4) and the possible participation of strong oxidizing sulfate radicals
264 ($SO_4^{\bullet-}$) in oxidation reactions with organic substrates (Neta et al., 1977).

265 The following reactions give rise to the formation of radical active species:

266



269

270 The sulfate radical anion can then attack organic compounds via: i) hydrogen atom abstraction
271 from saturated carbon, ii) addition to unsaturated or aromatic carbon, iii) removal of electrons from
272 some reactive groups, such as carboxylate anion. These peculiar properties suggest the addition of
273 peroxydisulfate to enhance both the degradation rate and the mineralization extent in various
274 photocatalytic processes. This approach has been successfully applied to increase the photocatalytic
275 degradation/mineralization rates of different pollutants, such as organophosphorous compounds
276 (Gratzel et al., 1990), dioxins, chlorophenols and atrazine (Pelizzetti et al. 1991), chlorinated
277 hydrocarbons (Martin et al., 1995), anthraquinonic dyes (Bianco Prevot et al., 2001) and others.

278 On these basis we decided to perform photocatalytic experiments in the presence of $K_2S_2O_8$
279 (500 mg L^{-1}), added at the beginning of the runs. From the examination of profiles III in Figs. 3a
280 and 3b, the beneficial effect due to the additive is evident.

281 **iii) Treatment of the soil washing waste in the photoreactor:** Table 3 reports the evolution of
282 substrates degradation as a function of irradiation time (up to 6 h), in the presence of both TiO_2 and
283 $K_2S_2O_8$ (500 mg L^{-1}). It can be seen that, under the examined conditions, the removal of Group 1

284 compounds (naphthol and chloroanilines) and of some components of Group 2 (anthraquinone, 1,4-
285 dichlorobenzene and benzanthrone) is effective, whereas the much slower degradation of
286 polychlorinated benzenes is evident. For these last mentioned compounds longer irradiation times
287 become necessary in order to obtain their complete degradation.

288

289 **CONCLUSIONS**

290 Taking into account the complex composition of the examined wastes, their high content of
291 aromatic pollutants, the contribution to the total organic matter arising from the organic soil fraction
292 and the presence of relevant amounts of added surfactant (ca. 60 g L⁻¹), the reported results are
293 promising since they support the feasibility of the photocatalytic procedure based on the use of TiO₂
294 dispersions under simulated solar light irradiation, even under these unfavourable starting
295 conditions. The addition of K₂S₂O₈ to the wastes enhances remarkably the rate of degradation of the
296 examined substrates.

297 The different reactivities exhibited by the investigated pollutants can be, at least in part, related
298 to their tendency to partition between the surfactant micelles and the bulk aqueous phase before
299 their transfer to the active sites of the irradiated semiconductor, although other factors such as the
300 specific influence of substrate and surfactant structures and the nature and evolution of surfactant
301 layers adsorbed onto the semiconductor surface, should be also considered and examined more
302 deeply. Studies in these directions are actually in progress in our laboratory.

303

304 **Acknowledgements**

305 Financial support from MIUR (PRIN 05) is gratefully acknowledged.

306

307

308

309

310 **REFERENCES**

311 Alfano, O.M.; Bahneman, D., Cassano, A.E., Dillert, R., Goslich, R., 2000. Photocatalysis in water
312 environments using artificial and solar light. *Catal. Today* 58, 199-230.

313

314 Bahnemann, D., Cunningham, J., Fox, M.A., Pelizzetti, E., Pichat, P., Serpone, N., 1994.
315 Photocatalytic treatments of waters. In: Helz, G.R., Zepp, R.G., Crosby, D.G. (Eds.). *Aquatic and*
316 *Surface Photochemistry*. Lewis, Boca Raton (FL), pp. 261-316.

317

318 Bianco Prevot, A., Pramauro, E., De la Guardia, M., 1999. Photocatalytic degradation of carbaryl in
319 aqueous TiO₂ suspensions containing surfactants. *Chemosphere* 39, 493-502.

320

321 Bianco Prevot, A., Baiocchi, C., Brussino, M.C., Pramauro, E., Savarino, P., Augugliaro, V., Marci,
322 G., Palmisano, L., 2001. Photocatalytic degradation of Acid Blue 80 in aqueous solutions
323 containing TiO₂ suspensions. *Environ. Sci. Technol.* 35, 971-976.

324

325 Borgerding, M.F, Quina, F.H, Hinze, W.L, Bowermaster, J, McNair, H.M, 1988. Investigation of
326 the retention mechanism in nonionic micellar liquid chromatography using an alkylbenzene
327 homologous series. *Anal. Chem.* 60, 2520-2527.

328

329 Bunton, C.A., Sepulveda, L., 1979. Hydrophobic and coulombic interactions in the micellar binding
330 of phenols and phenoxide ions. *J. Phys. Chem.* 83, 680-683.

331

332 Chu, W., So, W.S., 2001. Modeling the two stages of surfactant-aided soil washing. *Water Res.* 35,
333 182-188.

334

335 Chu, W., Chan, K.H., 2003. The mechanism of the surfactant-aided soil washing system for
336 hydrophobic and partially hydrophobic organics. *Sci. Total Environ.* 307, 83-92.
337

338 Chu, W., Kwan, C.Y., 2003. Remediation of contaminated soil by a solvent/surfactant system,
339 *Chemosphere* 53, 9-15.
340

341 Desphande, S., Shiao, B.J., Wade, D., Sabatini, D.A., Harwell, J.H., 1999. Surfactant selection for
342 enhancing ex-situ soil washing. *Water Res.* 33, 351-360.
343

344 Edwards, D.A., Luthy, R.G., Liu, Z. B, 1991. Solubilization of polycyclic aromatic-hydrocarbons in
345 micellar nonionic surfactant solutions. *Environ. Sci. Technol.* 25, 127-133.
346

347 Fabbri, D., Bianco Prevot, A., Pramauro, E., 2004. Kinetic effects of SDS on the photocatalytic
348 degradation of 2,4,5-trichlorophenol. *Appl. Catal. B-Environ.* 49, 233-238.
349

350 Fabbri, D., Bianco Prevot, A., Pramauro, E., 2006. Effect of surfactant microstructures on
351 photocatalytic degradation of phenol and chlorophenols. *Appl. Catal. B-Environ.* 62, 21-27.
352

353 Gotlieb, I., Bozelli, J.W., Gotlieb, E., 1993. Soil and water decontamination by extraction with
354 surfactants. *Separ. Sci. Technol.* 28, 793-804.
355

356 Gratzel, C.K., Jirousek, M., Gratzel, M., 1990. Decomposition of organophosphorus compounds on
357 photoactivated TiO₂ surfaces. *J. Mol. Catal.* 60, 375-387.
358

359 Hidaka, H., Yamada, S., Suenaga, S., Zhao, J., Serpone, N., Pelizzetti, E., 1990. Photodegradation
360 of surfactants.6. Complete photocatalytic degradation of anionic, cationic and nonionic surfactants
361 in aqueous semiconductor dispersions. *J. Mol. Catal.* 59, 279-290.

362

363 Hoffmann, M.R., Martin, S.T., Choi, W., Bahnemann, D.W., 1995. Environmental application of
364 semiconductor photocatalysis. *Chem. Rev.* 95, 69-96.

365

366 Liu, Z.B., Edwards, D.A., Luthy, R.G., 1992. Sorption of non-ionic surfactants onto soil. *Water*
367 *Res.* 26, 1337-1345.

368

369 Malato, S., Blanco, J., Vidal, A., Richter, C., 2002. Photocatalysis with solar energy at a pilot-plant
370 scale: an overview. *Appl. Catal. B-Environ.* 37, 1-15.

371

372 Marina, M.L., Vera, S., Rodriguez, A.R., 1989. Determination of the micelle-solute association
373 constants of some benzene and naphthalene derivatives by micellar high performance liquid
374 chromatograph. *Chromatographia* 28, 379-384.

375

376 Martin, S., Lee, A.T., Hoffmann, M.R., 1995. Chemical mechanism of inorganic oxidants in the
377 TiO_2/UV process - increased rates of degradation of chlorinated hydrocarbons. *Environ. Sci.*
378 *Technol.* 29, 2567-2573.

379

380 Muneer, M., Bahnemann, D., 2002. Semiconductor-mediated photocatalyzed degradation of two
381 selected pesticide derivatives, terbacil and 2,4,5-tribromoimidazole, in aqueous suspension. *Appl.*
382 *Catal. B-Environ.* 36, 95-111.

383

384 Neta, P., Madhavan, V., Zemel, H., Fessenden, R.W., 1977. Rate constants and mechanism of
385 reaction of sulfate radical anion with aromatic compounds. *J. Am. Chem. Soc.* 99, 163-164.
386

387 Ollis, D.F., Pelizzetti, E., Serpone, N., 1989. Heterogeneous photocatalysis in the Environment:
388 Application to Water Purification. In: Serpone, N., Pelizzetti, E. (Eds.). *Photocatalysis.*
389 *Fundamentals and Applications.* Wiley, New York, pp. 603-637.
390

391 Pelizzetti, E., Carlin, V., Minero, C., Gratzel, M., 1991. Enhancement of the rate of photocatalytic
392 degradation on TiO₂ of 2-Chlorophenol, 2,7-Dichlorodibenzodioxin and atrazine by inorganic
393 oxidizing species. *New. J. Chem.* 15, 351-359.
394

395 Pichat, P., Guillard, C., Maillard, C., Amalric, L., D'Oliveira, J. C., 1993. TiO₂ photocatalytic
396 destruction of water aromatic pollutants. Intermediates, properties-degradability correlation, effect
397 of inorganic ions and TiO₂ surface area. In: Ollis, D. F., Al-Ekabi, H. (Eds.). *Photocatalytic*
398 *Purification and Treatment of Water and Air.* Elsevier, Amstedam, pp. 207-223.
399

400 Pramauro, E., Bianco Prevot, A., Vincenti, M., Gamberini, R., 1998. Photocatalytic degradation of
401 naphthalene in aqueous TiO₂ dispersions: Effect of nonionic surfactants. *Chemosphere* 36, 1523-
402 1542.
403

404 Tada, H., Matsui, H., Shiota F., Nomura, M., Ito, S., Yoshihara, M., Esumi, K., 2002.
405 Heterosupramolecular photocatalysis: oxidation of organic compounds in nanospaces between
406 surfactant bilayers formed on TiO₂. *Chem. Commun.* 16,1678-1679.
407

408 Yang, K., Zhu, L., Xing, B., 2006. Enhanced soil washing of phenanthrene by mixed solutions of
409 TX100 and SDBS. *Environ. Sci. Technol.* 40, 4274-4280.

410 Zheng, Z.M., Obbard, J.P., 2002. Evaluation of an elevated non-ionic surfactant critical micelle
411 concentration in a soil/aqueous system. *Water Res.* 36, 2667-2672.

412

413 Zhu, L.Z., Feng, S.L., 2003. Synergistic solubilization of polycyclic aromatic hydrocarbons by
414 mixed anionic-nonionic surfactants. *Chemosphere* 53, 459-467.

415

416 **Captions**

417 **Figure 1** Surface tension versus dilution factor of Brij 35 in washing solution (○) and in washing
418 solution after contact with TiO₂ in the dark (☆).

419

420 **Figure 2** Linear plots of $-\ln A/A_0$ versus time of degradation, obtained for analytes of Group 1
421 (dashed lines) and Group 2 (continuous lines). (□ 2-naphtol; △ 3,4-dichloroaniline; ○ 2,4-
422 dichloroaniline, ◆ 1,4-dichlorobenzene; ★ 1,2,4-trichlorobenzene; ● 1,2,3,4-tetrachlorobenzene; ■
423 9,10-antraquinone, ▲ benzanthrone)

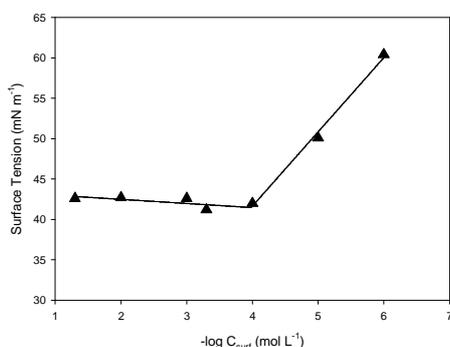
424

425 **Figure 3** HPLC profiles of soil washing extract following the chromatographic conditions
426 employed for Group 1 (a) and Group 2 (b). Profile I): sample diluted 1:2 with water; II) after 1 h of
427 degradation in the presence of TiO₂ (500 mg L⁻¹); III) after 1 h of degradation in the presence of
428 TiO₂ (500 mg L⁻¹) and K₂S₂O₈ (500 mg L⁻¹). Group 1: 1) 2-naphthol, 2) 3,4-dichloroaniline, 3) 2,4-
429 dichloroaniline. Group 2: 4) chlorobenzene; 5) 9,10-anthraquinone, 6) 1,4-dichlorobenzene; 7)
430 7[H]-benz[de]-anthracen-7-one (benzanthrone), 8) 1,2,4-trichlorobenzene, 9) 1,2,3,4-
431 tetrachlorobenzene, 10) 1,2,4,5-tetrachlorobenzene.

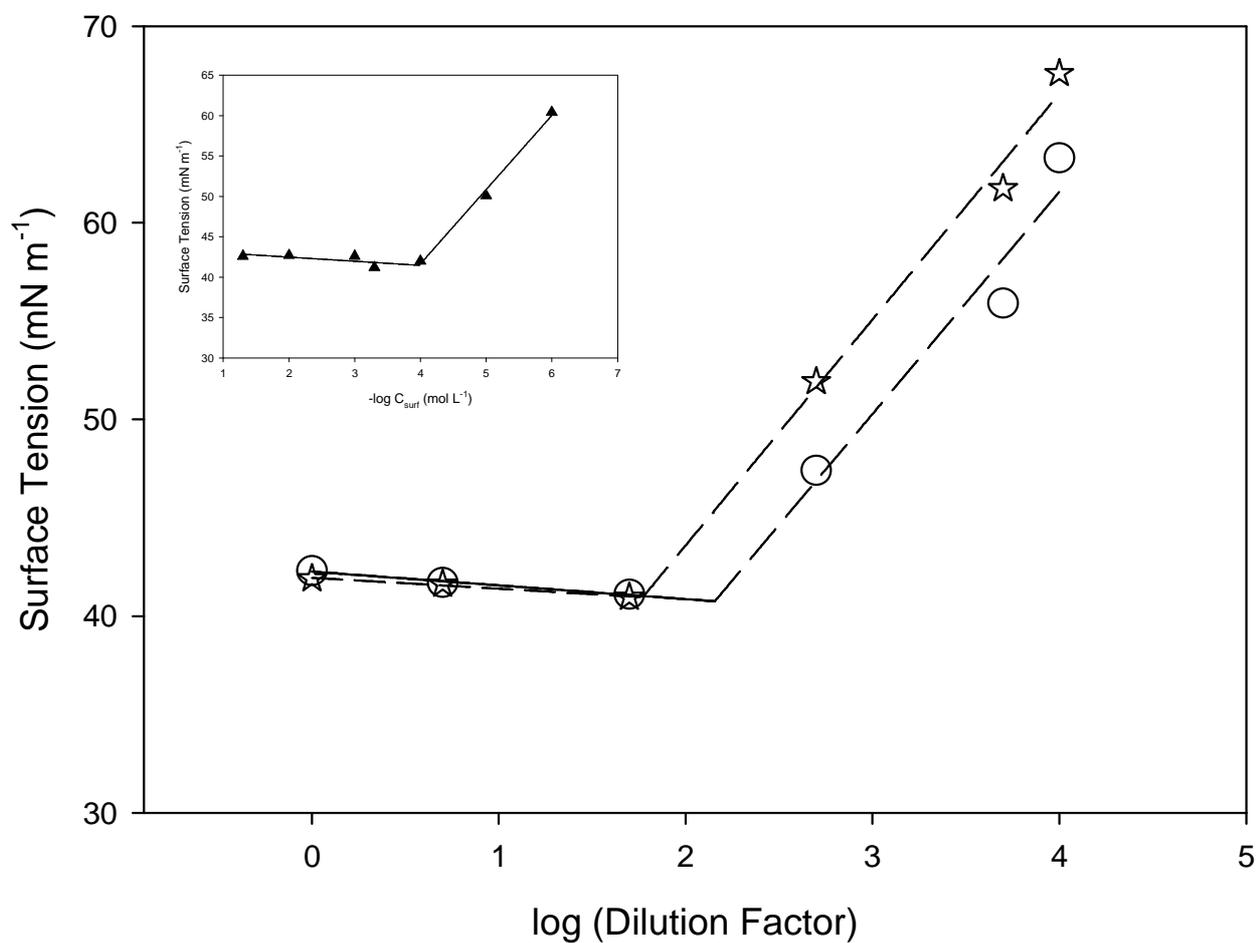
432

433

434



435 Figure 1



436
437

438

439

440

441

442

443

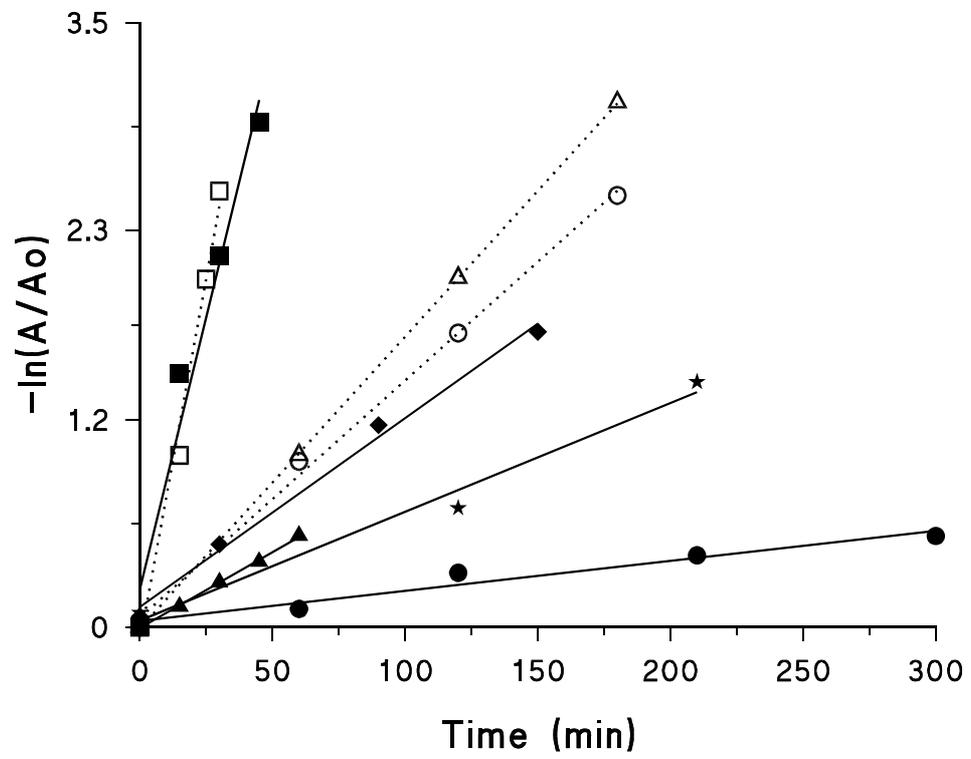
444

445

446

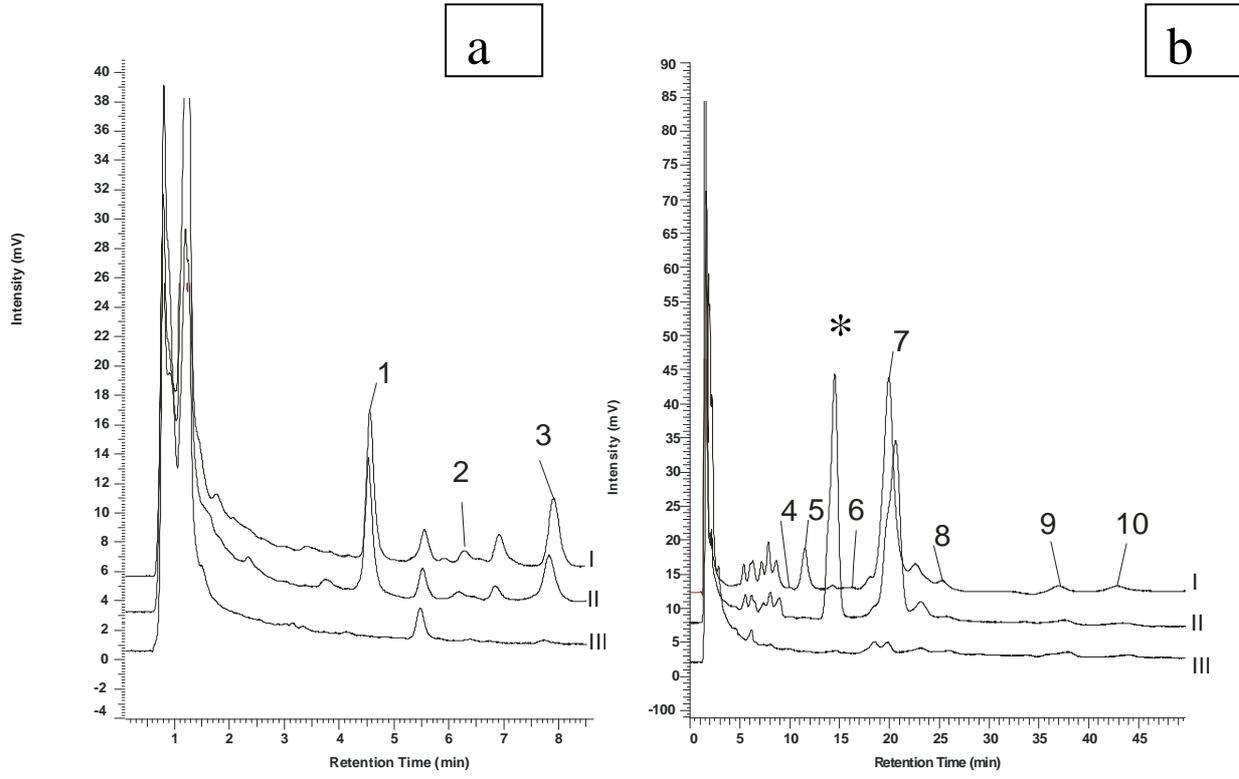
447

448 Figure 2



449
450
451

452 Figure 3
453
454



455

456 Table1: Aromatic pollutants found in the contaminated soil.

Pollutant	Concentration in soil (mg kg⁻¹)
2-naphtol	66
2,4-dichloroaniline	126
3,4-dichloroaniline	30
Chlorobenzene	76
1,4-dichlorobenzene	114
1,2,4-dichlorobenzene	76
1,2,3,4-tetrachlorobenzene	79
1,2,4,5-tetrachlorobenzene	67
9,10-anthraquinone	670
Benzanthrone	1706
Benzene	traces

457

458

459 Table 2: Amount of pollutant recovered (mg kg⁻¹) after 5 h extraction with Brij35 0.05 M and
460 recovery yields in respect to the exhaustive extraction.

461

Pollutant	Amount recovered (mg kg⁻¹)	% Recovery
2-naphtol	39	59
2,4-dichloroaniline	87	69
3,4-dichloroaniline	13	43
Chlorobenzene	7	≈ 9
1,4-dichlorobenzene	29	25
1,2,4-dichlorobenzene	30	40
Tetra chlorobenzenes	72	49
9,10-anthraquinone	92	14
Benzanthrone	761	45

462

463

464 Table 3: Percent of pollutants removal as a function of the irradiation time. Photoreactor runs.

465

Pollutant	Time (h)		
	2	4	6
Group 1	2	4	6
2-naphtol	98	100	100
2,4-dichloroaniline	99	100	100
3,4-dichloroaniline	87	93	95
Group 2			
1,4-dichlorobenzene	31	54	100
1,2,4-trichlorobenzene	28	40	50
Tetrachlorobenzenes	37	47	60
9,10-anthraquinone	100	100	100
Benzanthrone	91	93	94

466

467

468

469

470

471

472

473

474

475