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Research Article

Heterogeneous Nucleophilic Transformation of Metolachlor by Bisulfide on Alumina Surface

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The present research elucidates the accelerating effect of alumina minerals on metolachlor transformation using sulfur nucleophiles and also determines the metolachlor transformation mechanisms in the heterogeneous reaction systems. Metolachlor transformation was first systematically investigated under different conditions. Then, the Fourier transform infrared (FTIR) spectra were used to characterize the changes in the surface bonds of the aluminas. The transformation products were qualitatively identified using LC/MS. The results showed that bisulfide can produce efficient metolachlor transformation rates, and the presence of the aluminas can further accelerate the transformation by achieving complete transformation in <21 days. In addition, a higher pH and higher bisulfide concentration are more favorable for metolachlor transformation. When normalized to the surface area, the metolachlor transformation rates were found to follow the order of α -Al₂O₃ > γ -AlOOH > γ -Al₂O₃ in the presence of different aluminas. FTIR results indicated that the enhancement of metolachlor transformation rates by bisulfide with aluminas can be attributed to the surface active nucleophiles on alumina surfaces formed through Al–S and Al–O bonds. The substitution of chlorine on the metolachlor followed the S_N2 mechanism by bisulfide with accelerated rate through mediating the heterogeneous reactions with aluminas.

Keywords: Aluminum oxide; Chloroacetanilide herbicides; Heterogeneous nucleophiles; Nucleophilic reagent; Nucleophilic substitution

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1 Introduction

Metolachlor, 2-chloro-N-(2-ethyl-6-methyl-phenyl)-N-(1-methoxypropyl)acetamide (Fig. 1), is one of the important chloroacetanilide herbicides and acts as a pre-emergent herbicide widely used to control certain broadleaf weed species, annual grassy weeds, barnyard grass, crabgrass, fall panicum, and foxtails [1]. The annual use of metolachlor was estimated to be higher than all the other chloroacetanilide herbicides, and only lower than that of atrazine among all herbicides [2]. Hence, serious groundwater and soil pollutions are frequently found because of the intensive application of this herbicide. Metolachlor is among the top five most frequently detected pesticide in soils and groundwater [3] and is considered persistent in soils, as well as groundwater, with a reported average field dissipation half-life of approximately 120 days [4]. Integrating the widely realized ecotoxicity [5, 6], exploring the decontamination methods for environments polluted by herbicides is important.

Chloroacetanilides have been reported to undergo transformation processes with artificial-like actions, such as oxidative degradation, photolysis, and biotransformation. However, the essential reaction conditions for these compounds may be penurious in the anaerobic and dark environments, resulting in negligible or much slower

processes [7]. The fundamental transformation of chloroacetamides in the environments is hydrolysis [8]. However, although hydrolysis is the important process in accelerating the transformation and decomposition of chloroacetamides, long transformation half-lives of chloroacetamides, ranging from 1 year to 7 years, were obtained in the hydrolysis processes [9, 10].

Active nucleophiles are important for accelerating the self-transformation and self-detoxification of pollutants in the natural environment. The natural sulfur species are important nucleophiles and have received increasing attention in recent years for their roles in accelerating herbicide transformation [11, 12]. The reduced sulfur species, e.g., HS⁻, S_n²⁻, S₂O₃²⁻, and S₂O₄²⁻, are reportedly active environmental “reagents” that can react with a wide array of organic pollutants, including chloroacetanilide herbicides, which undergo nucleophilic substitution and dehalogenation processes [12–16]. However, all these previous studies were conducted in homogeneous conditions. Many active solid components, such as minerals, are important for pollutant transformation in different environments, especially in soil. However, only a few investigations have been conducted on the nucleophilic substitution of chloroacetanilide herbicides by active sulfur compounds at the interface of minerals.

Aluminum is the most abundant metallic element in the earth's crust with 8.1% of the total weight, only lower than O and Si among all the earth elements [17]. Although an excessively high

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Abbreviations: FTIR, Fourier transform infrared; LAS, Lewis acid sites

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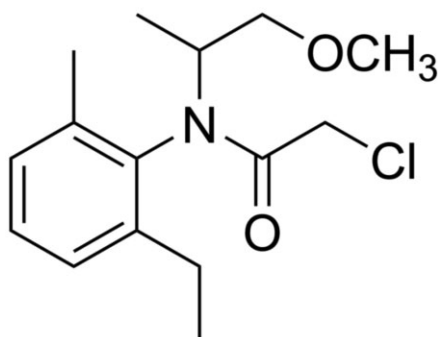


Figure 1. Chemical structure of metolachlor.

concentration of aluminum would cause aluminum toxicity to plant growth and even to human health [18], the over 270 types of soil aluminum minerals are usually environmental friendly and beneficial for geochemical processes of contaminants [19]. Aluminum minerals play an important role in regulating the composition of soil–water, sediment–water, and other soil systems. Compared with other minerals in soils, the surfaces of alumina are particularly more reactive [20, 21].

Aluminum (hydr)oxides, as the common soil aluminum minerals, show the purest and representative properties of aluminum minerals [22]. Given their special surface properties and thermal stability, aluminas have been widely applied as adsorbents [23] as well as catalysts and catalyst supports of ozonation and wet air oxidation [24, 25]. The surface chemistry of aluminas plays a key role in their performance as adsorbents and catalysts [26]. The protonated surface of an alumina renders it to be easily adsorbed by negatively charged compounds as a result of electrostatic attraction. When the surfaces of aluminas are hydrated, water would be chemisorbed on the aluminas, and the top layer oxide ions would be converted to hydroxyl ions with square and filled lattice proven to be active nucleophiles in the environment [22]. Furthermore, the aluminum on the top layer of aluminas are usually unsatisfied and are positively charged, in which the aluminum sites act as Lewis acid sites (LAS) and the surface OH groups act as Lewis bases. The solid acid and base sites on alumina surfaces are extremely active, and the acid–base properties of alumina are mainly responsible for the active functions in geochemical processes [27].

Therefore, as the abundant and active minerals in the environment, aluminas are expected to exhibit an important effect on the transformation of chloroacetanilide herbicides when presented together with active nucleophiles. To elucidate the transformation mechanism of chloroacetanilide herbicides in an alumina-rich environment, the nucleophilic transformation of metolachlor by bisulfide in the presence of aluminas under different conditions were systematically investigated in the present study using batch experiments. The primary aims were to elucidate the role of alumina surfaces in metolachlor transformation by bisulfide for obtaining the heterogeneous metolachlor transformation mechanism. To achieve these goals, we firstly conducted experiments to determine the kinetics of metolachlor transformation with the simultaneous action of bisulfide and aluminas. Then, the main transformation products were identified to reveal the metolachlor transformation mechanisms in the heterogeneous reaction systems.

2 Materials and methods

2.1 Materials

Metolachlor (analytical reagent grade) and methanol (GC grade, $\geq 99.8\%$) were purchased from Sigma–Aldrich (St. Louis, MO, USA). The sodium bisulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and other chemicals were of analytical grade and obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). All chemicals were used as received, including the methanol, which was not deoxygenated before use. A Milli-Q water purification system was used to produce ultrapure water ($18\text{ M}\Omega\text{ cm}$) and the obtained water were deoxygenated by purging with O_2 -free N_2 overnight before being used for the preparation of all chemical solutions. Three aluminas, i.e., $\gamma\text{-AlOOH}$, $\gamma\text{-Al}_2\text{O}_3$, and $\alpha\text{-Al}_2\text{O}_3$, were used in this study. Boehmite ($\gamma\text{-AlOOH}$) was received as HiQ-7223 alumina (Alcoa, PA, USA). $\gamma\text{-Al}_2\text{O}_3$ was prepared from HiQ-7223 alumina powder by thermal treatment at 650°C for 3 h. Corundum ($\alpha\text{-Al}_2\text{O}_3$) was obtained by further calcining the as-formed $\gamma\text{-Al}_2\text{O}_3$ at 1500°C for 6 h [28]. The surface areas of the obtained $\gamma\text{-AlOOH}$, $\gamma\text{-Al}_2\text{O}_3$, and $\alpha\text{-Al}_2\text{O}_3$ were measured using a surface area analyzer (Coulter SA 3100; Beckman Coulter, Fullerton, CA, USA) as 299.4 , 88.6 , and $1.65\text{ m}^2\text{ g}^{-1}$, respectively. The pH at the points of zero charges (pH_{pzc}) of the aluminas was determined by a zeta-potential analyzer (Coulter Delsa 440SX; Beckman Coulter).

2.2 Experimental procedures

$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was used to prepare the Na_2S stock solutions with deoxygenated ultrapure water. The solution was prepared within an anaerobic glove box. The reduced sulfur reaction solutions were prepared by diluting reduced Na_2S stock solution into 50 mM phosphate pH buffer containing 5% methanol and 100 mM NaCl. The NaCl in the solvent was used to establish an ionic strength of $0.15\text{ equiv. L}^{-1}$, and methanol was used as a co-solvent to reduce the surface tension of the electrolyte. Then, 250 mg of metolachlor were dissolved in 250 mL deoxygenated ultrapure water to obtain the metolachlor stock solution (1000 mg L^{-1}). Other stock solutions were also prepared with ultrapure water. All solutions were stored at 4°C before the experiments. The total volume of reaction solution was 100 mL that contained in borosilicate glass serum bottles that with the volume of 125 mL , in which the reaction components with the sequence of alumina ($\gamma\text{-AlOOH}$, $\gamma\text{-Al}_2\text{O}_3$, or $\alpha\text{-Al}_2\text{O}_3$), bisulfide stock solution, and aqueous metolachlor stock solution being added consequently. In the reaction suspensions, the dosages of alumina were controlled at 10 g L^{-1} , the concentrations of metolachlor were at 10 mg L^{-1} , and the concentrations of bisulfide were at 1 , 3 , 5 , and 10 mM according to the experimental design. The reaction pH was controlled with 0.02 M phosphate buffer at pH 6 , 7 , and 9 as designed. After being covered with Teflon-lined butyl rubber septa and aluminum crimp seals, the reaction bottles were placed onto an orbital shaker at 250 rpm . At the designated sampling time, a 4 mL filtrate was collected from each bottle in the anaerobic glove box after being passed through a $0.22\text{ }\mu\text{m}$ PTFE filter (Millipore, MA, USA). Then, excess methanol (36 mL) was immediately added to the filtrate to quench further reaction before compositional analyses [29, 30]. The samples prepared for analyses were stored at 4°C in a refrigerator and analyzed daily. The rest of the reaction solutions after sampling were covered with Teflon-lined butyl rubber septa and aluminum crimp seals in the anaerobic glove box for followed

reactions. The stopped reaction between metolachlor and bisulfide in solvent of mixed methanol and phosphate buffer, 10:1 v/v, was also verified in our experiments (data not presented). Controlled samples consisting of only bisulfide and metolachlor in the buffer solution were also prepared with the same treatment procedure. All the batch experiments were conducted in duplicate and the variability of the data were reported as the error bars in the figures. For the Fourier transform infrared (FTIR) study, the alumina sample was collected by centrifuging at 4000 rpm and then being freeze-dried for 12 h. The dried samples were stored in a sealed borosilicate glass serum bottle with nitrogen protection before test. The bisulfide concentrations were obtained by calculation based on total sulfide concentration measurement. First, the total concentration of sulfide species, $[S]_T$, representing $[H_2S] + [HS^-] + [S^{2-}]$, was measured by iodometric titration using a starch endpoint. Then, the bisulfide ion concentrations were calculated from $[H_2S]_T$ and the measured pH values via the ionization constants for H_2S at 25°C [31] that being corrected by ionic strength using the activity coefficients γ_{HS^-} and $\gamma_{S^{2-}}$ determined from the Davies approximation.

2.3 Chromatographic analyses of metolachlor and its transformation products

Quantitative determination of the metolachlor concentrations in the aqueous solutions during the transformation processes were conducted using a HPLC system (Waters 1525/2487, USA). The mobile phase with 1% acetic acid in a solvent mixture of water and methanol with a ratio of 15:85 v/v at a flow rate of 1.0 mL min⁻¹ was used with an Xterra C18 reverse-phase column. The column temperature was set at 35°C, and a UV detector was applied at 230 nm. The limit of detection was 7 µg L⁻¹, and the relative standard deviation was within 5%. The qualitative determination of the metolachlor transformation intermediates was performed by LC/MS analysis using an HPLC system (Shimadzu, Japan) accompanying an API 3000 mass analyzer with the detailed procedure described in our previous study [32].

2.4 Infrared spectroscopy study

An FTIR spectrometer (Bruker Vector 33, Germany) was used to record the FTIR spectra of the three aluminas before and after reaction. In each measurement, 64 scans were collected in the spectral range of 4000–400 cm⁻¹ with the resolution of 4 cm⁻¹. The specimens for the FTIR analyses were prepared by mixing the dried target sample with spectroscopic grade KBr and then compressing the mixtures to form pellets.

3 Results and discussion

3.1 Metolachlor transformation by bisulfide on aluminas

The kinetic results of metolachlor transformation on the three kinds of aluminas, i.e., γ -AlOOH, γ -Al₂O₃, and α -Al₂O₃, with or without bisulfide are shown in Fig. 2. Metolachlor was stable in the buffer solutions (pH 9) without bisulfide, and all the aluminas showed none adsorption abilities for metolachlor. As shown in the results, the metolachlor concentrations in the reaction solutions remain unchanged when only aluminas were present. The bisulfide is a strong nucleophile and can result metolachlor an efficient transformation rate, in which the complete transformation was achieved at the reaction time of 28 days in the presence of 3 mM bisulfide, with the pseudo-first-order kinetic constant value k of 0.112 ± 0.0082 days⁻¹ ($R^2 = 0.970$). The efficient transformations of chloroacetanilide herbicides, including metolachlor, by bisulfide were also reported in the previous report [13]. However, the transformation rate of metolachlor in our study was significantly higher than that reported by Loch et al. [13], with the calculated second order rate constant of $1.0 \times 10^{-2} M^{-1} s^{-1}$ compared with $0.25 \times 10^{-2} M^{-1} s^{-1}$, which may resulted from the reaction systems with different buffer solution for formation rate of bisulfide from Na₂S.

The presence of aluminas can further accelerate the metolachlor transformation with all the three types of aluminas as shown in the

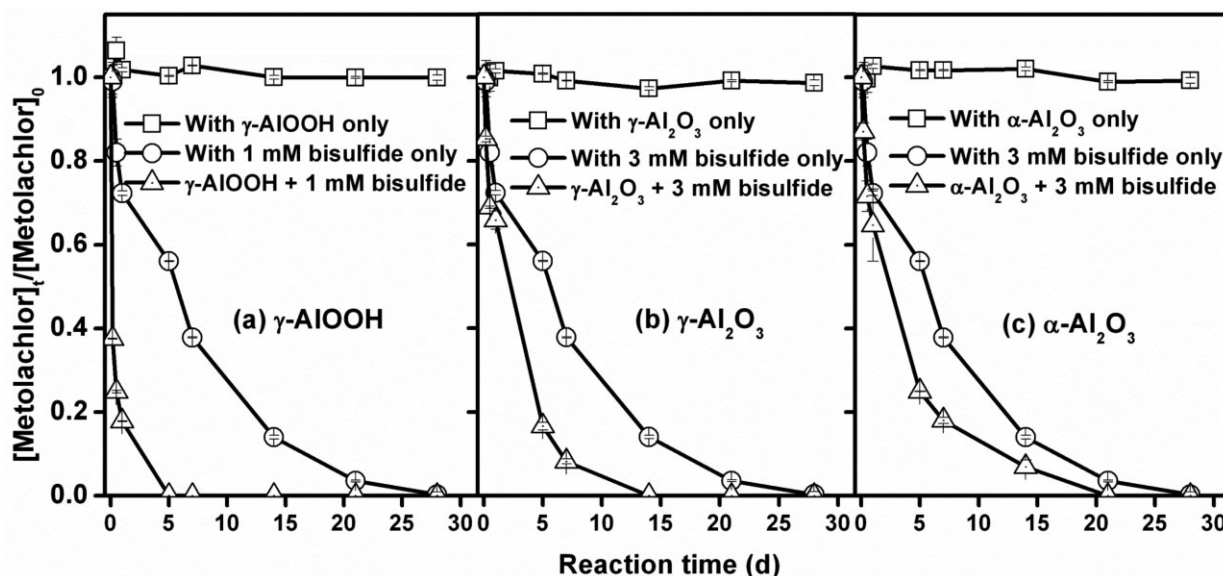


Figure 2. Transformation of metolachlor with an initial concentration of 10 mg L⁻¹ using 3 mM bisulfide on three aluminas (10 g L⁻¹) at 25°C and pH 9.

figure. Metolachlor can be completely transformed in 5, 21, and 14 days when with γ -AlOOH, γ -Al₂O₃, or α -Al₂O₃, respectively. Pseudo-first-order kinetics was also used to characterize the metolachlor transformation before the process was completed, and the k values were achieved to be 0.914 ± 0.0396 ($R^2 = 0.943$), 0.237 ± 0.0096 ($R^2 = 0.935$), and 0.164 ± 0.0074 days⁻¹ ($R^2 = 0.964$), with γ -AlOOH, γ -Al₂O₃, or α -Al₂O₃, respectively. For the studied three aluminas, the metolachlor transformation rates also increased with the increasing bisulfide concentration when 10 g L⁻¹ aluminas were introduced into the reaction system. Metolachlor transformations with different bisulfide concentrations at the same alumina dosages were also studied, and the kinetic constant k values when with different bisulfide concentrations are illustrated in Fig. 3 (all the reaction times for kinetic study were similar to that before the complete transformation of metolachlor). As shown by Fig. 3, the k values of experiments without any alumina show a linear relationship with the bisulfide concentrations, whereas in the presence of alumina, the k values show nonlinear relationships with bisulfide concentrations and exhibit an exponential-like increase. This result indicated the significant enhancement effect of the alumina surface on the metolachlor transformation by bisulfide. The metolachlor transformation rates were also differentiated in the presence of the three kinds of aluminas under the same conditions. When normalized to the surface area of the aluminas, the surface area-normalized-rate constants of γ -AlOOH, γ -Al₂O₃, and α -Al₂O₃ were obtained as 0.0031, 0.0027, and 0.0999 g m⁻² d⁻¹, respectively, indicating that α -Al₂O₃ had the most active surface sites, and then followed by γ -AlOOH and γ -Al₂O₃.

Bisulfide is one type of active reduced sulfur species and can act as a strong nucleophilic reagent for accelerating herbicide transformation [13]. This compound also plays an important role in the transformation of chloroacetanilide herbicides, especially in the heterogeneous reaction systems with the presences of aluminas. As indicated by the results of the present study, the presence of the three aluminas can evidently accelerate the metolachlor transformation with bisulfide in the heterogeneous reaction systems, as a result from the action of their active surface properties, especially the surface LAS, which have been reported to play important roles in their active performance as adsorbent, catalyst, and catalyst

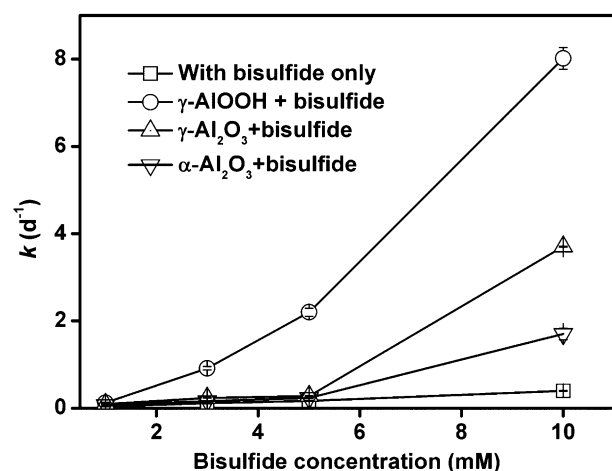


Figure 3. Variations in the pseudo-first-order kinetic parameters of metolachlor transformation at different concentrations of bisulfide with 10 g L⁻¹ aluminas at 25°C and pH 9.

supports [27]. The results also indicated that all the three kinds of aluminas, i.e., γ -AlOOH, γ -Al₂O₃, and α -Al₂O₃, showed very little adsorption abilities for metolachlor. In the aqueous solution, aluminas have relatively high points of zero charge that varied from approximately 7 to 10 [22] (the pH_{pzc} values here were determined to be 8.4, 8.5, and 8.7 for γ -AlOOH, γ -Al₂O₃, and α -Al₂O₃, respectively), whereas metolachlor was about either neutral or positively charged in the investigated pH range that was investigated in the present study. The positively charged surface of the alumina resulted in an electric double layer electrostatic on the surface of aluminas [27]. Therefore, the electrostatic adsorption did not occur, and metolachlor was stable in the alumina suspensions.

3.2 Metolachlor transformation under different pH

The different reaction conditions may exert effects on the surface properties of aluminas, consequently affecting the metolachlor transformation processes with bisulfide in the heterogeneous reaction systems. Therefore, the fundamental reaction conditions, especially the pH of the solution during metolachlor transformation by bisulfide on alumina were investigated for disclosing the transformation mechanisms. The transformation processes under different pH conditions were also modeled by pseudo-first-order kinetics. The concentration variation during the metolachlor (10 mg L⁻¹) transformation processes at different pH values is shown in Figures 4a–c for γ -AlOOH, γ -Al₂O₃, and α -Al₂O₃, respectively. In the absence of bisulfide, the metolachlor concentration remained stable within the studied pH range of 6–10, which indicates that metolachlor did not undergo hydrolysis transformation under acidic, neutral, or basic conditions. In the presence of bisulfide, metolachlor achieved efficient transformation possesses under all the studied pH conditions for all the three aluminas. Figure 4d shows the k value variations at different pH values. Minor differences in metolachlor transformation rates were observed among the acidic, neutral, and basic conditions in the presence of aluminas. Notably, for all α -Al₂O₃ setups, metolachlor achieved 100% transformation at a reaction time of 28 days and with k values of 0.103 ± 0.0044 ($R^2 = 0.895$), 0.127 ± 0.0113 ($R^2 = 0.949$), and 0.164 ± 0.0074 days⁻¹ ($R^2 = 0.964$) under acidic, neutral, and basic conditions, respectively. In the presence of aluminas, metolachlor underwent an efficient transformation process via bisulfide whether under acidic, neutral, or basic conditions, although the more basic conditions were slightly more favorable for metolachlor transformation compared with the more acidic ones.

Basic conditions were also reported to be more favorable for propachlor dechlorination by dithionite, and base hydrolysis is one of the routes for propachlor transformation [16]. In the presence of aluminas, metolachlor transformation rates by bisulfide were all highly efficient due to the active properties of the alumina surface. However, metolachlor transformation with bisulfide on aluminas under different pH were observed to follow the same trend (Fig. 4) as that of propachlor transformation by dithionite, i.e., the higher transformation rates were achieved under higher pH reaction conditions, although with slight differences among the different pH conditions. The mechanisms of base-catalyzed reactions may parallel with the reactions of environmental nucleophiles (such as reduced sulfur species) catalyzed by (hydr)oxide minerals as important counterpart reactions through base-catalyzed processes [8]. Furthermore, in alkaline conditions containing active minerals, some of the bisulfide was integrated to form polysulfides through

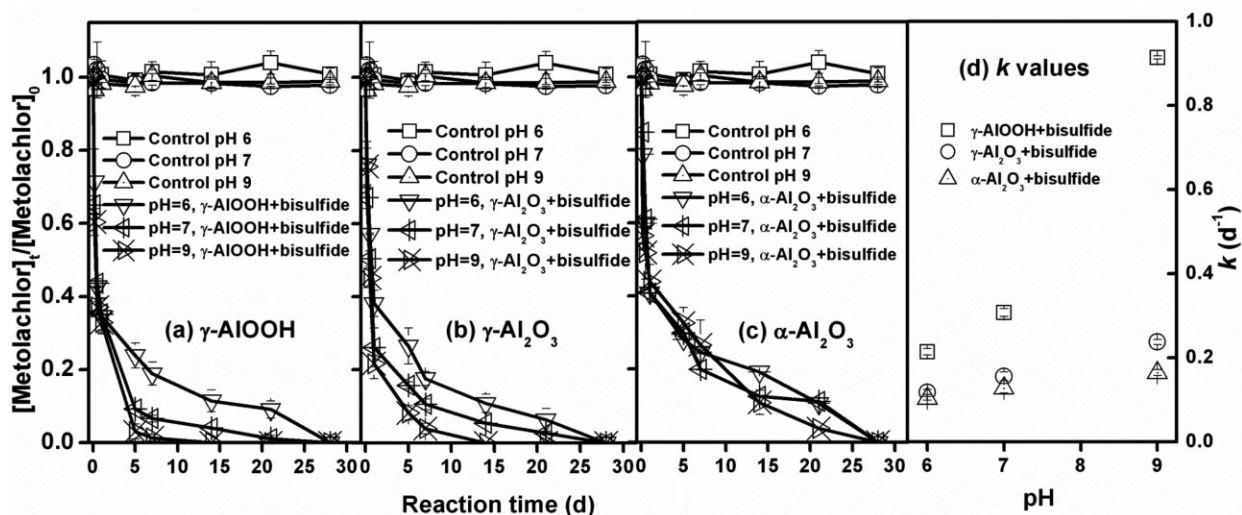


Figure 4. Transformation of metolachlor with an initial concentration of 10 mg L^{-1} using 3 mM bisulfide on the three aluminas (10 g L^{-1}) at 25°C and different pH conditions. (a) γ -AlOOH; (b) γ -Al₂O₃; (c) α -Al₂O₃; (d) the k value variations in the presence of the three aluminas at different pH conditions.

oxidation by residue O₂ that probably dissolved in the solvent of methanol, which are more reactive as nucleophiles than bisulfide [12].

3.3 FTIR studies of the interfacial mechanism on aluminas

Figure 5 shows the FTIR spectra of the three aluminas studied under three different circumstances, i.e., the original samples with no reactions, after reaction with metolachlor only, and after reaction with both metolachlor and bisulfide. For the original γ -AlOOH with no reactions (curve a₁), the bands at high wave numbers of 3304 and 3090 cm^{-1} (two split broad bands) are attributed to $-\text{OH}$ bond stretching vibration, whereas the bands at 2101 and 1640 cm^{-1} are attributed to $\text{H}-\text{O}-\text{H}$ bond stretching vibration. The band at 1072 cm^{-1} corresponds to the $\delta_s \text{Al}-\text{O}-\text{H}$ of boehmite, and the four bands at 884 , 740 , 623 , and 488 cm^{-1} are attributed to the $\text{Al}-\text{O}$ band stretching vibration of boehmite [33]. For γ -Al₂O₃ sample with no reactions (curve b₁), the $\text{H}-\text{O}-\text{H}$ and $-\text{OH}$ bonds were also found but with much lower transmittance intensities in the spectra. Meanwhile, for α -Al₂O₃ sample before any reactions (curve c₁), the abovementioned bands were not completely detected, which indicate no $\text{H}-\text{O}-\text{H}$ and $-\text{OH}$ bonds on the α -Al₂O₃ surface before hydration. For the stretching vibration of bands at low wave numbers on γ -Al₂O₃ and α -Al₂O₃, i.e., the bands at 766 , 656 , 620 , 615 , 603 , 562 , 553 , and 465 cm^{-1} , they are all attributed to the pseudoboehmite stretching [34, 35]. After reacting with metolachlor, almost no changes were found for all the bands in the spectra for γ -AlOOH (curve a₂) and γ -Al₂O₃ (curve b₂) except for the increase in very small intensities. For α -Al₂O₃ (curve c₂), the bonds corresponding to $-\text{OH}$ and $\text{H}-\text{O}-\text{H}$ appeared, although with lower intensities, which resulted from the hydration of the α -Al₂O₃ surface with the water when reacted with the metolachlor solution. After reacting with bisulfide and metolachlor for 24 h, the new bands at 1162 and 1397 cm^{-1} associated with surface sulfur species were detected on all the three aluminas, although with low intensities on γ -Al₂O₃

(curve b₃) and α -Al₂O₃ (curve c₃). These two new bands on γ -AlOOH (curve a₃) are more prominent than those on γ -Al₂O₃ and α -Al₂O₃. The band at 1162 cm^{-1} was reported to be resulted from $\text{Al}-\text{S}$ bond stretching, whereas the band at 1397 cm^{-1} was identified in the literature as aluminum sulfur compounds with $\text{Al}-\text{O}$ stretching [36, 37].

Outer-sphere and inner-sphere complexes are two types of surface complexes of anions on metal (hydr)oxides [38, 39], the property distinctions of which are very important for determining their chemical behavior at the water/solid interface [40]. When bisulfide reacted with alumina surfaces, the bisulfide anion would form inner- or outer-sphere surface sulfur species through different adsorption behaviors [40]. Figure 6 shows the significant concentration decreases of the total sulfur species when bisulfide was presented with the three aluminas in the absence of metolachlor. We also find that the adsorbed amount of total sulfur species on the three aluminas were almost similar although the surface area of these three aluminas were differentiated significantly, which may be resulted from the integrated factors from different physicochemical properties of aluminas, such as the particle size, pore size distribution, and the acidity of surface aluminol groups [27]. Overall, the disappearance of sulfur species in the solution clearly indicated the adsorption or adhesion of sulfur species on the aluminas. The reaction between bisulfide and aluminas are important for the accelerated transformation of metolachlor. Aluminum ions that bonded with bisulfide were able to facilitate metolachlor transformation by acting as inner-sphere surface complexes. After bisulfide was adsorbed by chemically bonding with aluminum ions on the surface of the aluminas, the surface protonation and reactivity of alumina oxide were enhanced accordingly. The surface $\text{Al}-\text{S}$ compounds would become more negative and polar by pulling a proton from the sulfur in the structure. Therefore, the surface sulfur compounds are stronger nucleophiles and give metolachlor a higher transformation rate. The intensities of the surface $\text{Al}-\text{S}$ compounds on aluminas are assumed mainly responsible for the metolachlor transformation rates in the heterogeneous reaction systems. As the FTIR results indicate, the $\text{Al}-\text{S}$ and $\text{Al}-\text{O}$ bond stretching on γ -AlOOH

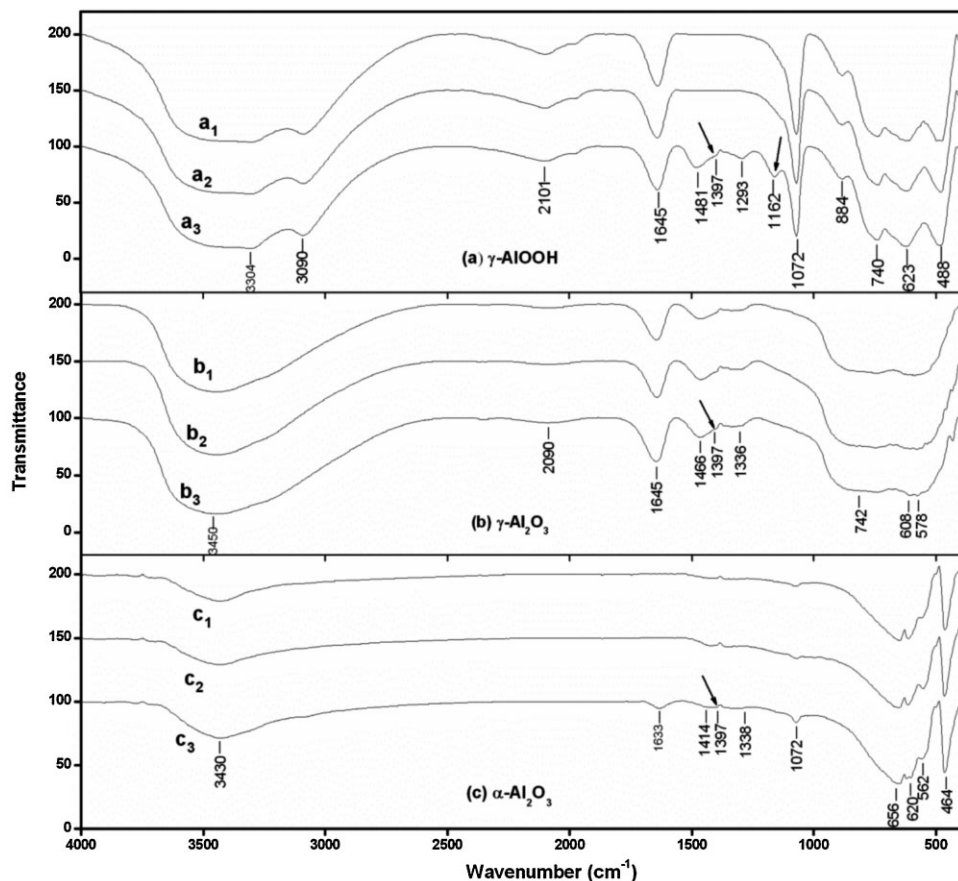


Figure 5. FTIR spectra of (a) γ -AlOOH, (b) γ -Al₂O₃, and (c) α -Al₂O₃. All the three figures each include three curves: the original sample with no reaction (curves a₁, b₁, and c₁), after reaction with metolachlor for 10 h (curves a₂, b₂, and c₂), and after reaction with metolachlor and dithionite simultaneously for 10 h (curves a₃, b₃, and c₃).

after undergoing the reaction achieved higher transmittance compared with those of γ -Al₂O₃ and α -Al₂O₃, which resulted in a higher metolachlor transformation rate with γ -AlOOH. With regard to γ -Al₂O₃ and α -Al₂O₃, only Al–O bond stretching was found after

the reaction and the intensities on these two aluminas also varied slightly. However, according to our previous report, the higher intensity of active LAS on γ -Al₂O₃ than on α -Al₂O₃ may lead to the higher metolachlor transformation rate with γ -Al₂O₃ [32].

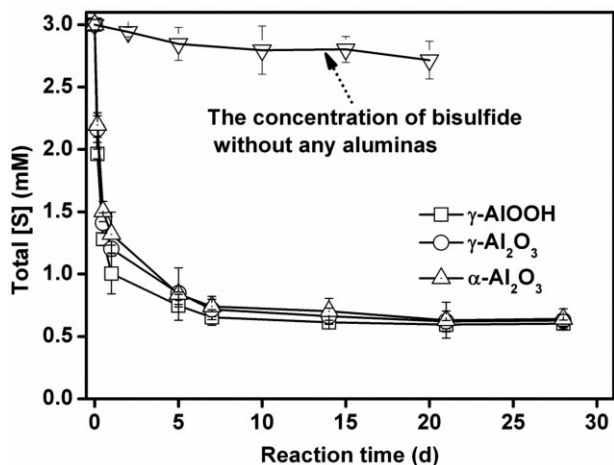


Figure 6. Concentration changes of the total sulfur species (3.0 mM initial concentrations) when reacted with the three alumina materials (10 g L⁻¹) without metolachlor at 25°C and pH 9.

3.4 Products of metolachlor transformation by bisulfide on aluminas

As shown in Fig. 7, the mass spectrum was obtained from the LC/MS analysis using the positive ion mode with [M+H]⁺ ion. Mercaptometolachlor with chlorine substituted by HS at *m/z* 281 was determined to be the main transformation product of metolachlor by bisulfide on alumina (γ -AlOOH). In the heterogeneous alumina systems with bisulfide under basic conditions, the dechlorination by nucleophilic substitution, which releases chloride ions, is the first step in nucleophilic transformation of chloroacetanilide herbicides [12, 14]. Metolachlor also reacted with bisulfide via the displacement of chlorine to form mercaptometolachlor [2-chloro-2'-ethyl-6'-methyl-N-(1-methyl-2-methoxyethyl) acetanilide]. Besides the mass at *m/z* 281, two unidentified minor peaks clearly relating to metolachlor were also observed at *m/z* 297 and 313. As reported in a previous paper [13], polysulfides may be formed through oxidation under alkaline conditions in heterogeneous reaction systems. The formed two products are

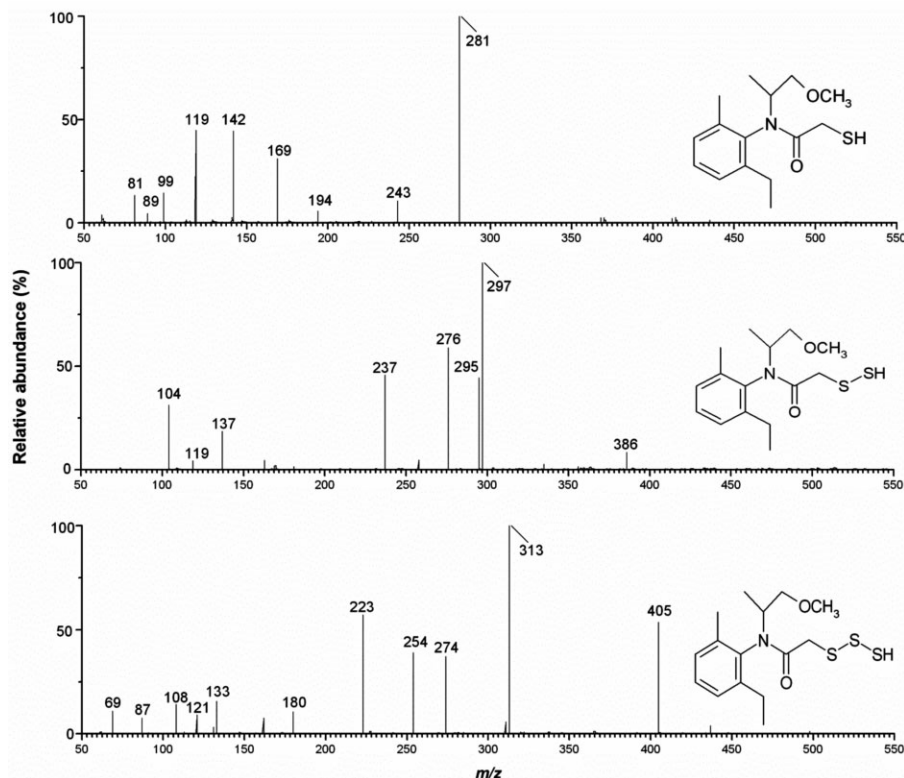


Figure 7. Mass spectra in positive mode for products of metolachlor transformation by 3mM bisulfide on γ -AlOOH (10gL^{-1}) for five days at 25°C and pH 9.

assumed to be disulfur (2S)-substituted and trisulfur (3S)-substituted derivatives, which are the products of metolachlor being reacted with the polysulfides that possibly formed in the alumina systems, although we did not detect polysulfide in the reaction systems possibly due to the low concentration or the decomposition of the little polysulfides. When treating metolachlor only with bisulfide, i.e., without alumina, in a homogeneous system, the ensuing metolachlor transformation obtained the same intermediates indicated by the total ion chromatogram, but the peak areas for all the three intermediates in the chromatogram were relatively lower than that obtained in the heterogeneous system (data not presented). The same products were also obtained in one previous study, which identified the polysulfur-substituted products in the nucleophilic reaction of chloroacetanilide herbicides with polysulfides (S_n^{2-}) [13]. The nature of the dechlorinated products substituted by nucleophiles suggests the bimolecular nucleophilic substitution (S_N2) mechanism being mainly responsible for metolachlor transformation by bisulfide [41], and the aluminas acting as the solid-mediator for accelerating the reactions between metolachlor and nucleophiles of bisulfide in the heterogeneous system [42, 43].

Chlorine dissociation from chlorinated organic pollutants can generate products that are more easily degraded, which is the important step in the decontamination of pollutants. The dechlorinated chloroacetanilides may be more biodegradable than the parent chloroacetanilides [44]. The toxicity of the chlorinated compounds also usually stems from the chlorine in the structure. Thus, the dissociation of chlorine from the organic compounds would largely reduce the toxicity. After dechlorination, chloroacetanilide herbicides would also be more readily biodegradable and the

toxicity, e.g., LC_{50} , would be largely reduced [12]. Therefore, understanding the transformation mechanism involving the initiation of metolachlor dechlorination by bisulfide is important for the detoxification of this herbicide in environments after application.

3.5 Proposed metolachlor transformation mechanism by bisulfide on aluminas

The effects of metal ions on the nucleophilic transformation of pesticides have been extensively studied in previous investigations. After adding the bisulfide and aluminas, aluminum ions on the aluminas coordinated with the bisulfide and raised surface reactivity toward the electrophilic site. The FTIR results indicate that the surface-active sulfur species through the Al–S and Al–O–S bonds may be formed on the alumina surface after reacting with bisulfide for 24 h. After adsorption via bond formation on aluminas, the adsorption reaction and protonation of surface groups can form surface Al–S compounds [37], such as $\equiv\text{AlOHSO}_2^{2-}$, $\equiv\text{AlSO}_2^{2-}$, $\equiv\text{AlSO}_2^-$, and $\equiv\text{AlSO}_3^{3-}$. The surface Al–S compounds would become more negative and polar by pulling a proton from the S in the structure. Therefore, they can act as the stronger reductants and nucleophiles in heterogeneous reaction systems and give metolachlor a higher transformation rate than bisulfide alone in homogeneous reaction systems. Furthermore, although the reaction atmosphere that with O_2 presence or not have been reported exerting little effect on nucleophilic stability of chloroacetanilide herbicides when with the same nucleophiles [16], the residue O_2 that probably came from the non-deoxygenated methanol can affect the

formation of heterogeneous nucleophiles, in which bisulfide can be integrated into polysulfides through oxidation by the residue O_2 especially in alkaline conditions in the presence of active minerals, which are more reactive as strong nucleophiles than bisulfide [13]. By reacting with the strong heterogeneous nucleophiles, the chlorine in the metolachlor structure is dissociated by nucleophilic substitution, and the sulfur compounds were combined in the molecular structure of the product.

4 Conclusions

In this study, the nucleophilic transformations of metolachlor by bisulfide in heterogeneous systems with different aluminas were investigated. The results suggest the important roles of alumina and bisulfide in accelerating the transformation rates of metolachlor in environments. As a strong nucleophile, bisulfide can facilitate efficient metolachlor transformation rates in the absence of aluminas. While with aluminas present in the system, metolachlor transformation rates were further significantly increased. As demonstrated subsequently, a higher reaction pH was more favorable for metolachlor transformation. The three aluminas varied in efficiency for accelerating the metolachlor transformation processes owing to the varied intensities of active sites on their respective surfaces, which can be ranked as $\gamma\text{-AlOOH} > \gamma\text{-Al}_2\text{O}_3 > \alpha\text{-Al}_2\text{O}_3$. In heterogeneous systems, the surface sulfur compounds formed through the Al–S and Al–O bonds on aluminas were responsible for the enhanced metolachlor transformation rates, given their stronger nucleophilic abilities compared with bisulfide. The metolachlor transformation products obtained through the molecular chlorine substitution by surface sulfur species were identified. The primary mechanism for metolachlor transformation with bisulfide involved S_N2 nucleophilic substitution, however, the overall reaction mechanisms with aluminas as the reaction mediators are still need to be further investigated with a thorough analysis on transformation products and an appropriate mass balance.

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References

- G. Chesters, G. V. Simsiman, J. Levy, B. J. Alhajjar, R. N. Fathulla, J. M. Harkin, Environmental Fate of Alachlor and Metolachlor, *Rev. Environ. Contam. Toxicol.* **1989**, *110*, 1–74.
- D. Donaldson, T. Kiely, A. Grube, *Pesticide Industry Sales and Usage: 1998 and 1999 Market Estimates*, USEPA, Washington, DC **2002**.
- D. W. Kolpin, E. M. Thurman, S. M. Linhart, Finding Minimal Herbicide Concentrations in Ground Water? Try Looking for Their Degradates, *Sci. Total Environ.* **2000**, *248*, 115–122.
- F. Rhoton, M. Shipitalo, D. Lindbo, Runoff and Soil Loss from Midwestern and Southeastern US Silt Loam Soils as Affected by Tillage Practice and Soil Organic Matter Content, *Soil Tillage Res.* **2002**, *66*, 1–11.
- L. J. Dziuk, Propachlor, *Encyclopedia of Toxicology*, 2nd ed. (Ed.: P. Wexler), Elsevier, Amsterdam **2005**, pp. 527–529.
- M. A. S. Aly, P. Schröder, Effect of Herbicides on Glutathione S-transferases in the Earthworm *Eisenia fetida*, *Environ. Sci. Pollut. Res.* **2008**, *15*, 143–149.
- O. Osano, D. Nzyuko, M. Tole, W. Admiraal, The Fate of Chloroacetanilide Herbicides and Their Degradation Products in the Nzoia Basin, Kenya, *Ambio* **2003**, *32*, 424–427.
- D. L. Carlson, K. D. Than, A. L. Roberts, Acid- and Base-Catalyzed Hydrolysis of Chloroacetamide Herbicides, *J. Agric. Food Chem.* **2006**, *54*, 4740–4750.
- T. C. Cavalier, T. L. Lavy, J. D. Mattice, Persistence of Selected Pesticides in Ground-Water Samples, *Ground Water* **1991**, *29*, 225–231.
- H. H. Zheng, C. L. Ye, Identification of UV Photoproducts and Hydrolysis Products of Butachlor by Mass Spectrometry, *Environ. Sci. Technol.* **2001**, *35*, 2889–2895.
- E. E. Moran, Q. K. Timerghazin, E. Kwong, A. M. English, Kinetics and Mechanism of S-Nitrosothiol Acid-Catalyzed Hydrolysis: Sulfur Activation Promotes Facile NO^+ Release, *J. Phys. Chem. B* **2011**, *115*, 3112–3126.
- X. Cai, G. Sheng, W. Liu, Degradation and Detoxification of Acetochlor in Soils Treated by Organic and Thiosulfate Amendments, *Chemosphere* **2007**, *66*, 286–292.
- A. R. Loch, K. A. Lippa, D. L. Carlson, Y. P. Chin, S. J. Traina, A. L. Roberts, Nucleophilic Aliphatic Substitution Reactions of Propachlor, Alachlor, and Metolachlor with Bisulfide (HS^-) and Polysulfides (S_n^{2-}), *Environ. Sci. Technol.* **2002**, *36*, 4065–4073.
- J. Y. Gan, Q. Q. Wang, S. R. Yates, W. C. Koskinen, W. A. Jury, Dechlorination of Chloroacetanilide Herbicides by Thiosulfate Salts, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5189–5194.
- H. Bian, J. Chen, X. Cai, P. Liu, Y. Wang, L. Huang, X. Qiao, L. Huang, Dechlorination of Chloroacetanilide Herbicides by Plant Growth Regulator Sodium Bisulfite, *Water Res.* **2009**, *43*, 3566–3574.
- C. S. Liu, K. Shih, L. Wei, F. Wang, F. B. Li, Kinetics and Mechanism of Propachlor Reductive Transformation through Nucleophilic Substitution by Dithionite, *Chemosphere* **2011**, *85*, 1438–1443.
- N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford **1997**.
- X. Y. Dong, R. F. Shen, R. F. Chen, Z. L. Zhu, J. F. Ma, Secretion of Malate and Citrate from Roots is Related to High Al-Resistance in *Lespedeza Bicolor*, *Plant Soil* **2008**, *306*, 139–147.
- H. G. Dill, The “Chessboard” Classification Scheme of Mineral Deposits: Mineralogy and Geology from Aluminum to Zirconium, *Earth Sci. Rev.* **2010**, *100*, 1–420.
- H. A. Al-Abadleh, V. H. Grassian, Oxide Surfaces as Environmental Interfaces, *Surf. Sci. Rep.* **2003**, *52*, 63–161.
- E. Álvarez, M. Fernández-Sanjurjo, X. L. Otero, F. Macías, Aluminum Speciation in the Bulk and Rhizospheric Soil Solution of the Species Colonizing an Abandoned Copper Mine in Galicia (NW Spain), *J. Soils Sediments* **2011**, *11*, 221–230.
- S. Goldberg, J. A. Davis, J. D. Hem, The Surface Chemistry of Aluminum Oxides and Hydroxides, in *The Environmental Chemistry of Aluminum*, Chapter 7, 2nd ed. (Ed.: G. Sposito), CRC Press, Boca Raton, FL **1996**, pp. 271–331.
- M. E. Essington, R. M. Anderson, Competitive Adsorption of 2-Ketogluconate and Inorganic Ligands onto Gibbsite and Kaolinite, *Soil Sci. Soc. Am. J.* **2007**, *72*, 595–604.
- M. Ernst, F. Lurot, J. Schrotter, Catalytic Ozonation of Refractory Organic Model Compounds in Aqueous Solution by Aluminum Oxide, *Appl. Catal. B* **2004**, *47*, 15–25.
- H. He, J. Liu, Y. Mu, Y. Yu, M. Chen, Heterogeneous Oxidation of Carbonyl Sulfide on Atmospheric Particles and Alumina, *Environ. Sci. Technol.* **2005**, *39*, 9637–9642.
- K. C. Hass, W. F. Schneider, A. Curioni, W. Andreoni, The Chemistry of Water on Alumina Surfaces: Reaction Dynamics from First Principles, *Science* **1998**, *282*, 265–268.

- [27] B. Kasprzyk-Hordern, Chemistry of Alumina, Reactions in Aqueous Solution and Its Application in Water Treatment, *Adv. Colloid Interface Sci.* **2004**, *110*, 19–48.
- [28] Y. Y. Tang, S. S. Y. Chui, K. M. Shih, L. R. Zhang, Copper Stabilization via Spinel Formation during the Sintering of Simulated Copper-Laden Sludge with Aluminum-Rich Ceramic Precursors, *Environ. Sci. Technol.* **2011**, *45*, 3598–3604.
- [29] J. Goerke, J. de Gier, P. P. M. Bonsen, Silica Gel Stimulates the Hydrolysis of Lecithin by Phospholipase A, *Biochim. Biophys. Acta* **1971**, *248*, 245–253.
- [30] J. A. Laszlo, D. L. Compton, X. L. Li, Feruloyl Esterase Hydrolysis and Recovery of Ferulic Acid from Jojoba Meal, *Ind. Crops Prod.* **2006**, *23*, 46–53.
- [31] F. J. Millero, The Thermodynamics and Kinetics of the Hydrogen Sulfide System in Natural Waters, *Mar. Chem.* **1986**, *18*, 121–147.
- [32] C. S. Liu, K. Shih, Y. X. Gao, F. B. Li, L. Wei, Dechlorinating Transformation of Propachlor through Nucleophilic Substitution by Dithionite on the Surface of Alumina, *J. Soils Sediments* **2012**, *12*, 724–733.
- [33] D. Y. Li, Y. S. Lin, Y. C. Li, D. L. Shieh, J. L. Lin, Synthesis of Mesoporous Pseudo-boehmite and Alumina Template with 1-Hexadecyl-2,3-Dimethyl-Imidazolium Chloride, *Microporous Mesoporous Mater.* **2008**, *108*, 276–282.
- [34] T. Z. Ren, Z. Y. Yuan, B. L. Su, Microwave-Assisted Preparation of Hierarchical Mesoporous–Macroporous Boehmite ALOOH and γ -Al₂O₃, *Langmuir* **2004**, *20*, 1531–1534.
- [35] G. Zu, J. Shun, X. Wei, X. Ni, Z. Zhang, J. Wang, G. Liu, Preparation and Characterization of Monolithic Alumina Aerogels, *J. Non-Cryst. Solids* **2011**, *357*, 2903–2906.
- [36] M. Skoglundh, A. Ljungqvist, M. Petersson, E. Fridell, N. Cruise, O. Augustsson, E. Jobson, SO₂ Promoted Oxidation of Ethyl Acetate, Ethanol and Propane, *Appl. Catal. B* **2001**, *30*, 315–328.
- [37] F. J. Gracia, S. Guerrero, E. E. Wolf, J. T. Miller, A. J. Kropf, Kinetics, Operant FTIR, and Controlled Atmosphere EXAFS Study of the Effect of Sulfur on Pt-Supported Catalysis during CO Oxidation, *J. Catal.* **2005**, *233*, 372–387.
- [38] K. Hayes, J. O. Leckie, Modeling Ionic Strength Effects on Cation Adsorption at Hydrous Oxide/Solution Interfaces, *J. Colloid. Interface Sci.* **1987**, *115*, 564–572.
- [39] S. J. Hug, In Situ Fourier Transform Infrared Measurements of Sulfate Adsorption on Hematite in Aqueous Solutions, *J. Colloid Interface Sci.* **1997**, *188*, 415–422.
- [40] H. Wijnja, C. P. Schulthess, Interaction of Carbonate and Organic Anions with Sulfate and Selenate Adsorption on an Aluminum Oxide, *Soil Sci. Soc. Am. J.* **2000**, *64*, 898–908.
- [41] K. A. Lippa, A. L. Roberts, Nucleophilic aromatic substitution reactions of chloroazines with bisulfide (HS⁻) and polysulfides (S_n²⁻), *Environ. Sci. Technol.* **2002**, *36*, 2008–2018.
- [42] S. Oh, P. C. Chiu, Graphite- and Soot-Mediated Reduction of 2,4-Dinitrotoluene and Hexahydro-1,3,5-Trinitro-1,3,5-Triazine, *Environ. Sci. Technol.* **2009**, *43*, 6983–6988.
- [43] W. Xu, K. E. Dana, W. A. Mitch, Black Carbon-Mediated Destruction of Nitroglycerin and RDX by Hydrogen Sulfide, *Environ. Sci. Technol.* **2010**, *43*, 6409–6415.
- [44] I. Scheunert, H. Parlar, *Terrestrial Behavior of Pesticides*, Springer-Verlag, New York **1992**.