Research Article

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The oxidative degradation of sulfadiazine at the interface of α-MnO_2 and water

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Abstract

BACKGROUND: Sulfadiazine (SD), a widely used antibiotic chemical, has been detected in contaminated water and soils. Manganese dioxides are common minerals with a high redox potential and can act as active oxidants for SD degradation in wastewater treatment.

RESULTS: α-MnO_2 was used to promote SD oxidative degradation. At pH 4.6 and 25 °C, 92.7% of SD (0.02 mmol L^{-1}) was degraded by 1.0 g L^{-1} α-MnO_2. SO_4^{2-} was detected as the inorganic end product from the mineralization of SD. The ecological toxicity index of average well color development (AWCD) in SD solution was 2.01 after the solution was degraded by α-MnO_2 for 2 h, while the AWCD was 0.48 for the solution without α-MnO_2 treatment. The degradation rate of SD can be improved by increasing the dosages of α-MnO_2 and the reaction temperature, but the rate was limited by increased initial SD concentration and reaction pH.

CONCLUSION: SD can be effectively degraded and mineralized with α-MnO_2. These results are helpful for removing antibiotics by manganese dioxides in the environment, and also for exploring new technology for wastewater treatment.

Keywords: manganese dioxide; antibiotics; oxidation; interface; cryptomelane

INTRODUCTION

Sulfonamide antibiotics include a class of synthetic, primarily bacteriostatic, sulfanilamide derivatives and are the most frequently detected antibiotics in surface waters.[1] Sulfonamide antibiotics was used in human therapy, livestock production, and aquaculture. Treated individuals excrete a fraction of the excess dose as the unaltered parent compound or an acetylated metabolite[2,3] susceptible to reactivation by bacterial deacetylation.[4] Disposal of domestic and hospital waste, fertilization with animal manure, runoff and infiltration from confined animal feeding result in the entry of sulfonamides into the environment.[5] Sulfonamide antibiotics have the potential to cause pathogenic bacteria drug-resistance and pose adverse health effects to humans.[6] To date, very little information is available on the fate and transformation of antibiotics in soil/water environments compared with other well-known xenobiotics.[7,8]

Sulfonamides are not readily biodegradable and incomplete degradation is a feature of biological treatment processes.[9,10] Thus, the chemical oxidation process for sulfonamides elimination has received increasing attention in the past several years.[11–13] Although significant transformation of sulfonamide occurs during disinfection of municipal wastewater and drinking water using free chlorine[11] and chlorine dioxide,[12] chlorination may result in disinfection byproducts that would remain in the treated water. Ozonation has great potential to remove sulfonamides,[13] but ozone can form the potent carcinogenic bromate ion by reacting with bromide present in water. Another advanced oxidation process is photocatalysis, which can transform sulfonamides on titanium dioxide.[14] One promising method may be the application of manganese dioxides, which can address issues associated with current methodologies, in treating sulfonamide antimicrobials.

Manganese is the third most abundant transition metal in the earth crust and is important in both biological and environmental processes.[15] Manganese dioxides, possibly the most important natural oxidants with redox potential of 1.23 V,[16] are reactive surfaces that play an important role in affecting the fate and degradation of organic pollutants in soil and aquatic environments.[16,17] In fact, manganese dioxides have been demonstrated to be powerful oxidizing agents in aqueous media to degrade a wide range of organic contaminants, such as phenol,[18] aniline,[19] aliphatic amine,[20] aromatic amine,[17] triazine,[21] benzothiazole,[22] and even antibiotics.[16]

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This work has studied for the first time, the degradation of sulfonamides by manganese dioxides. Cryptomelane (α-MnO_2), one of the most stable polymorph of manganese dioxides was synthesized to systematically investigate the oxidative degradation of sulfadiazine (SD, 4-amino-N-(2-pyrimidinyl) benzene sulfonamide, one of the sulfonamide class of antibiotics). The objectives are (a) to determine the kinetics of the sulfadiazine oxidation under different conditions (pH, initial concentration of sulfonamides and reaction temperature); (b) to evaluate the ecological toxicity of sulfonamides after degradation by MnO_2; (c) to propose a potential mechanism of sulfadiazine oxidation by MnO_2.

MATERIALS AND METHODS

Chemicals

SD chemical (A.R.) was purchased from Aldrich (Louis, MO, USA). Other chemicals (analytical grade) were obtained from Guangzhou Chemical Co., China. All chemicals were used as received without further purification. All solutions were prepared with high purity water obtained from a Milli-Q system (≥18 MΩ, Barnstead) and stored at less than 5 °C before use.

α-MnO_2 preparation and characterization

α-MnO_2 was prepared through a low-temperature liquid-phase comproportionation method.[23] 4.20 g of $KMnO_4$ and 1.79 g of $MnSO_4 \bullet H_2O$ were added to 80 mL of distilled water at room temperature to form a mixed solution, which was then transferred into a Teflon-lined stainless steel autoclave, sealed and maintained at 130 °C for 12 h. After reaction, the resulting solid product was filtered, washed with distilled water to remove ions possibly remained in the final products, and finally dried at 60 °C as α-MnO_2 powder.

The prepared α-MnO_2 powder was characterized by X-ray powder diffraction (XRD) and Brunauer–Emmett–Teller (BET). The XRD characterization of α-MnO_2 was recorded on a Rigaku D/Max-III A diffract meter at room temperature, operated at 30 kV and 30 mA with Cu$K\alpha$ radiation ($\lambda = 0.154$ nm). The BET surface area and total pore volume of α-MnO_2 were measured by the BET method, in which N_2 adsorption at 77 K was applied and a Carlo Erba Sorptometer used.[24] The average size of α-MnO_2 was determined by the Scherrer formula based on the (110) peak.[25]

EXPERIMENTAL PROCEDURES

SD degradation with α-MnO_2

The oxidative degradation of SD by α-MnO_2 in aqueous solution was conducted in borosilicate glass serum bottles (effective volume 20 mL) with aluminum crimps and Teflon-lined butyl rubber septa. The bottles were placed in an orbital shaker at 200 rpm in the absence of light during the reaction. Four batch experiments were involved to study the effect of various operational factors on oxidative degradation of SD with α-MnO_2. The first set was used to investigate the effect of initial SD concentrations, and experiments were conducted at an initial SD concentration of 0.004, 0.01, 0.02, 0.03 and 0.04 mmol L^{-1} with 20 mg α-MnO_2 (1.0 g L^{-1}) at pH 4.6. The second set was used to investigate the effect of α-MnO_2 dosages, and the tests were performed at a loading of 0.1, 0.3, 0.6, 1.0, 2.0 and 4.0 g L^{-1} with 0.02 mmol L^{-1} SD at pH 4.6. To study the effect of pH, a third set was performed over the pH range 3.6–9.0 with 0.02 mmol L^{-1} SD and 1.0 g L^{-1} α-MnO_2. The pH values were adjusted by buffer solutions as described previously.[22] To study the effect of reaction temperature, a fourth set was performed at temperatures of 15 ± 1 °C, 25 ± 1 °C, 30 ± 1 °C, 40 ± 1 °C and 50 ± 1 °C with 0.02 mmol L^{-1} SD and 1.0 g L^{-1} α-MnO_2.

Determination of ecological toxicity of SD degradation samples

Red soil was sampled at depths of 0–20 cm from the top on a field site near the laboratory. The soil sample collected was dried at 25 °C before being sieved through a 2 mm screen to remove stones and root fragments. Using the weighing method, the screened soil sample was adjusted to a water-holding capacity (WHC) of 50% and incubated in a polythene bottle at 25 °C for 7 days before soil microbial diversity analyses.

Soil microbial functional diversity was analyzed by developing community-level physiological profiles using Biolog® assays. The soil sample (10.0 g) was extracted in 100 mL of sterile saline solution (0.85%, m/v) with glass beads (I.D. 3.0 mm) on a rotary shaker at 200 rpm for 30 min at 25 °C. After being diluted 100-fold and settled for 10 min, 10.0 mL of the dilutions been mixed with 10.0 mL SD solution after 0.5 or 2 h degradation by MnO_2, and then the mixtures were added to 90 mL of sterile water. After mixing, 150 µL of the suspension was added to each cell of a Biolog-ECO plate. The light absorbance at 590 nm was recorded using a Biolog automated BIOLOG Microplate Reader (Biolog, Hayward, CA, USA) and the data were collected by Microlog 4.01 software (Biolog). The plates were then sealed inside a plastic bag and incubated at 25 °C in the dark, and recorded every 24 h over 7 days. During the incubation, no contamination was found in the control cells (only water).

Analytical methods

The SD concentration in the collected samples was determined by high performance liquid chromatography (HPLC, Waters 2487, Milford, Ma, USA). A mobile phase consisting of 30% methanol, 69% water and 1% (v/v) acetic acid was operated at a flow rate of 1.0 mL min^{-1}, and a UV detector (UV-vis SPD-10AVP) was used to determine SD concentration at 265 nm. The mineralized products of SO_4^{2-} from SD degradation in the collected samples were determined by ion chromatography (IC Dionex, ICS-90, Sunnyvale, CA, USA), coupled with a RFIC™ IonPac® AG14A-7 µm Guard Column (4 mm, 50 mm), AMMS III micromembrane suppressor, IonPac® AS14A-7 µm Analytical Column (4 mm, 250 mm), and a DS5 Detection Stabilizer conductivity detector. An eluent solution, containing 8.0 mmol L^{-1} Na_2CO_3 and 1.0 mmol L^{-1} $NaHCO_3$, was pumped at a flow rate of 1.0 mL min^{-1}. Chemical oxygen demand (COD) determination was performed directly on the sample according to Standard Methods.[26] The concentration of released Mn^{2+} ion was determined by flame atomic absorption spectrophotometry (WFX-130, Beijing Rayleiah Analytical Instrument Co., China). All experiments were conducted in triplicate, and the experimental results presented in the text are the average values.

RESULTS AND DISCUSSION

Properties of α-MnO_2

The prepared α-MnO_2 sample was examined by XRD. The XRD pattern (Fig. 1) indicated that the sample exhibited all seven peaks ((110), (200), (310), (211), (301), (411) and (521)) that are attributable to α-MnO_2 (JCPDS 44–0141).[27] The average crystal size of α-MnO_2 was determined to be 24.8 nm using the Scherrer formula with the (110) peak.[25] Using the BET method, the specific surface area of β-MnO_2 was determined to be 61.75 m^2 g^{-1} and the total pore volume, 0.15 cm^3 g^{-1}.[24]

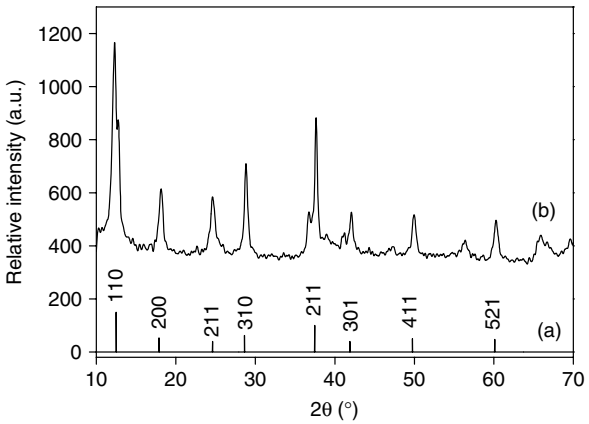

Figure 1. XRD patterns of standard α-MnO_2 (a) and the prepared α-MnO_2 powder (b).

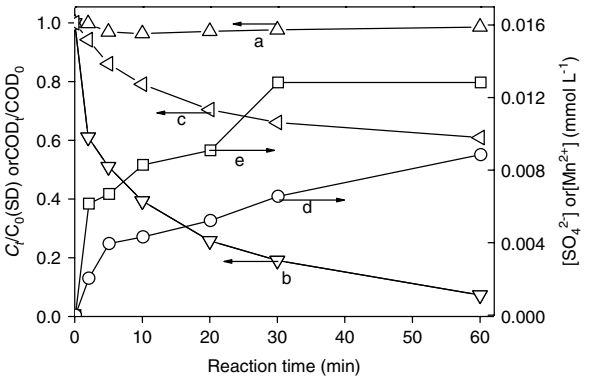

Figure 2. Degradation of SD with initial concentration of 0.02 mmol L^{-1} by α-MnO_2 at 25 °C and pH 4.6: (a) in the absence of α-MnO_2; (b) in the presence of 1.0 g L^{-1} α-MnO_2; and (c) COD removal; (d) concentration of final product of SO_4^{2-}; and (e) concentration of generated Mn^{2+}, in the presence of 1.0 g L^{-1} α-MnO_2.

Oxidative degradation of SD with α-MnO_2

The results of SD degradation at pH 4.6 and 25 °C are presented in Fig. 2. The results fitted pseudo-first-order kinetics well. In the absence of α-MnO_2 (curve *a*), SD concentration remained almost unchanged after 60 min reaction. However, in the presence of 1.0 g L^{-1} α-MnO_2, the concentration of SD was dramatically degraded by 92.7% after 60 min (curve *b*). It was found that SD can be mineralized by α-MnO_2, indicated by the observed COD removal of 39.1% after 60 min (curve *c*). Also, the SO_4^{2-} ion was detected as one of the main final products of SD mineralization. The final concentration of SO_4^{2-} was determined to be 0.009 mmol L^{-1}, representing 45% of the total sulphur in the original SD solution (curve *d*). Furthermore, solid α-MnO_2 dissolved slightly and was reduced to Mn^{2+} ions through the SD oxidation reaction. The amount of Mn^{2+} in solution was determined to be 0.013 mmol L^{-1} after 60 min (curve *e*), suggesting that the consumption of 0.0075 mmol L^{-1} MnO_2 can completely mineralize 0.008 mmol L^{-1} organic-S into SO_4^{2-}. The formation of Mn^{2+} indicated that SD degradation was a consequence of oxidation by α-MnO_2, which was reduced to Mn^{2+} by SD.

Toxicity reduction

Because of its toxicity, SD may have a negative ecological effect and inhibit the diversity of communities.[8] The toxicity evaluation of SD degradation process is thus of crucial importance. The intermediates of SD oxidative degradation, such as 4-hydroxysulfadiazine and N-acetylsulfadiazine,[28] may be more toxic than SD itself.[29] In this study, the average well color development (AWCD) was used as an indicator of microbial activity to evaluate the effect of the SD degradation process on the functional diversity of microbiology (Fig. 3). The samples for toxicity evaluation were taken from the batch containing 0.02 mmol L^{-1} SD with 1.0 g L^{-1} α-MnO_2 at pH 4.6 after 0.5 and 2 h incubation. AWCD in the control (only water without SD) increased rapidly after 24 h and reached 2.01 after 144 h incubation. In the test with SD itself, AWCD increased slowly to 0.48 after 144 h, indicating that SD has a significant negative effect on microbial diversity. In the incubation with SD treated with α-MnO_2 for 0.5 h, the rate of AWCD increase was much greater than that of SD itself and approached a maximum AWCD of 1.10. The sample after 2 h incubation can further decrease the toxicity, with a maximum AWCD of 1.64. It is clear that the toxicity of SD solution may be significantly decreased after degradation by α-MnO_2.

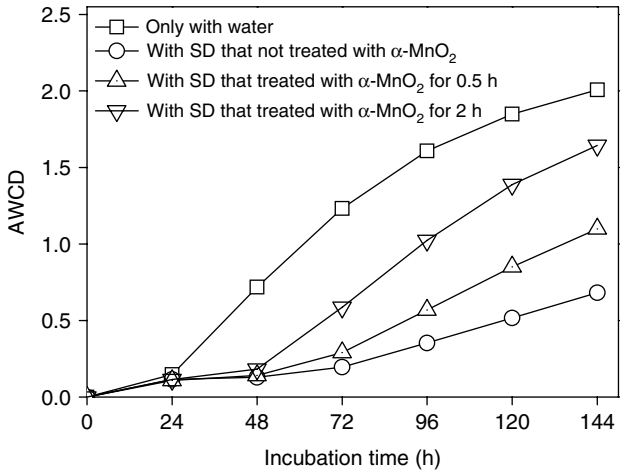

Figure 3. Effect of SD and its intermediate products on soil microbial diversity (two samples taken from the batch with 0.02 mmol L^{-1} SD and 1.0 g L^{-1} α-MnO_2 at pH 4.6 after 0.5 and 2 h incubation).

Effect of SD initial concentration, α-MnO_2 dosages, and pH values on SD degradation by α-MnO_2

The dependence of SD oxidative degradation on the initial SD concentration with 1.0 g L^{-1} α-MnO_2 at pH 4.6 and 25 °C is shown in Fig. 4(A). On increasing the SD initial concentration from 0.004 to 0.04 mmol L^{-1}, the SD removal decreased from 93.2% to 72.3%. This suggested that the lower initial concentration of SD was more favorable for degradation, since the adsorbed SD on α-MnO_2 can be more efficiently oxidized by α-MnO_2. With an excess amount of SD, α-MnO_2 with limited specific surface area (61.75 m^2 g^{-1}) cannot provide enough active sites for SD, which leads to a lower degradation rate.

The dependence of SD degradation on the dosages of α-MnO_2 at pH 4.6 and 25 °C is shown in Fig. 4(B). With increased α-MnO_2 dosages, degradation rate increased accordingly. The SD removals were 33.5%, 55.0%, 71.6%, 92.7%, 96.3%, and 97.2% for α-MnO_2 at loadings of 0.1, 0.3, 0.6, 1.0, 2.0, and 4.0 g L^{-1}, respectively. With a fixed amount of SD, a higher dosage of α-MnO_2 can provide more oxidative active sites for SD oxidation, resulting in a higher SD degradation rate. At low α-MnO_2 dosages, an increase in α-MnO_2 amount can improve the degradation rate to a greater extent.

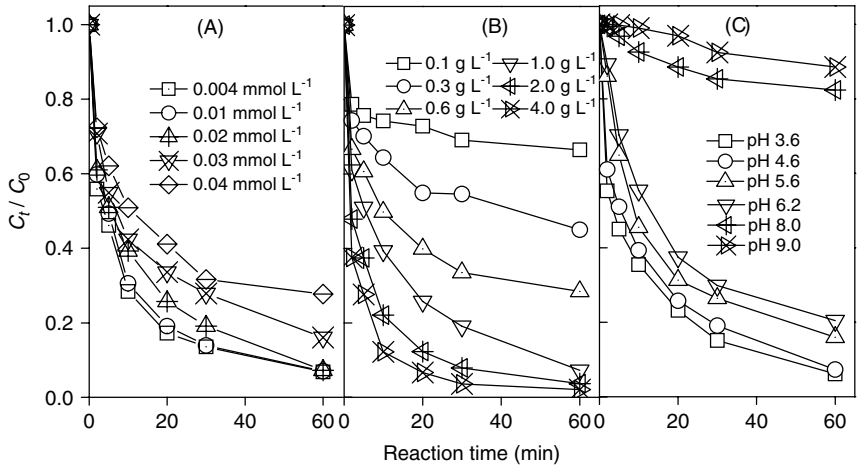

Figure 4. (A) Effect of initial concentration of SD on SD degradation by 1.0 g L^{-1} α-MnO_2 at 25 °C and pH 4.6. (B) Effect of α-MnO_2 dosage on 0.02 mmol L^{-1} SD degradation by 1.0 g L^{-1} α-MnO_2 at 25 °C and pH 4.6. (C) Effect of pH on 0.02 mmol L^{-1} SD degradation by 1.0 g L^{-1} α-MnO_2 at 25 °C.

SD oxidative degradation by α-MnO_2 also strongly depended on the reaction pH. The results of SD (0.02 mmol L^{-1}) degradation with α-MnO_2 (1.0 g L^{-1}) under different reaction pH values (controlled by buffer solutions) are presented in Fig. 4(C). At reaction pH values of 3.6, 4.6, 5.6, 6.2, 8.0, and 9.0, the SD removal was 93.9%, 92.7%, 84.0%, 79.6%, 17.6%, and 11.4%, respectively; i.e. SD degradation rates decreased as pH was increased. SD has a pK_a of 6.52 at 25 °C and thus it is present in the protonated form under acidic conditions.[30] Increased pH would favor the dissociated form of SD, which has less affinity for the negatively charged α-MnO_2.[31] As a result, increasing pH values would decrease the SD degradation rate. Furthermore, as Zhang and Huang reported,[32] the Mn^{2+} generated can reabsorb onto the surface of MnO_2 and thus reduce the active sites available for SD. Some adsorbed Mn^{2+} would be released by H^+ when the acidity of the reaction suspension increased. Accordingly, more active sites on α-MnO_2 could be available for SD degradation, so as to increase the degradation rate of SD.

SD degradation kinetics

From the curves of SD degradation versus reaction time, it can be seen that SD concentration decreased markedly during the early stage of the reaction and then to a lesser extent at the later stage. This pattern indicates that SD degradation by α-MnO_2 does not follow the pseudo-first-order kinetics well. A similar departure from the pseudo-first-order kinetics was also reported by previous investigations[31,32] and it was proposed that the oxide surface had been changed due to adsorption of reaction products resulting in lower activity.[31] Therefore, the reaction rates (r, mmol min^{-1}) were used to determine the reaction order with respect to three key factors, [SD], [α-MnO_2] and pH, and the SD degradation reaction can be expressed as[16,22]

$$k = \frac{-r}{[SD]^a \times [\alpha - MnO_2]^b \times [pH]^c} \quad (1)$$

where r is the SD degradation rate, [SD] is the initial concentration of SD, [α-MnO_2] is the dosage of α-MnO_2, and [pH] is the reaction pH values, which were controlled by buffer solutions.

As shown in Fig. 5(A) and 5(B), the reaction orders of SD degradation were determined to be 0.44 with respects to the initial concentration of SD and 0.30 with respects to α-MnO_2 dosage in this study. The SD degradation rates were also estimated at various pH values and the reaction order was determined to be −0.43 in the pH range of 3.6–9.0, as shown in Fig. 5(C). From these results, Equation (1) can be redefined as Equation (2) with particular reaction orders to these three key variables. From this rate law, the rate constant (k) for 0.02 mmol L^{-1} SD degradation with 1.0 g L^{-1} α-MnO_2 was calculated to be 3.64×10^{-6} $mmol^{-0.17}$ min^{-1} at pH 4.6.

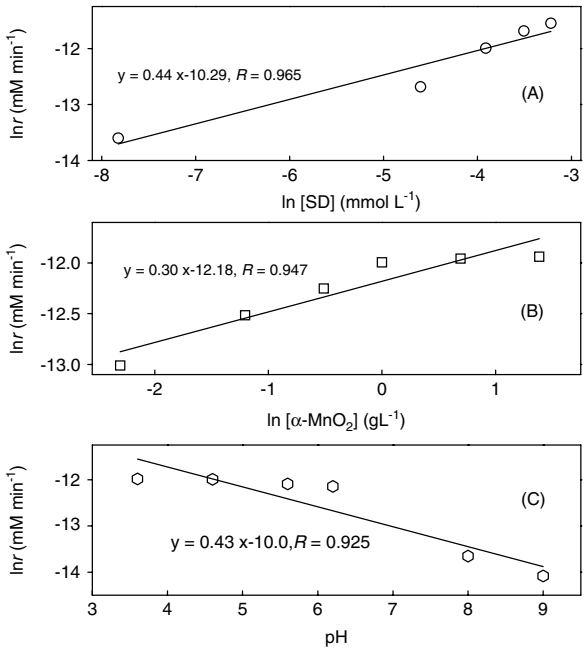

Figure 5. Determination of reaction orders with respect to reaction conditions: (A) initial concentration of SD; (B) α-MnO_2 dosage; and (C) pH values.

$$k = \frac{-r}{[SD]^{0.44} \times [\alpha - MnO_2]^{0.30} \times [pH]^{-0.43}} \quad (2)$$

The effect of reaction temperatures

The reaction temperature can obviously affect the SD degradation rate. The effect of temperature on the oxidative degradation

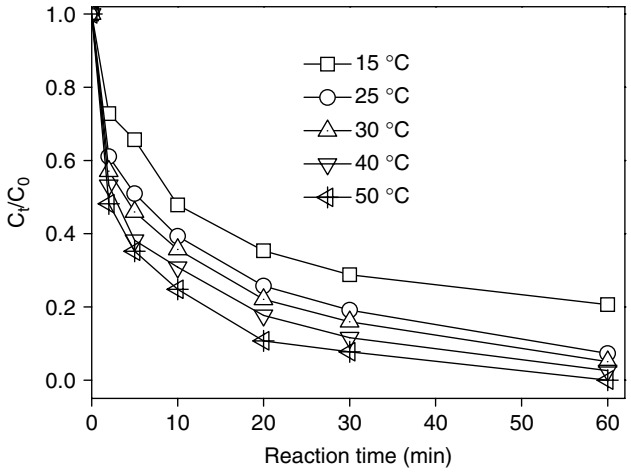

Figure 6. Effect of reaction temperatures on 0.02 mmol L^{-1} SD degradation by 1.0 g L^{-1} α-MnO_2 at pH 4.6.

of 0.02 mmol L^{-1} SD by 1.0 g L^{-1} of α-MnO_2 at pH 4.6 was investigated in the range 15 °C to 50 °C (Fig. 6). The SD degradation rate increased gradually with increasing temperature. At temperatures of 15, 25, 30, 40 and 50 °C, the k values for SD degradation were 3.12×10^{-6}, 3.64×10^{-6}, 3.73×10^{-6}, 3.83×10^{-6} and 3.93×10^{-6} $mmol^{-0.17}$ min^{-1}, respectively. Obviously, there is a significant positive correlation between k and the reaction temperatures. The apparent activation energy of α-MnO_2 was estimated to be 11.6 kJ mol^{-1} for SD degradation by fitting rate constants obtained at various temperatures according to the Arrhenius equation:

$$\ln(k) = \frac{E_a}{RT} + \ln(A) \quad (3)$$

where R is the universal gas constant, E_a (kJ mol^{-1}) is the activation energy, T (K) is the temperature, and A is the pre-exponential factor. This activation energy indicated that the degradation of SD by α-MnO_2 follows a mechanism of sorption, reaction and desorption.[33] The increased degradation rate of SD with increased reaction temperature suggested that the degradation of SD by α-MnO_2 was endothermic. However, due to its low positive value of activation energy, SD degradation with α-MnO_2 occurred spontaneously,[34] also indicating that SD degradation rates will be faster in warmer environments such as sun-exposed surface water.

CONCLUSIONS

In this work, cryptomelane (α-MnO_2) has been used to evaluate the treatment of water contaminated with sulfadiazine (SD). SD can be efficiently oxidized and even mineralized by α-MnO_2. Furthermore, the ecological toxicity of SD for microbial functional diversity could be effectively decreased after degradation by MnO_2. SD oxidative degradation with α-MnO_2 depended on the operational conditions. Increased α-MnO_2 dosages and reaction temperatures can promote SD degradation, while increased SD initial concentration and pH values would lower the oxidative degradation rate by α-MnO_2. More acidic reaction conditions and higher reaction temperatures are more favorable for SD degradation.

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