Dechlorination of chloroacetanilide herbicides by plant growth regulator sodium bisulfite

Haitao Biana, Jingwen Chenb, Xiyun Caia,*, Ping Liua, Ying Wanga, Liping Huanga, Xianliang Qiaoa, Ce Haoa

aKey Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education), Department of Environmental Science and Technology, Dalian University of Technology, Linggong Road 2, Dalian 116024, P.R. China
bState Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, P.R. China

1. Introduction

Chloroacetanilide herbicides are among the most commonly used pesticides in agriculture for pre-emergence control of annual grasses and broadleaf weeds in corn, soybeans, and many other crops. About 15,900 metric tons of acetochlor was used in the United States in 2001, followed by 10,900 metric tons of S-metolachlor and 4100 metric tons of alachlor (Kiely et al., 2004). The consumption of acetochlor is more than 10,000 metric tons every year in China (Ye, 2003). Due to

the prevalent use of these herbicides and their relatively high solubility in water, the herbicides and their degradation products have been frequently detected in groundwater and surface waters (Kolpin et al., 1996; Boyd, 2000; Cerejeira et al., 2003; Xue et al., 2005; Hildebrandt et al., 2008).

Alachlor and acetochlor are characterized as class B2 human carcinogens by the U. S. Environmental Protection Agency, whereas metolachlor is viewed as a class C human carcinogen (USEPA, 1995, 1998, 2006). Chloroacetanilide herbicides have moderate to high chronic toxicity to aquatic biota.
vertebrates and invertebrates, high toxicity to aquatic plants (USEPA, 1998) and some green algae (Junghans et al., 2003; Cai et al., 2007). The concentrations reported in surface waters could result in extensive adverse effects on aquatic plants (USEPA, 1998). Therefore, the removal of these pesticides’ contaminations from wastewater effluent and the environment is of great importance.

Chloroacetanilide herbicides can be attenuated naturally in the soil–water system. The ethane sulfonic acid (ESA) and oxanilic acid derivatives of alachlor, acetochlor and metolachlor have been frequently detected as the major transformation products of chloroacetanilide herbicides in water at higher levels than those of their parent compounds (Kalkhoff et al., 1998; Kolpin et al., 2000; Spalding et al., 2003). However, the transformation may be very slow under the relatively dilute or nutrient-limited conditions such as some groundwater and river water (Larson et al., 1995; Potter and Carpenter, 1995). Recently, it has been reported that some sulfur compounds could rapidly transform chloroacetanilide herbicides to less toxic products (Gan et al., 2002; Loch et al., 2002; Zheng et al., 2004b). This provides a new strategy for the remediation of chloroacetanilide-contaminated aqueous environments.

Sodium bisulfite (NaHSO₃) is used as a plant growth regulator in China (Zhang and Peng, 1984; Wang et al., 2000a,b). Given that NaHSO₃ is an agrochemical with low toxicity, using NaHSO₃ as the remediation reagent of chloroacetanilide herbicide contamination would have minimal impact on the agricultural system and the environment. The specific objectives of this study were to (i) determine reaction rates of three chloroacetanilide herbicides (alachlor, acetochlor and S-metolachlor) with sodium bisulfite in water, (ii) explore reaction mechanisms by evaluating reaction kinetics and activation parameters, identifying transformation products, and using hybrid density functional theory (DFT) calculation, and (iii) investigate the changes of toxicity of transformation products following the degradation of the parent herbicides.

2. Materials and methods

2.1. Chemicals

Technical grade alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide, 95.5%] and acetochlor [2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide, 95.2%] were purchased from Shandong Binnong Technology Co., Ltd. (Binzhou, China). S-metolachlor [S-2-chloro-N-(2-ethyl-6-methylphenyl)-N-(1-methoxypropan-2-yl)acetamide, 96%] was purchased from Syngenta (Suzhou) Crop Protection Co., Ltd. (Suzhou, China). All were used as received. NaHSO₃ and Na₂SO₃ were reagent grade.

Alachlor ESA (purity > 96.4%), acetochlor ESA (purity > 99.1%) and S-metolachlor ESA (purity > 96.9%) were prepared by the following procedures (Aga and Thurman, 2001) and used in acute toxicity assays. Briefly, the herbicides were refluxed with excess sodium sulfite in 10% ethanol/water (10/90, v/v) solution until the mixture became homogeneous. Following acidification with sulfuric acid, the products were dissolved in hot ethanol. The hot ethanol mixture was filtered and allowed to stand undisturbed for recrystallization of the ESAs. The crystals obtained were washed several times with cold ethanol and identified as alachlor ESA, acetochlor ESA or S-metolachlor ESA by high-pressure liquid chromatography–mass spectroscopy (HPLC–MS).

2.2. Experimental systems

A series of experiments were conducted to understand the reaction kinetics between the herbicides and sodium bisulfite. In the first experiment, disappearance of herbicides was determined by HPLC in aqueous solutions containing sodium bisulfite at various concentrations. Sodium hydroxide was used to adjust 45 mL of sodium bisulfite solution to pH 7.3. After the solution was transferred to a 100 mL volumetric flask, 50 mL of phosphate buffer solutions (pH 7.3) was also added into the volumetric flask. Stock solutions of herbicides (20.0 mM) were prepared in methanol. To initiate the reaction, 1.0 mL of each herbicide solution was separately added into the volumetric flasks, and the volume was brought to the 100-mL mark with deionized water. The initial herbicide concentration was 0.2 mM. The initial NaHSO₃ concentration was 0, 5.0, 10.0, 20.0, 30.0 and 50.0 mM, respectively. The final concentration of total phosphate was 0.1 M. The flasks were immediately transferred to an incubator at 25 ± 0.5 °C under darkness. At intervals, 1.0-mL aliquots of solution were withdrawn from volumetric flasks and transferred to glass vials followed by HPLC analysis.

In the second experiment, the effect of pH values on the reaction rate of the herbicides was studied. The procedures were the same as those described in the first experiment to prepare and analyze the samples. The initial concentrations of herbicide and sodium bisulfite were set at 0.2 and 20.0 mM, respectively. The solution pH was 3.8, 6.1, 7.3 and 8.5, respectively. The control vials contained only herbicides in buffer solutions. All samples were incubated at 25 ± 0.5 °C in the dark.

Buffer solution at pH 3.8 was prepared by combining appropriate volumes of 0.2 M citric acid and 0.2 M sodium citrate. Solutions of pH 6.1 and 7.3 were prepared from 0.2 M phosphate buffer. Buffer solution at pH 8.5 was prepared from 0.2 M boric acid and 0.05 M sodium tetraborate. Sulfite ion concentrations were computed from the total sodium bisulfite concentration [HSO₃⁻] and measured pH values via ionization constants for sulfurous acid at 25 °C (Lide, 2002) that were corrected for ionic strength using activity coefficients γ₃H₂SO₃ and γ₅SO₄²⁻ determined from the Davies approximation. Sulfite ion concentrations at other temperatures were computed using pKₐ values of temperature corrections performed with the Van’t Hoff equation.

The effect of temperature on the reaction rate of the herbicides was also investigated. The procedures were the same as those described in the above experiment. The initial herbicide concentration was 0.2 mM. The initial sodium bisulfite concentration was 20.0 mM. The solution pH was 7.3. The samples were incubated at 15, 20, 25, 30, and 35 °C, respectively. Variation in temperature was less than 0.5 °C. The control experiments were conducted in the absence of sodium bisulfite at each temperature. All the experiments were carried out in triplicate.
2.3. Analytical determinations

The herbicides and chloroacetanilide ESAs were analyzed using an Agilent 1100 HPLC equipped with a diode-array UV detector and a YWG C-18 reversed-phase column (4.6 × 250 mm; Dalian Elite Analytical Instruments Co., Ltd., Dalian, China). The wavelength was set at 220 nm. The mobile phase was composed of acetonitrile and water (65/35, v/v), which was acidified to pH 3 with phosphoric acid. The flow rate of mobile phase was 1.0 mL/min, and the temperature of which was kept at 30 °C. The herbicides and their ESAs were eluted at 7.9 min (alachlor) and 2.0 min (alachlor ESA), 8.0 min (acetochlor) and 2.0 min (acetochlor ESA), and 8.2 min (S-metolachlor) and 2.0 min (S-metolachlor ESA), respectively.

Reaction products were identified by HPLC–MS after purification using solid phase extraction (SPE). Extraction was performed using C-18 SPE cartridges using similar protocols to Aga et al. (1994). The SPE cartridges were preconditioned with sequential washings of methanol, ethyl acetate, methanol, and deionized water. Then 50 mL of the reaction solutions was passed through the cartridge and eluted first with ethyl acetate followed by methanol. The HPLC–MS analysis of the methanol extract was injected. The mobile phase consisted of 65% acetonitrile and 35% water with a flow rate of 0.2 mL/min. The column was a 15-cm C-18 column with an internal diameter of 2.1 mm and a particle size of 5 μm. Column temperature was set at 35 °C. The MSD was used operating the electrospray chamber in negative ion mode. The drying gas flow was set at 8 L/min, the nebulizer pressure was 40 psi, the drying gas temperature was 350 °C, and the fragmentor voltage was 50 V.

2.4. Calculation of electrophilicity index of the three chloroacetanilide herbicides

The electrophilicity index (ω), which has been suggested to characterize the ability of a chemical to accept electron, is described in terms of the electronic chemical potential μ and the chemical hardness η as (Parr et al., 1999)

\[ \omega = \frac{\mu^2}{2\eta} \]

in which

\[ \mu = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2} \]

\[ \eta = E_{\text{LUMO}} - E_{\text{HOMO}} \]

where \( E_{\text{HOMO}} \) and \( E_{\text{LUMO}} \) are the energies of the highest occupied and lowest unoccupied molecular orbitals respectively.

All the calculations on chemical structures were performed using Gaussian 03 program system (Frisch et al., 2003). The geometries of chloroacetanilide herbicide molecules were optimized using DFT, B3LYP, with the 6-31+G(d) basis set. Solvent effects were modeled using the polarized continuum model (PCM) within self-consistent reaction field (SCRF) theory. Optimized structures were confirmed by frequency analyses at the same level. \( E_{\text{LUMO}} \) and \( E_{\text{HOMO}} \) values were obtained from single-point calculations at B3LYP/6-31+G(d,p) level.

2.5. Acute toxicity assays

The freshwater unicellular green alga Scenedesmus obliquus was obtained from the Institute of Wuhan Hydrobiology, Chinese Academy of Sciences. Algae were cultured in an incubator at 24 ± 0.5 °C and a 14 h light and 10 h dark photoperiod.

The algal growth-inhibition tests of three herbicides and their ESA transformation products were carried out according to the updated Organization for Economic Co-operation and Development (OECD) guideline (OECD, 2002). All experiments were conducted under the same conditions as the culture. The algae were taken from the exponentially growing pre-culture and inoculated into the test solution in flasks at the density of approximately 10^5 cell/mL. Three replicates were included for each treatment. The flasks were gently shaken four times per day to prevent the settling of algae. Percentages of growth inhibition of the treated cultures with respect to the control cultures were determined by measuring the optical density at 680 nm using a Hitachi UV2800 spectrophotometer. The 96 h EC_50 (medium effective concentration) values for the algae were calculated as the concentration of herbicides inhibiting 50% growth of the algae relative to controls.

3. Results and discussion

3.1. Kinetics of chloroacetanilide herbicides reactions with sodium bisulfite at 25 °C

The time courses for reactions of alachlor, acetochlor, and S-metolachlor with NaHSO_3 at pH 7.3 are shown in Fig. 1. Regression of the herbicide concentration with time showed a good first-order relationship with \( R^2 > 0.98 \). All chloroacetanilide herbicides were very stable in the control containing only herbicides, and the half-life \( (t_{1/2}) \) for each herbicide was \( >200 \) d (Table 1). As a result, NaHSO_3 caused the dissipation of the herbicides in the aqueous system. The reaction of chloroacetanilide herbicides accelerated remarkably as NaHSO_3 concentration was increased. At an initial NaHSO_3 concentration of 50 mM, \( t_{1/2} \) of alachlor and acetochlor were shortened to <3 d (Table 1).

At the same level of NaHSO_3, the herbicides exhibited different reactivity (Table 1), indicating the presence of substrate dependence. The reactivity of the herbicides decreased in the following order: alachlor > acetochlor > S-metolachlor. This was in accordance with the reactivity trend of the herbicides reported for other sulfur compounds such as HS^- (Loch et al., 2002) (alachlor > metolachlor), polysulfides (Loch et al., 2002) (alachlor > metolachlor), thiosulfate (Gan et al., 2002) (alachlor > acetochlor > metolachlor) and dithionite (Boparai et al., 2006) (alachlor > acetochlor > metolachlor) via S_2O_4^2- reaction. These results suggest a similar reaction between chloroacetanilide herbicides and reactive sulfur compounds.

3.2. Products of chloroacetanilide herbicides reactions with NaHSO_3

As the reaction proceeded, polar breakdown products appeared in HPLC spectra with shorter retention time, and increased in
peak area with time. The products were identified as chloroacetanilide ESAs by HPLC–MS. The mass spectra are shown in Fig. 2. Moreover, herbicide consumption was accompanied by the formation of almost equi-molar ESA, e.g., the average triplicate samples. Experiment data: control (○, 0.2 mM). Curves are fitted lines by using the first-order kinetics model. Error bars represent standard deviation of

<table>
<thead>
<tr>
<th>C0 (NaHSO3)</th>
<th>t1/2 (d)</th>
<th>alachlor</th>
<th>acetochlor</th>
<th>S-Metolachlor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&gt;200</td>
<td>&gt;200</td>
<td>&gt;200</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>26.2 ± 1.7</td>
<td>28.6 ± 2.0</td>
<td>68.6 ± 4.0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>12.5 ± 0.3</td>
<td>12.5 ± 0.6</td>
<td>43.2 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>6.0 ± 0.2</td>
<td>5.6 ± 0.1</td>
<td>33.4 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>4.3 ± 0.1</td>
<td>4.2 ± 0.1</td>
<td>23.2 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>2.2 ± 0.0</td>
<td>2.2 ± 0.0</td>
<td>13.6 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 – First-order half lives t1/2 (d) for the disappearance of different chloroacetanilide herbicides in solutions of different NaHSO3 concentrations at 25 °C and pH 7.3.

The reaction between chloroacetanilide herbicides and SO32− can be described as SN2 reactions, similar to the reaction of chloroacetanilides, along with the nature of ESAs in which the reaction is a stoichiometric substitution. The rate of reaction can hence be represented by the following expression:

\[ \frac{-d[\text{herbicide}]}{dt} = k_{\text{obs}}[\text{herbicide}] = k_{\text{SO3}^2−}[\text{SO3}^2−][\text{herbicide}] \]  

(1)

\[ k_{\text{obs}} = k_{\text{SO3}^2−}[\text{SO3}^2−] \]  

(2)

A significant linear relationship (R2 > 0.94) between kobs and [SO32−] was found for all tested herbicides (Fig. 5), indicating the reactions are also first-order in SO32− concentrations. The overall second-order nature of the reactions of SO32− with chloroacetanilides, along with the nature of ESAs in which chlorine has been substituted by SO32−, indicates the reactions can be described as S2,2 reactions, similar to the reaction of these herbicides with other sulfur compounds (Gan et al., 2002; Loch et al., 2002; Zheng et al., 2004b). The reactivity potencies of alachlor (kSO32− = 9.29(±0.27) × 10−5 M−1 s−1) and acetochlor (9.45(±0.27) × 10−5 M−1 s−1) with SO32− at 25 °C were four times greater than that of S-metolachlor (kSO32− = 1.62(±0.10) × 10−5 M−1 s−1). For alachlor, the

Fig. 1 – Dissipation of chloroacetanilide herbicides in solutions of varying NaHSO3 concentrations at 25 °C and pH 7.3. (a) alachlor, (b) acetochlor and (c) S-metolachlor. C0 is the initial concentration of chloroacetanilide herbicides (0.2 mM). Curves are fitted lines by using the first-order kinetics model. Error bars represent standard deviation of triplicate samples. Experiment data: control (■), 5 mM (□), 10 mM (▲), 20 mM (△), 30 mM (●) and 50 mM (○).
reactivity of the sulfur compounds decreased in the following order: polysulfides (Loch et al., 2002) > HS$^-$ (Loch et al., 2002) > thiosulfate (Lippa et al., 2004) > SO$_3^2$\(^-\). The relative order differs from that of S$_2$2 reaction between methyl bromide and them previously reported except for polysulfides (polysulfides > thiosulfate > HS$^-$ ≈ SO$_3^2$\(^-\)) (Larson and Weber, 1994; Schwarzenbach et al., 2003). It is quite likely that steric hindrance is responsible for the lower reactivity of the larger thiosulfate and SO$_3^2$\(^-\) nucleophile toward alachlor. A relatively reduced nucleophilicity of thiosulfate for the nucleophilic substitution reaction of chlorpyrifos-methyl with reduced sulfur species is also reported by Wu and Jans (2006).

The characteristics of the reactions between NaHSO$_3$ and chloroacetanilide herbicides indicate that many other halogenated organic contaminants and electrophilic contaminants may also be transformed via a similar process. Previous studies have determined that these contaminants can be dehalogenated or transformed by other reduced sulfur nucleophiles such as bisulfide, polysulfides (Lippa and Roberts, 2002; Wu and Jans, 2006), thiosulfate (Wang et al., 2000c) and thiourea (Zheng et al., 2004a).

3.4. Activation barriers for reaction with SO$_3^2$\(^-\)

No transformation of chloroacetanilide herbicides occurred in the absence of SO$_3^2$\(^-\) over the temperature range of 15.0–35.0 °C in the buffer control experiments ($p < 0.05$). Data for each herbicide were analyzed by regression (Fig. 6) according to a linearized version of the Eyring equation:

$$
\ln(kSO_3^2^-/T) = \ln(k/h) - \Delta H/RT + \Delta S/R
$$

where $k$ is Boltzmann’s constant, $h$ is Planck’s constant, $R$ is the gas constant, $T$ is temperature in Kelvin, and $\Delta H$ and $\Delta S$ are the enthalpic and entropic contributions, respectively, to the overall activation barrier $\Delta G$. Linear regression analyses of the data yielded $\Delta H$ and $\Delta S$ values (Table 2).

$\Delta H$ and $\Delta S$ for the reactions of alachlor and acetochlor with SO$_3^2$\(^-\) were statistically indistinguishable at the 95% confidence level, whereas these were significantly different from those of S-metolachlor. Judging from the results of the reaction kinetics, reactivity differences stemmed primarily from entropic factors. $\Delta S$ is related to the “freedom” or latitude of orientation, configuration, and translation of the molecule. Such negative $\Delta S$ values suggest that the transition states have more ordered or more rigid structures than the reactants in the ground state. The variations in $N$-alkoxyalkyl substituents or phenyl ring substituents would result in different
ordered transition states. The larger steric hindrance for S-metolachlor probably makes it more difficult for nucleophilic attack (Fig. 7). Loch et al. (2002) have demonstrated that

**Fig. 4** – Dissipation of chloroacetanilide herbicides in 20 mM NaHSO₃ solutions at different pH values (25 °C). (a) alachlor, (b) acetochlor and (c) S-metolachlor. C₀ is the initial concentration of chloroacetanilide herbicides (0.2 mM). Curves are fitted lines by using the first-order kinetics model. Error bars represent standard deviation of triplicate samples. Experiment data: pH 3.8 (●), pH 6.1 (□), pH 7.3 (○) and pH 8.5 (●).

**Fig. 5** – Plot of pseudo-first-order rate constant k_obs versus C(SO₃²⁻) for reactions of SO₃²⁻ with alachlor (●), acetochlor (○) and S-metolachlor (▲).

ΔS could account for appreciable differences in the overall reaction barrier of HS⁻ reaction with chloroacetanilide herbicides and the steric hindrance of herbicide molecules stemming from variations in N-alkyl (or N-alkoxyalkyl) substituents or phenyl ring substituents could cause the observed 20-fold difference in reactivity. This finding is also similar to the data for the reaction of chloroacetanilide herbicides with thiosulfate previously reported, in which the relatively slow dechlorination of metolachlor was also ascribed to its large steric hindrance (Gan et al., 2002).

**Fig. 6** – Temperature dependence of reactions of SO₃²⁻ with alachlor, acetochlor and S-metolachlor. alachlor (●), acetochlor (○) and S-metolachlor (▲). The experiments were conducted in pH 7.3, 20 mM NaHSO₃, 0.2 mM herbicides and 100 mM phosphate buffer over 15-35 °C. Solid line represents linear regression of data.
3.5. Electrophilicity index of the three chloroacetanilide herbicides

Electrophilicity indices of the three chloroacetanilide herbicides decreased in the following order: alachlor ≈ acetochlor > S-metolachlor (Table 2), which revealed a decrease in the ability of them to accept electron. This was confirmed by the above observed reactivity potencies for these herbicides in S₈₂ substitution. The reactivity trend of these herbicides with other sulfur-contained chemicals such as HS⁻ (Loch et al., 2002), polysulfides (Loch et al., 2002), dithionite (Boparai et al., 2006) and thiosulfate (Gan et al., 2002) is also in accordance with their electrophilicity indices. Electrophilicity index could characterize the energy lowering associated with maximal electron flow and the ability of a chemical to accept electron, and hence characterize susceptibility of electrophiles to nucleophilic attack in electrophile–nucleophile interaction processes. It has been found to be helpful in analyzing the reactivity of various chemical compounds as well as the reaction mechanisms of diverse classes of chemical processes (Domingo et al., 2004; Galabov et al., 2004; Campodonico et al., 2005; Contreras et al., 2005; Enoch et al., 2008). The results of this study suggest that the electrophilicity of chloroacetanilide herbicides represents the reaction potencies when they are treated by reactive sulfur compounds.

3.6. Acute toxicity of chloroacetanilide herbicides and chloroacetanilide ESAs

Three chloroacetanilide herbicides have high toxicity to green alga S. obliquus, with EC₅₀ values ranging from 0.008 to 0.156 mg/L (Table 3). Junghans et al. (2003) also reported high toxicity of chloroacetanilide herbicides to green alga Scenedesmus vacuolatus. In surface waters, 0.025 mg/L acetochlor and 0.143 mg/L metolachlor have been detected (Battaglin et al., 2000), which could result in adverse effects on some sensitive aquatic organisms.

EC₅₀ values of the major degradation products (ESAs) increased significantly compared with those of the chloroacetanilides (Table 3), suggesting that ESAs were less toxic than the parent herbicides. For instance, the EC₅₀ values of ESAs were greater by 4 orders of magnitude than those of the herbicides.

Chloroacetanilide ESAs have been frequently detected as major degradation products of chloroacetanilide herbicides in water and soils at levels often higher than those of their parent compounds (Kolpin et al., 2000; Dagnac et al., 2002). They are metabolites yielded by glutathione conjugation with chloroacetanilide herbicides and subsequent in vivo transformation, which are common metabolic pathways as well as detoxification processes, carried out by aquatic and terrestrial plants and soil microorganisms (Field and Thurman, 1996). ESAs have been of concern because they are more mobile and persistent than the parent herbicides (Kalkhoff et al., 1998). Compared to the availability of toxicological data for the parent chloroacetamide herbicides, those of ESAs are relatively limited. They are generally considered non-mutagenic and non-genotoxic, while some other chloroacetanilide degradates are more teratogenic and genotoxic than the parent herbicides (Tessier and Clark, 1995; Heydens et al., 1996, 2000; Osano et al., 2002). Similar with the results obtained in this study, Cai et al. (2007) observed that

![Fig. 7 – Nucleophilic transformation reaction between chloroacetanilide herbicides and SO₃²⁻.](image-url)
Acetochlor ESA had similar reduction of toxicity to other two green algae upon acetochlor dechlorination. If these results were indicative of a reduction in human and ecological toxicity, the facilitated dechlorination by NaHSO₃ provides a selective route for formation of chloroacetanilide ESAs, results in the enhanced detoxification of chloroacetanilide herbicides and would be an environmentally beneficial process.

4. Conclusions

Sodium bisulfite can accelerate the transformation of the chloroacetanilide herbicides (alachlor, acetochlor and S-metolachlor) to chloroacetanilide ESAs via SN₂ nucleophilic substitution reaction. The reaction rates are associated with herbicides, pH, temperature and sodium sulfite concentrations. The reactivity of the herbicides decreases in the following order: alachlor > acetochlor > S-metolachlor, which is related to steric hindrance and electrophilicity of the herbicides. ESAs are less toxic to green algae than the parent compounds, suggesting that chloroacetanilide herbicides dechlorination by NaHSO₃ may be a detoxification process.

NaHSO₃ is a plant growth regulator and readily available commercial product. The reaction of NaHSO₃ with these herbicides seems to be highly specific and may have less influence on the systems that are being treated, in contrast to nonselective methods such as solvent flushing and thermal treatments. In addition, NaHSO₃ can be oxidized to sulfate with time in the environment. Therefore, NaHSO₃ is potentially feasible for removing chloroacetanilide herbicides from wastewater effluent, spill sites and accidental discharge. Future researches on the detailed investigation on human and ecological toxicity of ESA and the methods and rates for in situ applications should be conducted, and the cost-effectiveness and engineering feasibility must be considered before this strategy is adopted.

Acknowledgements

This study was supported by the National Key Project for Basic Research (2006CB403302), the Fok Ying Tung Education Foundation (No. 114042), the National Natural Science Foundation of China (No. 20707002), and the International Foundation for Science (No. F/4580-1).

References


