

Degradation of the Herbicides Clomazone, Paraquat, and Glyphosate by Thermally Activated Peroxydisulfate

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Activated sodium peroxydisulfate has the potential to *in situ* destruct many organic contaminants because of the generation of the stronger oxidant sulfate radical. From photochemical activation of peroxydisulfate in flash-photolysis experiments, the bimolecular rate constants for the reaction of sulfate radical with glyphosate ($1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and paraquat ($1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) at 25 °C were obtained. Thermal activation of peroxydisulfate was shown to degrade the herbicides clomazone, paraquat, and glyphosate. Although the herbicide degradation was observed to take place in less than 1 h, the mineralization of the organic carbon required longer reaction times, because of the formation of stable organic intermediates. For similar initial total organic carbon (TOC) values, TOC profiles were similar for experiments with different substrates (the herbicides, humic acids, and a mixture of glyphosate and humic acids), which indicates that the mineralization of all of the samples is limited by the production of $\text{SO}_4^{\bullet-}$ radicals. A linear correlation between the initial amount of $\text{SO}_4^{\bullet-}$ needed per mole of C and the average oxidation state was found.

KEYWORDS: Peroxydisulfate; sulfate radical; glyphosate; clomazone; paraquat; average oxidation state

INTRODUCTION

Activated sodium peroxydisulfate (PS) has the potential to *in situ* destruct many organic contaminants commonly encountered in soil and groundwater. These properties combined with its safe handling and its solubility in water make it an excellent additive for waste treatment (1).

Although a strong oxidant, peroxydisulfate anion, $\text{S}_2\text{O}_8^{2-}$, slowly reacts with many organics. It can be chemically (2), photochemically (3), or thermally activated (4) to generate the stronger oxidant sulfate radicals, $\text{SO}_4^{\bullet-}$, with a redox potential $E(\text{SO}_4^{\bullet-}/\text{SO}_4^{2-}) = 2.6 \text{ V}$ (5). Generation of these radicals can significantly accelerate the kinetics of oxidation in a wide range of matrix conditions. Thermally activated peroxydisulfate has been demonstrated to decompose many contaminants in aqueous systems. Substrate degradation rates increase with an increasing temperature and oxidant concentration and are strongly affected by background matrix components (1).

During recent years, an intensive use of herbicides has raised increasing concern mainly because of their massive pollution of the environment. In particular, glyphosate (GS), clomazone (CLO), and paraquat (PQ) are among the most widely used broad-spectrum herbicides. They have very different mechanisms of action because of their differences in chemical structures: GS controls weeds by inhibiting the synthesis of aromatic amino acids necessary for protein formation in susceptible plants (6);

CLO inhibits synthesis of chlorophyll and carotenoids in sensitive plants, resulting in foliage devoid of pigmentation (7); and PQ inhibits photosynthesis by accepting electrons from photosystem I in light-exposed plants (8).

PQ is poisonous to humans and animals and is a well-characterized pneumotoxicant. It is also able to induce chromosomal aberrations and gene mutations in several living systems (12). CLO is relatively nontoxic to vertebrate animals, slightly toxic to fish, moderately toxic to water fleas, and highly toxic to some crustaceans (13). Recent studies reported that GS formulations induce apoptosis and necrosis in human umbilical, embryonic, and placental cells (14).

While CLO has moderate tendency to adsorb to soil particles, PQ and GS are strongly sorbed on a great variety of soils, where they are prone to biodegradation (9). The low mobility in soil indicates a minimal potential for the contamination of groundwater. However, the water-rinsed solutions produced during the formulation, dilution, mixing, transfer, and application of commercial herbicides may pollute the wastewater lines and may reach the sources of fresh water (10, 11).

To minimize the pollution of water lines containing the herbicides, technologies and management practices need to be developed. Thus, we investigate here the ability of thermal activated PS to degrade GS, PQ, and CLO in aqueous solutions. Because $\text{SO}_4^{\bullet-}$ radicals are the main oxidant species, their reactivity with the contaminants studied is the first parameter to be considered to minimize the pollution of water lines containing the herbicides; new technologies and management practices need to be developed.

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Thus, the bimolecular rate constant of the reaction between sulfate radicals and the herbicides GS and PQ were measured. The bimolecular rate constant of the reaction between sulfate radicals and CLO was reported in the literature (13).

The presence of dissolved organic matter (DOM) in natural waters may decrease the effectiveness of oxidants and may lead to the formation of inorganic and organic byproducts of health concern (15). To investigate their effect, degradation experiments of the insecticides in the presence of humic acid (HS), taken as models for DOM, were also performed.

MATERIALS AND METHODS

GS [*N*-(phosphonomethyl)glycine, monoisopropylamine salt solution (40 wt %) in H₂O from Aldrich], CLO [2-(2-chlorobenzyl)-4,4-dimethyl-1,2-oxazolidin-3-one from Clariant, Brazil], PQ (*N,N'*-dimethyl-4,4'-bipyridinium dichloride from Aldrich), potassium biphthalate (KHC₈H₅O₄, UCB), humic acid (Aldrich), Na₂S₂O₈ (Merck), Na₂CO₃, and NaHCO₃, (all J.T. Baker ACS) were used without further purification. Distilled water [$> 18 \text{ M}\Omega \text{ cm}$, < 20 parts per billion (ppb) of organic carbon] was obtained from a Millipore system.

The photochemical and thermal-activation experiments were performed with aqueous solutions of pH in the range of 4–5 (measured at 25 °C). According to the reported p*K*_a values of GS [0.78, 2.29, 5.96, and 10.98 (16)], the main GS species corresponds to the form with the first phosphonic and carboxylic groups ionized.

Flash-photolysis experiments were carried out with a conventional Xenon Co. model 720C equipment (Wilmington, MA) with modified optics and electronics (3). To avoid product accumulation, each solution was irradiated only once. Photolysis of S₂O₈²⁻ ($\lambda < 300 \text{ nm}$) was used as a clean source of SO₄^{•-} (3).

In the thermal-activation experiments, the temperature was controlled to ± 1 °C with a Vicking Masson D thermostat. Freshly prepared solutions of the reactants were separately heated for 15 min to the desired temperature and mixed in a 250 mL volume reactor immersed in the thermostat bath.

After the reactants were mixed, 5 mL sample aliquots were periodically collected from the reactor, cooled in an ice-bath, and thermostated to 25 °C before pH, high-performance liquid chromatography (HPLC), ultraviolet–visible (UV–vis) absorption, and total organic carbon (TOC) analysis.

GS and aminomethylphosphonic acid (AMPA) determinations were performed according to the United States Environmental Protection Agency (U.S. EPA) 547 method (derivatization, HPLC injection, and fluorescence detection). Detection limits were 2 and 3 μM , respectively.

CLO was analyzed by HPLC with a Hewlett-Packard HPLC model 1050 (Ti series) chromatograph with multiwavelength detection and a C18 Restek Pinacle II column (particle size, 5 μm ; 2.1 mm inner diameter \times 250 mm) and using a 65/35 methanol/water mixture as the eluent at 1 mL min⁻¹ constant flux. Detection limits were 0.1 mM for CLO.

TOC was measured with a Shimadzu TOC-5000A analyzer. Detection limits were 8×10^{-5} mol of C L⁻¹.

PQ was analyzed by its characteristic absorption band centered at 257 nm (10) with a Shimadzu UV-1800 spectrophotometer. The detection limit was 5 μM .

The chemical oxygen demand (COD) was determined with a Nanocolor COD 1500 test based on a silver-catalyzed oxidation with potassium dichromate/sulfuric acid at 148 °C for 2 h. The changes of absorbance quantified the concentration of Cr₂O₇²⁻ and Cr³⁺.

The average oxidation state (AOS) was calculated from TOC and COD values with eq 1

$$4(\text{TOC} - \text{COD})/\text{TOC} \quad (1)$$

where TOC and COD are expressed in moles of C per liter and moles of O₂ per liter, respectively. AOS takes values between +4 for CO₂, the most oxidized state of C, and -4 for CH₄, the most reduced state of C (17).

RESULTS AND DISCUSSION

Time-Resolved Photochemical Experiments. The reported bimolecular rate constant for the reaction of the SO₄^{•-} radical

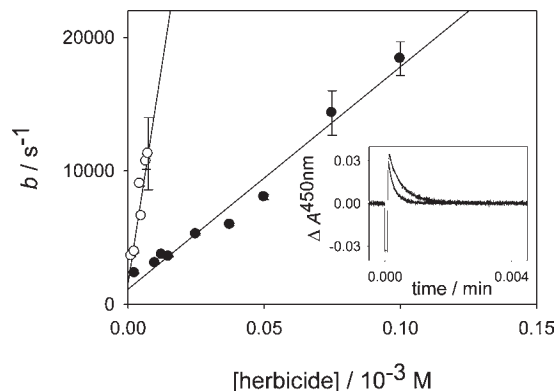


Figure 1. Plot of the pseudo-first-order rate constant b versus the molar concentration of GS (●) and PQ (○). (Inset) Sulfate radical decays obtained at 450 nm with 2.5×10^{-2} M PS, in the presence of 2.5×10^{-6} M (upper trace) and 2.5×10^{-5} M (lower trace) GS. Lines correspond to exponential fittings.

with CLO at 25 °C is $9.4 \pm 0.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (13), but there are no reported data for the rate constants of the reactions of the SO₄^{•-} radical with GS and PQ. To measure their values, flash-photolysis experiments were performed. For that purpose, sulfate radicals were generated by irradiation of PS solutions (2.5×10^{-2} M) containing the herbicides in the concentration range from 0 to 1×10^{-4} M.

Experiments showed absorption traces at $\lambda > 350 \text{ nm}$, whose spectrum immediately after the flash of light agreed with that of the SO₄^{•-} radical. The experimental absorption traces at a given observation wavelength, $A(\lambda)$, could be well-fitted according to eq 2, as shown in the inset of **Figure 1**.

$$A(\lambda) = a(\lambda)\exp(-bt) \quad (2)$$

The calculated constant b was independent of the detection wavelength and linearly dependent upon [herbicide] (**Figure 1**), as expected for the reaction of the SO₄^{•-} radical with PQ and GS. The slope of the straight line shown in **Figure 1** yielded the bimolecular rate constants $k(\text{PQ} + \text{SO}_4^{\bullet-}) = 1.2 \pm 0.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ($r^2 = 0.90$) and $k(\text{GS} + \text{SO}_4^{\bullet-}) = 1.6 \pm 0.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ($r^2 = 0.98$) at 25 °C. The error bars show the standard errors.

According to the reported p*K*_a values of GS [0.78, 2.29, 5.96, and 10.98 (16)], the rate constant obtained for GS at pH 4 corresponds to the form with the first phosphonic and carboxylic groups ionized.

The bimolecular rate constant determined in this work for the reaction of GS with SO₄^{•-} is lower than that reported for the reaction of GS with the less selective hydroxyl radicals [$2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (16)], as found for most substrates (18).

Thermally Activated Peroxydisulfate Experiments. All of the experiments were performed with solutions prepared with deionized water to evaluate the efficiency of thermally activated peroxydisulfate to degrade the herbicides in the absence of scavengers of the sulfate radicals. The composition of the specific matrix may affect the efficiency of this method.

Experiments performed at 80 °C with air-saturated solutions containing 0.1–1 mM GS and 1–5 mM Na₂S₂O₈ (PS) showed considerable GS degradation to carbon dioxide in less than 2 h. TOC time profiles could be well-fitted to a first-order law with apparent rate constants $k_{\text{app}}(\text{TOC})$. As shown in **Figure 2**, the degradation of GS only was observed in the presence of PS and both the rate of degradation and the grade of mineralization increased with the initial concentration of PS, [PS]₀. The rates of

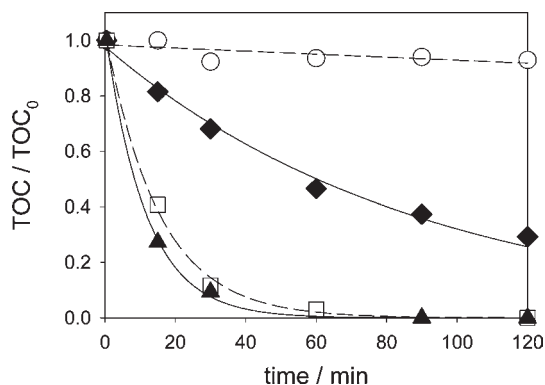


Figure 2. Time profiles of TOC/TOC₀ at 80 °C for solutions of [GS]₀ = 1 × 10^{−4} M without PS (○) and with [PS]₀ at 1 × 10^{−3} M (◆), 2 × 10^{−3} M (□), and 3 × 10^{−3} M (▲). Lines correspond to exponential fitting.

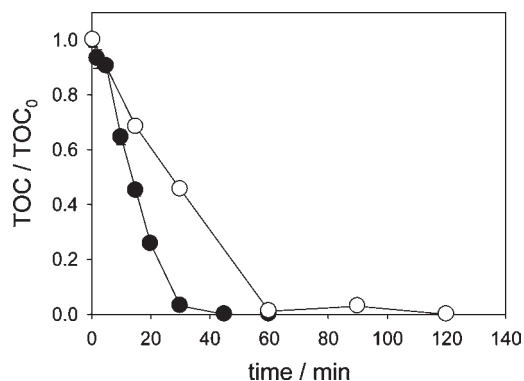


Figure 3. Time profiles of TOC/TOC₀ at 80 °C for O₂-saturated (●) and Ar-saturated (○) solutions of [GS]₀ = 1 × 10^{−4} M with [PS]₀ = 2 × 10^{−3} M.

TOC depletion appeared to be similar for [PS]₀ = 2 × 10^{−3} and 3 × 10^{−3} M. The value of [PS]₀ = 2 × 10^{−3} M was chosen as the [PS]₀ employed for most of the experiments performed in the present work.

The similar TOC degradation rates of GS solutions containing 2 × 10^{−3} and 3 × 10^{−3} M [PS]₀ could be explained by considering that, in the latter case, both the amount of sulfate radical formed and the rate of the reaction between the sulfate radical and the peroxydisulfate anion increase (4). As a result, the effective sulfate radical concentration that reacts with GS remains almost constant.

To determine the effect of molecular oxygen on the rate of TOC depletion, experiments with Ar- and O₂-saturated solutions were performed (see Figure 3). Although both systems reach complete mineralization, the presence of O₂ increased the rate of TOC depletion. Therefore, air-saturated solutions were used in the experiments.

The effect of the temperature on the rate of TOC depletion was studied in experiments with solutions containing 1 × 10^{−4} M [GS]₀ and 2 × 10^{−3} M [PS]₀ performed at 50, 60, 70, 75, and 80 °C (see Figure 4). The degradation rate of GS by activated PS was increased with an increasing temperature. Experiments at 50 and 60 °C showed no significant GS degradation after 2 h. Time profiles of TOC at 70, 75, and 80 °C could be well-fit with an exponential decay, as shown in Figure 4. The dependence of the apparent rate constant k_{app} upon the temperature (T) followed the Arrhenius equation (eq 3), as shown in the inset of Figure 4

$$\ln(k_{app}) = \ln(A) - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (3)$$

where A was the pre-exponential factor, R was the ideal gas constant, and E_a was the activation energy.

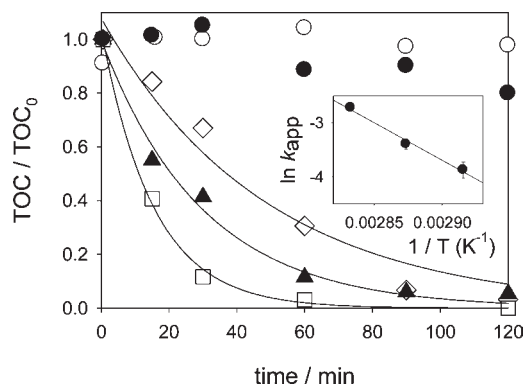


Figure 4. Time profiles of TOC/TOC₀ at 50 °C (○), 60 °C (●), 70 °C (◇), 75 °C (▲), and 80 °C (□), for solutions of [GS]₀ = 1 × 10^{−4} M with [PS]₀ = 2 × 10^{−3} M. Solid lines correspond to exponential fitting. (Inset) Plot of ln(k_{app}) versus T^{-1} for TOC profiles of the main figure at 70, 75, and 80 °C.

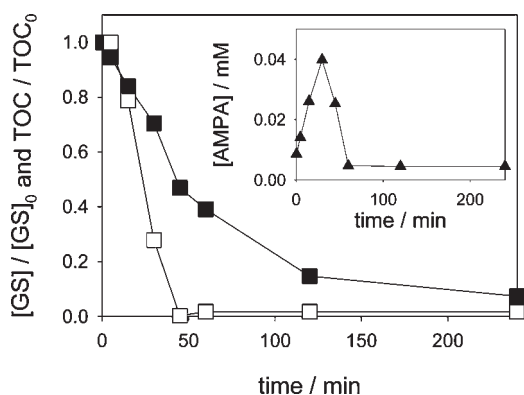


Figure 5. Time profiles of [GS]/[GS]₀ (□) and TOC/TOC₀ (■) at 80 °C for solutions of [GS]₀ = 1.7 × 10^{−4} M with [PS]₀ 2 × 10^{−3} M. (Inset) Evolution of the concentration of AMPA.

The slope of the Arrhenius plot for the range of 70–80 °C yielded $E_a = 116 \pm 6 \text{ kJ mol}^{-1}$ ($r^2 = 0.99$). This parameter corresponds to the overall reaction because k_{app} was a measure of TOC depletion. This value is in agreement with the value reported for the degradation of trichloroacetic acid with thermally activated peroxydisulfate (4). The observed activation energy is in the range reported for the thermal homolysis of PS, and as also concluded in ref 4, such an activation energy may be explained by a radical mechanism involving sulfate radicals. Any elemental thermal reaction between the herbicides and PS is expected to be of lesser significance.

Most experiments were performed at 80 °C to achieve measurable reactant consumption in a few hours of reaction time.

Experiments performed at 80 °C with air-saturated solutions containing 1.7 × 10^{−4} M GS and 2 × 10^{−3} M PS showed a significant degradation of GS, as shown in Figure 5. Although the concentration of GS was below the chromatographic detection limit already after 45 min of treatment, the complete mineralization of the mixture takes much longer (about 4 h). The formation and further degradation of AMPA was observed in HPLC chromatograms. This compound is the main oxidation product from GS and is more toxic than the herbicide (11). The contribution of GS and AMPA to the TOC is not enough to explain the experimental TOC values; therefore, other undetected intermediates that are degradable at longer reaction times were likely present in the reaction mixture. Reported products for the degradation of GS by the electro-Fenton-like process with Mn²⁺ as the catalyst include AMPA, glycolic, glyoxylic, formic, and oxalic

acids (16). In fact, these low-molecular-weight carboxylic acids are reported to efficiently react with $\text{SO}_4^{\bullet-}$ radicals (19).

A similar behavior was observed for experiments at 80 °C with 2×10^{-3} M PS and 1×10^{-4} M PQ or 1×10^{-4} M CLO. As shown in **Figure 6**, the concentrations of the herbicides rapidly reached values below the detection limits and the mineralization of the mixture took about 3 h. These observations indicate the formation of organic intermediates that required longer times to be oxidized by the $\text{SO}_4^{\bullet-}$ radical.

Photochemical experiments for the degradation of CLO with $\text{SO}_4^{\bullet-}$ radicals (at 25 °C) lead to the formation of 2-chlorobenzylalcohol and 2-chlorobenzaldehyde as reaction products. Under these conditions, the rate of CLO degradation was also found to be faster than that of TOC depletion (13).

As far as we know, the reaction of PQ with the sulfate radicals was not previously investigated. Photocatalytic degradation of this herbicide with UV light over titanium oxide at high pH values was found to occur in about 1 or 2 h of reaction (depending upon the experimental conditions), but the intermediate products (monoquat, monopyridone, picolinic acid, and succinic acid) stayed in the mixture for 3 h (10).

TOC profiles for experiments at 80 °C with $[\text{PS}] = 2 \times 10^{-3}$ M and the three herbicides in experiments performed with the same initial value of TOC are similar. Because of the relevance of humic substances in environmental studies and the known reactivity of $\text{SO}_4^{\bullet-}$ with them (20, 21), comparative experiments with an Aldrich humic acid (AHA) solution and with a mixture of GS and AHA (with similar TOC_0 values) were performed. The concentration of AHA used in these experiments corresponded to an amount of moles of C per liter similar to those found in underground, marine, and river waters, i.e., $8\text{--}200 \times 10^{-5}$ mol of C L^{-1} (22). The behavior observed for both experiments was coincident with those with the herbicides. The plot of the amount of carbon

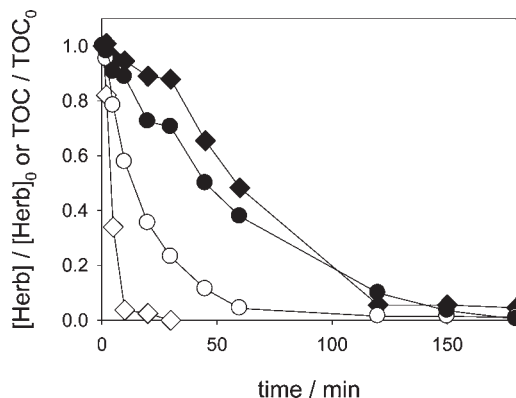


Figure 6. Time profiles of $[\text{PQ}]/[\text{PQ}]_0$ (\circ) and TOC/TOC_0 (\bullet) for solutions of $[\text{PQ}]_0 = 1 \times 10^{-4}$ M with $[\text{PS}]_0 = 2 \times 10^{-3}$ M and $[\text{CLO}]/[\text{CLO}]_0$ (\diamond) and TOC/TOC_0 (\blacklozenge) for solutions of $[\text{CLO}]_0 = 1 \times 10^{-4}$ M with $[\text{PS}]_0 = 2 \times 10^{-3}$ M.

Table 1. Correlation between TOC Mineralized and Amount of $\text{SO}_4^{\bullet-}$ Released from the Activation of PS at 80 °C Corresponding to Solutions of $[\text{PS}]_0 = 2 \times 10^{-3}$ M and Herbicides^a

	TOC_0 (10^{-3} mol of C L^{-1})	a (mol of C L^{-1})	b (mol of C/mol of $\text{SO}_4^{\bullet-}$)	r^2
$[\text{GS}]_0 = 2 \times 10^{-4}$ M	1.01	$3 \pm 3 \times 10^{-5}$	0.50 ± 0.04	0.96
$[\text{CLO}]_0 = 1 \times 10^{-4}$ M	0.91	$-6 \pm 3 \times 10^{-5}$	0.46 ± 0.05	0.93
$[\text{PQ}]_0 = 1 \times 10^{-4}$ M	0.97	$1 \pm 14 \times 10^{-5}$	0.56 ± 0.03	0.99
$[\text{AHA}]_0 = 8.50 \times 10^{-6}$ M ^b	1.25	$4 \pm 3 \times 10^{-5}$	0.49 ± 0.03	0.99
$[\text{GS}]_0 = 1 \times 10^{-4}$ M and $[\text{AHA}]_0 = 4.25 \times 10^{-6}$ M ^b	1.07	$-8 \pm 4 \times 10^{-5}$	0.60 ± 0.1	0.87
mean value \pm standard error		$2 \pm 2 \times 10^{-5}$	0.52 ± 0.03	0.96 ± 0.02

^a The TOC values were fitted to the following equation: $(\text{TOC}_0 - \text{TOC}) = a + b \times n(\text{SO}_4^{\bullet-})$, where $n(\text{SO}_4^{\bullet-})$ is the number of moles of the $\text{SO}_4^{\bullet-}$ radical released per liter (see the text). ^b Calculated taking the molecular weight of AHA = 4700 g/mol (20).

mineralized ($\text{TOC}_0 - \text{TOC}$) against the amount of $\text{SO}_4^{\bullet-}$ radical released from the thermal activation of PS, as calculated from the rate constant reported for 80 °C (4), yielded a linear correlation for all of the experiments, as shown in **Table 1**. The global linear correlation ($r^2 = 0.96$), with a slope of 0.52 ± 0.03 mol of C mol^{-1} of $\text{SO}_4^{\bullet-}$ means that, for the mineralization of 1 mol of C, 2 mol of $\text{SO}_4^{\bullet-}$ is required. This behavior indicates that the mineralization of all of the samples is limited by the production of $\text{SO}_4^{\bullet-}$ radicals from thermal decomposition of PS and is independent of the chemical nature of the substrate.

However, the initial slope is different for each compound or mixture. To obtain more information, the initial AOS was determined for each compound or mixture by combining TOC and DQO values. A linear correlation between the reciprocal value of the average initial slope (initial amount of $\text{SO}_4^{\bullet-}$ needed per mole of C) and AOS was found (see **Figure 7**). Because the sulfate radical is a one-electron oxidant, 1 mol of the $\text{SO}_4^{\bullet-}$ radical is needed to change in 1 unit the oxidation state of 1 mol of C. Thus, the expected slope of the plot shown in **Figure 7** is -1 (see dashed line in **Figure 7**). As shown in **Figure 7**, the experimental trend is not coincident with the predicted line, which indicates that the oxidation is more efficient, possibly because of the presence of molecular oxygen and chain reactions.

All of the data shown in **Figure 7** were obtained from experiments performed at 80 °C with the same initial concentration of PS and initial TOC values. On the other hand, for experiments performed with GS at 80 °C on the whole range of PS and GS initial concentrations, the plot of TOC consumed versus $\text{SO}_4^{\bullet-}$ radicals released shows a quite good correlation, as shown in **Figure 8**. The slope of the plot is 0.56 ± 0.02 mol of C/mol of $\text{SO}_4^{\bullet-}$, very similar to the value obtained in **Table 1**.

The thermal activation of PS at 80 °C is a convenient method for the degradation of the three herbicides: GS, CLO, and PQ.

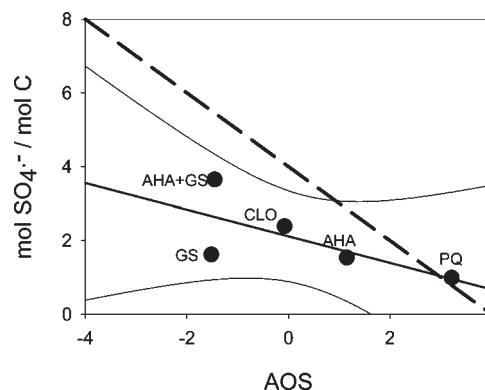


Figure 7. Initial amount of $\text{SO}_4^{\bullet-}$ needed for 1 mol of C versus the AOS. The solid lines correspond to the lineal correlation and confidence intervals (95%). The dashed line corresponds to the estimated amount of the $\text{SO}_4^{\bullet-}$ radical needed to change in 1 unit the oxidation state of 1 mol of C.

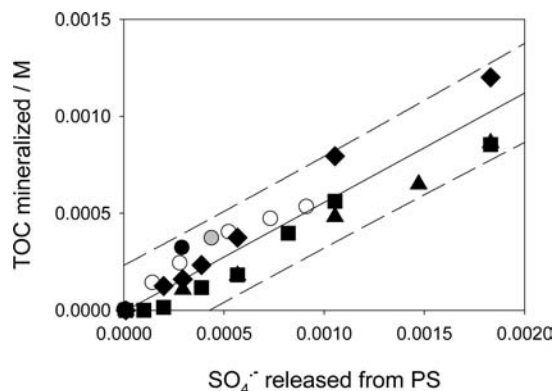


Figure 8. TOC mineralized versus the amount of $\text{SO}_4^{\bullet-}$ released from the activation of PS at 80 °C. Black symbols correspond to $[\text{PS}]_0 = 2 \times 10^{-3}$ M and $[\text{GS}]_0 = 1 \times 10^{-4}$ M (●), 2×10^{-4} M (■), 5×10^{-4} M (◆), and 1×10^{-3} M (▲). Circles correspond to $[\text{GS}]_0 = 1 \times 10^{-4}$ M and $[\text{PS}]_0 = 1 \times 10^{-3}$ (○), 2×10^{-3} (●), and 3×10^{-3} (gray circle). The solid line is the linear regression for all of the data, and the dashed lines show the 95% prediction intervals.

Although the herbicide degradation was observed to take place in less than 1 h, the complete mineralization of the organic carbon required longer reaction times, ca. 3 h.

The temperature required for this method (80 °C) can be considered moderate for a thermal treatment, and sodium peroxydisulfate is an unexpensive and stable solid, which can be easily handled. Thus, this method seems to be appropriate to clean the equipment employed for the application of the commercial herbicide.

ABBREVIATIONS USED

AHA, Aldrich humic acid; AMPA, aminomethylphosphonic acid; CLO, clomazone; GS, glyphosate; PQ, paraquat; PS, sodium peroxydisulfate.

ACKNOWLEDGMENT

M.C.G. and J.A.R. are research members of CONICET, Argentina. D.O.M. is a research member of CICPBA, Argentina. The authors thank Prof. Dr. André M. Braun for the donation of part of the analytical equipment used in this work.

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Received for review August 5, 2010. Revised manuscript received November 5, 2010. Accepted November 9, 2010. This work has been supported by Grants PICT 2007 00308 and PICT 2006 00876 from ANPCyT, Argentina. E.M.D.K. thanks Red de Macrouiversidades de America Latina y el Caribe for a graduate studentship.