Effects of montmorillonite on the chemical degradation kinetics of metsulfuron methyl in aqueous media

Maximiliano Brigante [a,*], Graciela Zanini [a,b], Marcelo Avena [a,b]

[a] INQUISUR-CONICET, Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina
[b] Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina

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ABSTRACT

The degradation kinetics of the sulfonylurea herbicide metsulfuron methyl (MM) has been studied in batch experiments by UV–VIS spectroscopy, and the effects of pH and the presence of a clay mineral (Na-montmorillonite) are reported. The proposed UV–VIS method gives kinetic results that are comparable to those obtained with chromatographic methods. In aqueous solutions, the chemical degradation of MM is undetectable at pH 6.5–9.5, but increases about 500 times by decreasing the pH from 6 to 2, and 300 times by increasing pH from 9.5 to 11.5. For example, the half-life of MM is shorter than 1 d at pH 2 and 11.5, but longer than a year at pH 6. Na-montmorillonite has an inhibitory effect on MM degradation. A combination of adsorption–desorption studies and degradation kinetic measurements demonstrates that in the presence of Na-montmorillonite only MM that remains in solution is subject to degradation; adsorbed MM is protected by the clay from being degraded. However, since adsorption only occurs at low pH (around 3) it can be envisaged that montmorillonite and supposedly other phyllosilicate clays do not affect significantly the chemical degradation rate of MM in soils and other natural systems.

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1. Introduction

Metsulfuron methyl (MM) is a sulfonylurea herbicide that can control an ample spectrum of weeds (Fletcher et al., 2003; Zhu et al., 2002). MM and other sulfonylurea herbicides have widespread use in farms around the world (Nyström et al., 1999; Ukrainczyk and Ajwa, 1996; Walker and Jurado-Exposito, 1998), and they are also widely used in the Pampean Region of Argentina, (Bazzigalupi and Cepeda, 2005; Bedmar et al., 2006; Castro et al., 2002). MM seems to be rather mobile in natural media (Zanini et al., 2009), raising concerns about contamination of surface water and groundwater.

Degradation is a very important process influencing the transport and fate of herbicides in nature (Bosten and van der Linden, 1991). It is known that MM is degraded in soils, and half-lives ranging from 38 to 84 d have been reported (Zanini et al., 2009). MM, like other sulfonylureas, degrades by chemical and microbial processes. In soil systems, chemical degradation appears to be a major factor at pH < 6, whereas at pH > 6 microbial degradation prevails (Sarmah and Sabadie, 2002). This is the case for the top centimeters of soils, where microorganisms are mainly located. However, since MM and other sulfonylureas are rather mobile, they may easily reach underlying sediments, where the microbial population is low, and where chemical processes can take

control of the herbicide degradation under all conditions. Chemical degradation of herbicides occurs through reactions such as photolysis, hydrolysis, oxidation and reduction (Caselli, 2005; Saha and Kulshrestha, 2002; Sarmah and Sabadie, 2002). The extent of degradation ranges from formation of metabolites to decomposition in inorganic products (Andreu and Picó, 2004; Sparks, 2003).

The chemical degradation of MM in aqueous solutions is rather well known (Sabadie, 1990; Sarmah and Sabadie, 2002) and involves three main pathways (Fig. 1). The first one is the cleavage (hydrolysis) of the sulfonylurea bridge, and was usually suggested as a main degradation mechanism under acidic conditions (Beyer et al., 1988). The second one is the O-demethylation of the methoxy-triazine moiety, as suggested by Pons and Barriuso (1998), followed by further hydrolysis of the product. The third degradation pathway, triazine ring opening (hydrolytic cleavage of the triazine ring), was evidenced by Li et al. (1999). The ring opening can also take place after O-demethylation in alkaline conditions (Sarmah et al., 2000). The rate of chemical degradation of MM in aqueous solutions strongly depends on pH, being relatively low around neutral pH and relatively high in acid and alkaline media (Sarmah and Sabadie, 2002).

Chemical degradation of sulfonylureas in the presence of various soil minerals was also investigated (Berger and Wolfe, 1996; Sabadie, 1990). Several studies were performed on dry minerals (Sabadie, 1997; Sabadie and Bastide, 1990; Sarmah and Sabadie, 2002), including silica, alumina, kaolinite, bentonite and montmorillonite, and the degradation pathways were found to be similar to those previously proposed for chemical degradation in solution. Some minerals resulted to be more

* Corresponding author at: Maximiliano Brigante, INQUISUR-CONICET, Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina. Tel.: +54 291 4595101x3593.
E-mail address: brigante@uns.edu.ar (M. Brigante).
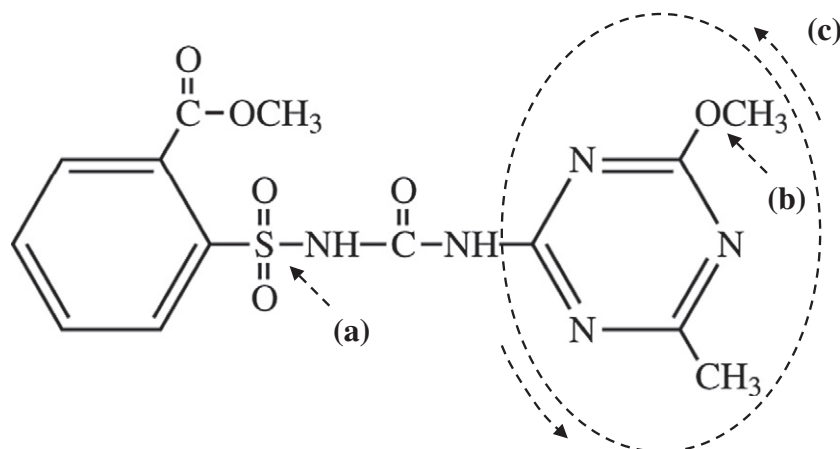
Fig. 1. Fully-protonated structure of MM. The arrows show the three possible metabolic pathways: (a) hydrolysis of sulfonylurea bridge; (b) O-demethylation; and (c) triazine ring opening.

active than others in the degradation of the herbicides. Minerals and other soil components may contribute to catalyze the chemical degradation of adsorbed herbicides, as it occurs with the degradation of chlorimuron on a sterile Canadian soil (Gaynor et al., 1997) and azimsulfuron on Fe(III) oxide and an Fe(III)-exchanged montmorillonite (Pinna et al., 2004). A catalytic effect will decrease the persistence of MM in nature and may lead to an undesired low herbicide activity. On the contrary, it is also possible that soil components may protect the herbicide and deactivate its degradation by adsorption on mineral surfaces. This protection will increase the persistence of MM in soils and may contribute to phytotoxicity effects (Bedmar et al., 2006; Wang et al., 2010) or to an undesired herbicide dissemination in natural waters. In the case of MM, it was reported by Sabadie (1990) that the presence of silica and specially montmorillonite produces a decrease in the hydrolysis rate of the herbicide as compared to the rate in solution, apparently due to adsorption on the solid surface. Although this explanation sounds reasonable, the author did not perform adsorption studies to corroborate that hypothesis, and thus the subject is still a matter of debate. All these findings show that a mineral surface can have a significant effect on MM and other sulfonylurea degradation, and that an important research effort is still necessary to gain a clearer understanding of the behavior of sulfonylurea herbicides in soil systems and sediments.

Reports about the degradation of sulfonylureas have involved several analytical methodologies such as chromatographic analyses (Bossi et al., 1999; Sarmah et al., 2000), bioassays (Ye et al., 2003), and enzyme-linked immunosorbent assays, ELISA (Knopp et al., 1999). Almost all these techniques are relevant to identify the degradation metabolites and to suggest a reaction mechanism, although they are sometimes rather complex and expensive, and require long times for analysis. In some cases, when the reaction pathways are rather well know and essentially reaction rates need to be measured, it is useful to apply simpler techniques, such as UV–VIS spectroscopy. This spectroscopic methodology has been continuously and successfully used in kinetic studies of several processes involving herbicides, such as adsorption–desorption on soil minerals, dissolution of humic acids in the presence of herbicides and herbicide degradation (Alves et al., 2012; Brigante et al., 2009; Fontecha-Camará et al., 2008).

The aim of this article is to present a study of the degradation kinetics of MM in aqueous solutions performed by UV–VIS spectroscopy. The data obtained at a variety of pH and in the absence and presence of varying concentrations of a sodium-exchanged montmorillonite are presented. The results provide relevant information about the effects of MM adsorption on the degradation rate. The originality of this work is also related to the use of UV–VIS spectroscopy

for evaluating and quantifying the amount of MM degraded as a function of time, which is a versatile, simple and fast method with a lower cost of analysis than chromatographic methods.

2. Materials and methods

2.1. Materials

The montmorillonite used in this study was obtained from a deposit in Cerro Banderita (province of Neuquén, Argentinean Patagonia). A general characterization of the sample was performed by Peinemann et al. (1972). The chemical formula of the solid is $M_{0.7}[Si_{7.94}Al_{0.06}]^{VI}(Al_{2.78}Fe_{0.40}Mn_{0.18}Mg_{0.64})^{IV}O_{20}(OH)_4$ where M is the monovalent exchangeable cation. This formula leads to a theoretical cation exchange capacity of 91.7 mEq·100 g^{-1} (91.7 cmol kg^{-1} in SI units), which is normal for montmorillonites and is the result of the negative structural charge located preferentially in the octahedral layer (Peinemann et al., 1972). Acid–base potentiometric titrations and electrokinetic measurements that corroborate the presence of these negative charges in the sample were reported by Avena and De Pauli (1998). Particles with a diameter of <2 μm were obtained by sedimentation and saturated with Na^+ by washing (successive centrifugal treatments) with 1 M NaCl solution in order to obtain a sodium-exchanged montmorillonite (Na-montmorillonite). The dispersion was then washed several times with doubly-distilled water to remove acidic and basic impurities until the conductivity of the supernatant was lower than 10 μScm^{-1}. Na-montmorillonite was then freeze-dried in order to obtain a dry powder. Its total surface area was 974.7 $m^2\ g^{-1}$ as determined by the methylene blue method (Yukselen and Kaya, 2008) and its external surface area was 6.7 $m^2\ g^{-1}$ as determined from BET-N_2 adsorption isotherms at 77 K using a Quantachrome NOVA 1200e surface area analyzer. The basal spacing of the solid was 12.6 Å, as determined by X-ray diffraction with a RIGAKU Geigerflex X-ray diffractometer.

An analytical standard grade MM (purity 99.3%, CAS number 74223-64-6) Riedel-de Haën, Sigma-Aldrich, was used in the experiments. All other chemicals were analytical grade.

2.2. MM degradation kinetics in solution

Since MM and its degradation products have different UV–VIS spectra, the degradation kinetics can be monitored by analyzing the spectral changes during the reaction. Degradation kinetics of MM in aqueous solution and in the absence of Na-montmorillonite was performed in batch experiments, using 50 mL polypropylene centrifuge tubes covered with polypropylene caps. 20 mL of a stock MM

solution (38.3 μM) was introduced in each centrifuge tube and mixed with a NaCl solution, which was used as supporting electrolyte. The total volume was 35 mL and the resulting concentrations of NaCl and MM were 0.01 M and 21.9 μM respectively. The pH of the solutions was then adjusted to the desired value in the ranges 2−11.5 by adding HCl or NaOH. The tubes were shaken with an end-over-end rotator (FAES, Argentina) and the pH was checked periodically and kept constant by adding small volumes (a few microliters) of HCl or NaOH solutions when necessary. At different reaction times, an aliquot of the solution was withdrawn and its UV–VIS spectrum was obtained. After registration of the spectrum, that took around 30 s, the solution was reintroduced into the tube. This procedure was repeated during several hours or even days in order to achieve a complete degradation of the herbicide or to gather enough data points. Normally, aqueous buffers (e.g. borate, phosphate, acetate, etc.) are employed to investigate the effect of pH on the herbicide degradation and its adsorption on several soils and soil minerals. However, it is also known that these molecules compete with the herbicide for adsorption on active sites (Wei et al., 2009; Zogorski and Faust, 1976). Moreover, Salvestrini et al. (2002) reported that phosphate buffer acts as efficient catalyst in the chemical degradation of the phenylurea herbicide diuron. Therefore, and taking into account these observations, we discarded the utilization of buffers in all (degradation and adsorption) experiments.

Spectra were obtained with an Agilent 8453 UV–VIS diode array spectrophotometer equipped with a Hellma 1 cm quartz cell. Linearity of the Absorbance vs. MM concentration curves (A vs. C_{MM}) was checked at different wavelengths and at all the investigated pH values using fresh MM solutions with a C_{MM} that ranged between 2 and 50 μM, although lower concentration can be also detected, e.g., up to 0.5 μM (76 ppb). This sensitivity is quite close to that of chromatographic methods for evaluating several sulfonylurea herbicides (10−50 ppb) including MM (Bossi et al., 1999). Good linearity was found in all cases ($r^2 > 0.998$). In all experiments, the pH was measured with a Crison GLP 22 pH meter and a Crison 52-02 combined pH electrode. The working temperature was 24 ± 2 °C.

2.3. MM degradation kinetics in the presence of Na-montmorillonite

Degradation kinetics of MM in the presence of Na-montmorillonite was performed in a way that was similar to that described above. Different volumes of a stock montmorillonite dispersion (18.9 g L^{-1}) were added to the centrifuge tubes in order to investigate the effects of montmorillonite concentration. The final volume, MM concentration and supporting electrolyte were always 35 mL, 21.9 μM and 0.01 M NaCl respectively. The range of montmorillonite concentration was 0−8.1 g L^{-1}. At different reaction times, an aliquot of the dispersion was withdrawn, the particles were separated from the supernatant by centrifugation at 5000 rpm (523.6 rad s^{-1} in SI units) during 20 min and the spectrum of the supernatant was immediately recorded. After this, the particles and the supernatant were reintroduced into the tube to maintain the same solid-to-solution ratio during the whole kinetic run.

2.4. MM adsorption kinetics

Adsorption kinetic experiments were carried out in order to establish the pH conditions where MM adsorption takes place. A cylindrical, water-jacketed reaction vessel covered with a glass cap was used in this case. Mixing was done by a magnetic stirrer, and the reaction temperature was maintained at 25 ± 0.2 °C by circulating water through the jacket with a FAC (Argentina) water bath/circulator. Before starting an adsorption kinetic experiment, a stock Na-montmorillonite dispersion (18.9 g L^{-1}) was prepared by adding the solid to a 0.01 M NaCl solution. The pH of the resulting dispersion was then adjusted to the desired value (either pH 3, 4.5 or 6) by adding HCl or NaOH solutions. At the

same time, 60 mL of a 0.01 M NaCl solution containing a known concentration of MM was placed in the reaction vessel, and the stirring (450 rpm or 47.1 rad s^{-1}) and water circulation were switched on. Once the temperature reached 25 ± 0.2 °C, the pH of the NaCl/MM solution was adjusted to the same pH value of the stock montmorillonite dispersion. The adsorption experiment was started by adding 10 mL of the stock dispersion to the NaCl/MM solution in the reaction vessel. This time was set as the initial time of the adsorption reaction. The total volume was 70 mL and the initial concentrations of montmorillonite and MM into the reaction vessel were 2.7 g L^{-1} and 21.9 μM respectively. At different reaction times, a 5 mL aliquot was withdrawn, centrifuged at 5000 rpm (523.6 rad s^{-1}) during 5 min and the supernatant was used for MM analysis. The reaction was followed for 180 min and the pH was continuously checked and kept constant with NaOH or HCl solutions. MM concentration was measured by UV–VIS, using the A vs. C_{MM} calibration curves described above. Adsorbed MM was calculated from the difference between the initial MM concentration and the concentration of the herbicide that remained in the supernatant solution.

A complementary adsorption–desorption kinetic experiment was performed by adsorbing MM at pH 3 followed by desorption at pH 6. The adsorption at pH 3 was carried out as described above, but after 25 min of adsorption, the pH of the dispersion was increased to 6 to promote desorption.

Adsorption–desorption times were much shorter than degradation times, thus degradation was negligible during all these adsorption–desorption experiments.

3. Results and discussions

3.1. Degradation kinetics of MM in solution

Fig. 2 shows the UV–VIS absorption spectra of a 45 μM MM solution at different pH values (pH ranges 2 to 11). All the spectra were recorded immediately after preparation of the MM solutions, thus they reflect the effects of pH on the UV–VIS behavior of pure MM, without degradation products. The spectrum at pH 11 shows an absorption maximum at 233 nm, a shoulder at 245 nm and a weak shoulder at 275 nm. Rafqah et al. (2004) assigned the maximum to a π → π* transition and the weak shoulder to a n → π* transition. The spectrum of MM gradually changes by decreasing the pH, and at pH 2 the absorption maximum appears at 225 nm. The observed spectral changes are the result of an acid–base equilibrium, since MM is a weak acid with $pK_a = 3.3$. The protonated molecule (Fig. 1) is uncharged and predominates at pH < 3.3; the deprotonation of the nitrogen atom of the −SO$_2$NHCO− group results in a negatively charged species that predominates at
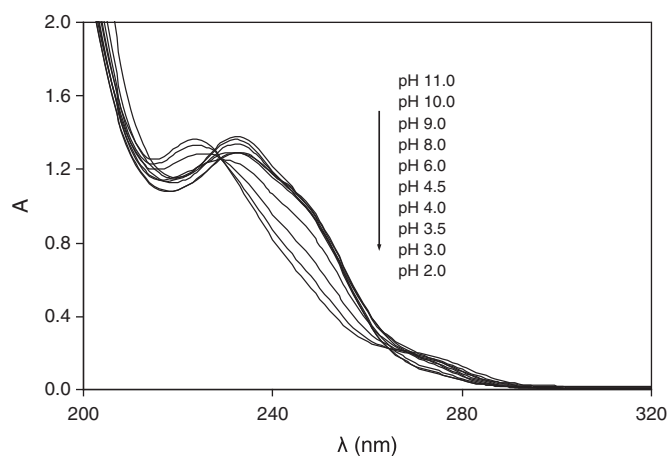
Fig. 2. UV–VIS absorption spectra of MM as a function of pH. Initial MM concentration: 45 μM.

pH > 3.3. Spectral changes due to acid–base equilibria are normally found with sulfonylureas (Vulliet et al., 2004).

Fig. 3 shows the changes in the UV–VIS spectra during typical degradation kinetic experiments of MM solutions at different pH values. At pH 6.5 (Fig. 3a) there are no significant changes in the spectra, showing that MM is stable at this pH during the investigated time (575 h). A very similar behavior, with no detectable degradation within 575 h, was observed at neutral and slightly alkaline pH (pH 7–9.5, data not shown). On the contrary, at pH 4.5 (Fig. 3b) there are significant changes in the spectra as the reaction time increases, showing that MM degrades at this pH. A rather well-defined isosbestic point is observed at 223 nm. The presence of this isosbestic point indicates that the stoichiometry of the degradation reaction remains unchanged and that no secondary reactions occur at a significant extent during the considered interval of time (McNaught and Wilkinson, 1997). A similar behavior, with spectral changes during reaction and the presence of isosbestic points (at 233 and 258 nm in this case), can be also observed at pH 10.5 (Fig. 3d). A more complicated behavior is observed at pH 3 (Fig. 3c) or lower. Although spectral changes are observed during reaction, no well-defined isosbestic points appear. At short reaction times (between 0 and 24 h), there is a decrease in the absorbance at all wavelengths as time increases. At intermediate times (between 24 and 55 h) a shoulder appears at 217 nm, shoulder that gradually decreases in intensity until a constant spectrum is observed after 200 h of reaction. The absence of well defined isosbestic points and the appearance of the mentioned shoulder suggest that a reaction intermediate is formed, having an UV–VIS absorption maximum at around 217 nm.

The behavior shown in Fig. 3 indicates that degradation of MM takes place at low and high pH and that no degradation is detected at intermediate pH. The results are consistent with those published by different authors (Hemmanada et al, 1994; Sarmah et al., 2000) for the degradation of MM as studied with chromatographic methods, and they are also similar to those reported for the degradation of other sulfonylureas (Braschi et al., 1997; Sarmah et al., 2000). According to the literature, the reaction products of MM are different in alkaline and acid media, which explains the spectral differences for experiments performed at different pH. Sarmah et al. (2000), for example, reported the formation

of 2-[(N-acetylcarbamoyl) carbamoylcarbamoylsulfamoyl] benzoic acid as the final product in alkaline degradation due to the O-demethylation of the methoxy-triazine moiety of MM followed by the triazine ring opening. At acid pH, on the contrary, 2-(aminosulfonyl)benzoate (a sulphonamide), 4-methoxy-6-methyl-2-amino-1,3,5-triazine, and carbon dioxide were reported as degradation products due to the hydrolysis of the sulfonylurea bridge (Beyer et al., 1988). Sabadie (1990) also reported the formation of 2-(4-hydroxy-6-methyl-1,3,5-triazin-2-ilcarbamoylsulfamoyl)benzoic acid by an alternative mechanism at acid pH.

It is clear that the UV–VIS technique used in this work cannot identify MM degradation products or intermediates, which are rather well known as discussed above. This simple and low-cost technique, however, is rather sensitive to MM degradation and is able to quantify its degradation kinetics. This kinetics can be evaluated by plotting C_{MM} as a function of the degradation time, t. C_{MM} was calculated as:

$$C_{MM} = C_i \left[\frac{A - A_f}{(A_i - A_f)} \right], \tag{1}$$

where C_i is the initial concentration of MM, A is the absorbance at time t, A_i is the initial absorbance at the working wavelength and A_f is the final absorbance, which corresponds to complete degradation. Complete degradation was observed in experiments at extreme pH values (2, 2.5 and 11.5), thus A_f could be well determined under these conditions. At less extreme pH, where the degradation was not complete in the studied time interval, A_f was obtained by degrading completely MM at either pH 2 or 11.5 and then changing the pH of the resulting solution to the pH value at which degradation was studied. The working wavelength for experiments performed at pH 10.5 and 11.5 was 245 nm, for experiments performed at 3.5–6.5 was 233 nm, and for experiments performed at 3, 2.5 and 2 was 240 nm. These wavelengths correspond to the UV–VIS region where the difference between A_i and A_f was the maximum at the working pH (lowest error in the value of calculated C_{MM}).

Fig. 4a shows the effect of pH on the degradation curves (C_{MM} vs. t curves) of MM. The degradation kinetics changes markedly with
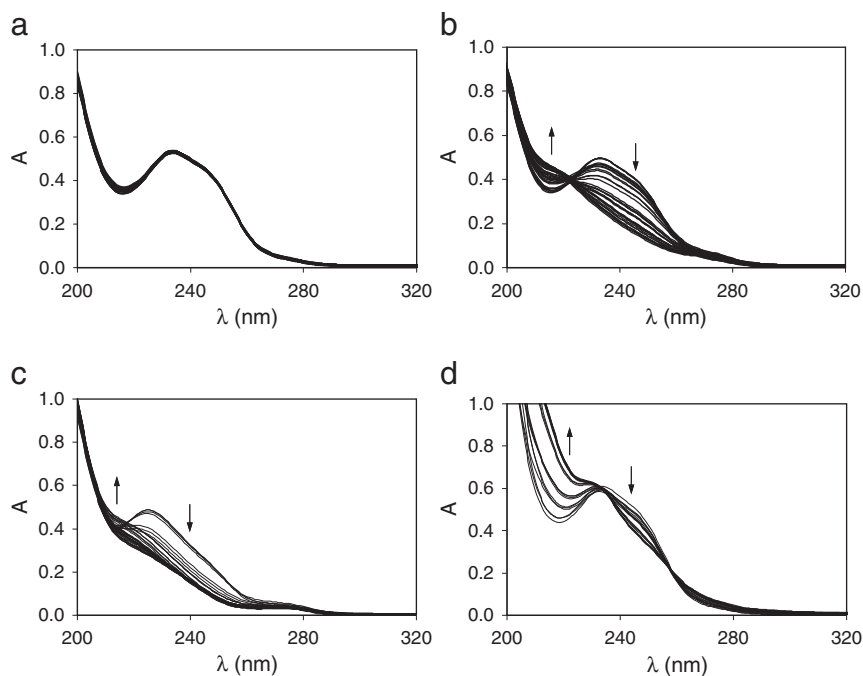

Fig. 3. UV–VIS spectra of 21.9 μM MM solutions at different degradation times and 25 °C. (a) pH 6.5; (b) pH 4.5; (c) pH 3; and (d) pH 10.5. The arrows indicate the direction of increasing time.

pH. It is relatively fast at pH 2, where only 24 h was necessary to degrade 80% of the initial MM and around 150 h to achieve complete degradation. The reaction becomes slower as the pH increases from 2 to 6.5. In fact, only 3%−4% of degradation could be achieved at pH 6 after 575 h. The rate increases again at high pH and almost complete degradation is achieved after 150 h at pH 11.5.

C_{MM} vs. t curves were analyzed in terms of a first-order kinetics:

$$R = -\frac{dC_{MM}}{dt} = kC_{MM} \tag{2}$$

$$\ln\left(\frac{C_{MM}}{C_i}\right) = -kt \tag{3}$$

$$t_{1/2} = \frac{-\ln(0.5)}{k} \tag{4}$$

where R is the degradation rate, k is the pseudo-first-order rate constant and $t_{1/2}$ is the half-life coefficient. A first-order kinetics has been commonly used to describe the degradation of several sulfonylureas (Brigante et al., 2005; Cambon et al., 1998). The obtained values of k and $t_{1/2}$ are listed in Table 1 and the effects of pH on k are plotted in Fig. 4b. The degradation is fast at low and high pH, but rather slow between pH 5 and 9.5. For example, the half-life of MM is shorter than 1 d at pH 2 and 11.5, but longer than a year at pH 6.

k vs. pH curves with shapes very similar to that shown in Fig. 4b were also reported by Sarmah et al. (2000), who developed a model to describe the pH-dependent degradation rate of several sulfonylureas. According to these authors, the first and rate determining step in the degradation process involves the cleavage of the sulfonylurea linkage via attack by water in acid or near neutral media, or by hydroxyl ions at higher pH. On the basis of this, the proposed model assumes that over the whole pH range the observed rate of sulfonylurea degradation is the sum of the following three simultaneous reactions: (a) hydrolysis of the protonated sulfonylurea molecule by water at low pH; (b) hydrolysis of the anionic species (deprotonated sulfonylurea) by water at near neutral pH; and (c) hydrolysis of the anionic species by hydroxyl ion at high pH. The model results in an equation that can be written as Eq. (3), with an explicit expression for k, which is given by the following equation (Sarmah et al., 2000):

$$k = \frac{\left[k_1 + \left[k_2 10^{(pH-pK_a)}\right] + \left[k_3 10^{(2pH-14-pK_a)}\right]\right]}{\left[1 + 10^{(pH-pK_a)}\right]} \tag{5}$$

where k_1, k_2, and k_3 are the first-order rate constants for each of the three hydrolysis reactions mentioned above respectively. At constant pH, the right-hand side of Eq. (5) becomes constant and the degradation rate follows a pseudo-first-order kinetics (Eq. (3)), as observed in our experiments. Predictions of Eqs. (3) and (5), with values of k_1, k_2 and k_3 listed in Table 2, are shown as a solid line in Fig. 4b. The values of the rate constants were obtained by fitting experimental k vs. pH data with Eq. (5) using least-squares. The model fits well the experimental data. The estimated rate constants increase in the order $k_3 > k_1 \gg k_2$, showing that the hydrolysis of MM occurs more rapidly via hydroxyl ion attack. These results are comparable to those obtained by Sarmah et al. (2000) in the study of degradation of MM solutions in sodium acetate and sodium hydrogen orthophosphate buffers in the pH range of 5.2−11.2. The differences between our results and those informed by Sarmah et al. (2000) are mainly observed in k_1 and k_3 values. The differences could be in principle attributed to the presence of aqueous buffers in the experiments by Sarmah et al. (2000). Similar differences can be deduced by analyzing the data reported by Dinelli et al. (1993) and later by Braschi et al. (1997), who studied the hydrolysis of triasulfuron in aqueous solution and in buffer solutions, respectively. The proposed UV–VIS method, therefore, gives kinetic results that are comparable to those obtained with chromatographic methods.

3.2. MM adsorption and effects of Na-montmorillonite on the degradation kinetics

Fig. 5 shows the adsorption kinetics of MM on Na-montmorillonite. At pH 3 MM is rapidly adsorbed on the clay, reaching adsorption equilibrium in a rather short time (10−20 min). Measurements were also performed at pH 4.5 and 6, but no adsorption was detected. MM adsorption (2.4 μmol g^{-1}) at pH 3 is almost 400 times lower than the cation exchange capacity of the clay. The behavior is understandable since MM exists predominantly as a neutral molecule at pH < 3.3 and thus interactions between MM and the clay surface are not
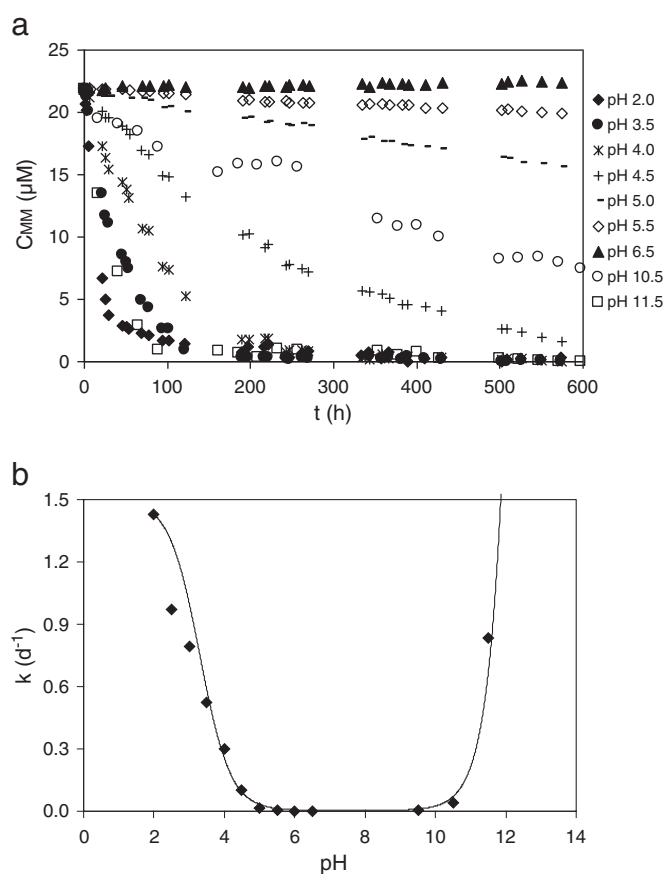
Fig. 4. Effect of pH on: (a) the degradation curves of MM at 25 °C and 10^{-2} M NaCl; and (b) the degradation rate constants. Line shows predictions of Eq. (5) with parameters in Table 2. Initial MM concentration: 21.9 μM.

Table 1
First-order rate constant (k) and half-life coefficient ($t_{1/2}$) values obtained in degradation experiments as a function of pH.

pH	k (d^{-1})	$t_{1/2}$ (d)
2.0	1.430	0.48
2.5	0.972	0.71
3.0	0.794	0.87
3.5	0.526	1.32
4.0	0.302	2.29
4.5	0.103	6.72
5.0	0.014	48.14
5.5	0.005	144.41
6.0	0.001	481.35
6.5	0.000	–
9.5	0.005	144.41
10.5	0.084	8.25
11.5	0.833	0.83

Table 2
Best-fit parameters for Eq. (5).

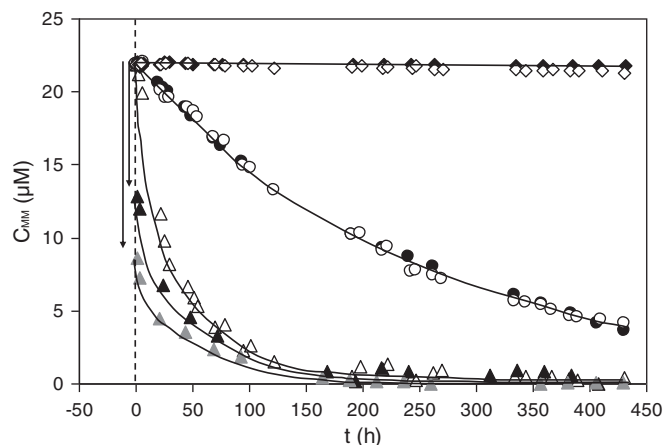|	Sarmah et al. [4]	This work
k_1 (d^{-1})	5.46	1.50
k_2 (d^{-1})	8.50×10^{-3}	4.00×10^{-3}
k_3 (d^{-1})	43.34	210

electrostatically driven. Interactions seem to be of the hydrogen-bond type or other kind of interaction, which are weaker than electrostatic attractions, leading to a lower adsorption than in the case of cationic species. Adsorption may be also suggested from the comparison of X-ray patterns of Na-montmorillonite before and after adsorption of MM, as shown in the supporting information (SI, see SI Fig. S1). The intensity of the (001) peak of the MM–Na-montmorillonite complex at pH 3 strongly decreases in comparison with the raw mineral, effect that may be due to a more irregular stacking of montmorillonite layers as a consequence of herbicide adsorption (Parolo et al., 2012). Since the (001) peak position of the complex does not change significantly in the presence of herbicide (from 7.64°2θ to 7.60°2θ), this adsorption seems to occur mainly on the outer surface of the clay mineral (Rytwo et al., 2010). This last suggestion is supported by the fact that the theoretical size of non-hydrated MM molecule is around 12.7 × 7.2 Å (Rivas et al., 2010), larger than the basal spacing of Na-montmorillonite at pH 3.3 (d_{001} = 6.6 Å). At pH > 3.3, on the contrary, MM exists mainly as an anion and repulsive interactions when the negative montmorillonite surface impedes significant adsorption. Similar results were reported by Ukrainczyk and Ajwa (1996) on the adsorption of primisulfuron on silica and Al-montmorillonite, which have a net negative charge above pH 2.

Fig. 5 also displays the results obtained with an adsorption–desorption experiment. After adsorption at pH 3, a rather fast and complete desorption of MM takes place by increasing the pH of the dispersion to 6. This adsorption–desorption behavior is reversible and can be repeatedly observed in the same kinetic run, pointing again to a weak interaction between MM and montmorillonite at pH 3. It is necessary to remark that during all these adsorption and adsorption–desorption experiments the shape of the UV–VIS spectra of MM in the supernatant did not change with respect to the spectrum of a fresh MM solution, indicating that no significant MM degradation took place and that adsorption–desorption is much faster than degradation.

Fig. 6 compares C_{MM} vs. t curves in the presence and absence of Na-montmorillonite at different pH. In all cases, the initial MM

Fig. 6. Evolution of the MM concentration in the supernatant as a function of time at 25 °C and 10^{-2} M NaCl. Initial MM concentration: 21.9 μM. Open diamonds, degradation in absence of clay pH 6; solid diamonds, degradation in 2.7 g L^{-1} clay pH 6; open circles, degradation in the absence of clay pH 4.5; solid circles, degradation in 2.7 g L^{-1} clay pH 4.5; open triangles, degradation in absence of clay pH 3; black triangles, degradation in 2.7 g L^{-1} clay pH 3; gray triangles, degradation in 8.1 g L^{-1} clay pH 3. Arrows show the fast decrease in MM concentration due to adsorption.

concentration was 21.9 μM. At pH 6, C_{MM} remains equal to 21.9 μM and thus no degradation takes place, even in the presence of Na-montmorillonite. At pH 4.5 some degradation is observed, but the presence of Na-montmorillonite does not modify the kinetics. The clay at this pH is acting as a spectator, without catalyzing or slowing down the process. At pH 3, on the contrary, there are significant differences between the curve in the absence of montmorillonite and the two curves in the presence of montmorillonite that are shown in the figure. The curve in absence of clay does not need much discussion because it is similar to the curves in Fig. 4, which correspond to a first order degradation kinetics. The curves obtained in the presence of Na-montmorillonite have a different shape. There is a fast decrease in C_{MM} from t = 0 to t = 10 min, which is the first data point that could be measured in the kinetic experiments. This initial and relatively fast process is marked in the figure with arrows. This process does not correspond to the degradation of the herbicide; it is the result of MM adsorption that takes place quickly at this low pH, as was verified with adsorption–desorption experiments. After this fast adsorption process the actual degradation of the herbicide takes place. The measured half-life of MM in the presence of 2.7 g L^{-1} of montmorillonite was 1.30 d, whereas in the
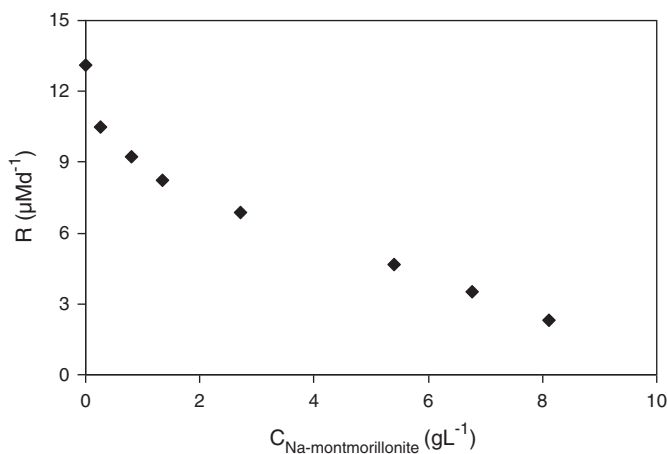

Fig. 5. Adsorption kinetics of MM on Na-montmorillonite as a function of pH at 25 °C and 10^{-2} M NaCl. Solid diamonds, pH 3; open circles, pH 4.5; and solid triangles, pH 6. Stars and line show the adsorption–desorption curve performed at pH 3 and 6, respectively. The arrows indicate the time where the pH was changed either to 6 or 3. Initial Na-montmorillonite and MM concentrations were 2.7 g L^{-1} and 21.9 μM respectively.

Fig. 7. Effect of the clay concentration on the degradation rate at pH 3 and 25 °C. Initial MM concentration: 21.9 μM.
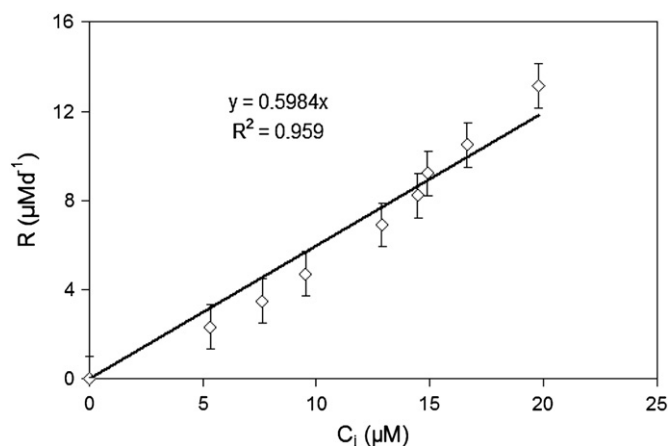
Fig. 8. Linear relationship between degradation rate (at pH 3 and 25 °C) and MM concentration remaining in the supernatant after adsorption.

presence of 8.1 g L^{-1} of montmorillonite was 1.60 d. These half-lives are longer than that obtained in the absence of montmorillonite under the same conditions (0.87 d), reflecting a protective effect of montmorillonite on the degradation of MM.

The effects of the presence of clay were further investigated by measuring the degradation rate at different clay concentrations. This is shown in Fig. 7, where the degradation rate at pH 3 is plotted as a function of clay concentration. The rate decreases by increasing clay concentration. It is clear that montmorillonite protects MM from being degraded. This protective action seems to be mainly due to adsorption, i.e., adsorbed MM molecules do not degrade whereas MM molecules that remain in solution degrade. Therefore, at low clay concentration, MM concentration in the supernatant is high and the degradation rate is relatively high; at high clay concentration, C_{MM} is low due to an important adsorption and then the degradation rate is low. This can be proved by plotting the relationship between degradation rate and MM concentration that remains in the supernatant after adsorption, which is shown in Fig. 8. R varies linearly with MM concentration in the supernatant, confirming that only MM molecules that remain in solution are subject to degradation.

Inhibitory effects of minerals on the degradation of herbicides have already been reported in the literature. Sabadie (2002, 1997), for example, informed a slow degradation of both bensulfuron and nicosulfuron in the presence of various minerals including a montmorillonite, a calcium-exchanged bentonite and a proton exchanged bentonite. Although the results are not directly comparable to ours because this author studied degradation of the herbicides under low moisture content, they agree qualitatively with our findings. A more direct comparison can be done for the case of MM. Sabadie (1990) reported a decrease in the degradation rate of the herbicide at pH 3.9 in the presence of montmorillonite K10 (Fluka), resembling the behavior shown here. There is so far no information on how adsorption is protecting MM from being degraded. As it was observed, the adsorption is rather low and thus MM molecules could be located in the interlayer space without being detected by XRD. The location in the interlayer is perhaps responsible for the herbicide protection. It is then possible to speculate that some reactive groups of MM become involved in the interaction with the clay surface and that these groups are not available for water attack and further hydrolysis. Although there is no information on the interaction modes of metsulfuron methyl and montmorillonite, some analogies could be observed with a related sulfonylurea, bensulfuron methyl. Infrared experiments with bensulfuron methyl adsorbed on montmorillonite performed by Si et al. (2004) show that the stretching frequency of the C=O bond and that the antisymmetric stretching frequency of the SO_2 group shifts upon adsorption, indicating molecular interactions between the molecule and the clay surface, interactions that

could be involved in the protection of the herbicide. More fundamental research in this direction is still necessary.

4. Conclusions

The results obtained with the proposed UV–Vis methodology agree with those obtained with chromatographic techniques, indicating that UV–Vis can be satisfactorily used to evaluate the degradation kinetics of MM. This simple and fast method, with a lower cost of analysis than chromatographic methods, could be used in laboratory experiments to obtain environmentally relevant information about the degradation rate of MM and other sulfonylureas under well controlled conditions.

The degradation rate of MM in solution strongly depends on pH. It is very slow at pH 6.5–9.5, but increases about 500 times by decreasing pH from 6 to 2, and 300 times by increasing pH from 9.5 to 11.5. The degradation rate also depends on the clay concentration, decreasing as Na-montmorillonite concentration increases. It is demonstrated that this deactivation is due to adsorption (on the montmorillonite surface), and thus adsorbed MM molecules do not degrade; only MM molecules that remain in solution are reactive.

Since adsorption only occurs at rather low pH, it can be envisaged that montmorillonite and supposedly other phyllosilicate clays do not affect significantly the chemical degradation rate of MM in soils and other natural system.

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