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REDUCTIVE REMOVAL OF TRICLOSAN BY Sn-BEARING MATERIALS AND CATHODE POWDER RECOVERED FROM SPENT LI-ION BATTERIES

Tin (Sn)-bearing materials, tin oxide (SnO) and elemental tin (Sn(0)), and cathode powder recovered from spent Li-ion batteries were examined as reductants to transform triclosan, a common antibiotic through batch experiments. The reductive removal of triclosan was rapidly observed within 1 h under the given conditions, however, the formation of a passivation layer, mainly composed of SnO₂. Tin dioxide inhibited the reduction reactions on the surfaces of SnO and Sn(0). In contrast, dissolved Sn²⁺, formed by the addition of SnCl₂, could rapidly reduce triclosan within 5 h, resulting in over 95% removal. The results supported the notion that the inhibition of Sn²⁺ formation by SnO₂ on the surface acted as a rate-limiting step in the reductive removal of triclosan by Sn(0) and SnO. Conversely, the removal of triclosan by cathode powder was due to sorption and reduction, and its efficacy was limited by increased pH. A synergistic combination of Sn-bearing materials and cathode powder significantly improved the reduction of triclosan. Our findings suggest that the application of cathode Sn(0)/SnO/cathode powder with SnCl₂ holds promise as an effective approach for the reductive transformation of triclosan in engineered systems.

1. INTRODUCTION

Tin, a metal relatively abundant on Earth, is used in various applications such as soldering, plating, chemical processes, and special alloys like brass and bronze [1]. Tin is known to be non-toxic when present in water, and elemental Sn(0) has been considered a reductant due to its relatively low redox potential ($E_h = 0.14$ V) [2]. Previous studies have reported the reductive transformation of carbon tetrachloride and trichloroethylene by Sn(0) [3, 4]. Sn(0) has also been found to reductively transform Orange II

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into discolored products [5]. While passivation layers hindered the reduction process in acidic solutions [5, 6], combining Sn(0) with ultrasound irradiation was suggested to enhance the reduction of nitrofunctional groups [7]. Furthermore, aromatic nitro compounds were shown to be reduced by SnCl₂ ($E_h = 0.15$ V) in acidic solutions [8]. Therefore, it is pertinent to investigate the potential Sn(0) and SnCl₂ as reductants for transforming oxidized contaminants.

To mitigate the release of CO₂ into atmospheric environments, efforts have been increasingly made to develop electric vehicles (EVs) equipped with Li-ion batteries to replace fossil fuels-derived vehicles [9]. As a result, millions of tons of spent Li-ion batteries are expected to be generated annually when EVs are scrapped. For the sustainable management of spent Li-ion batteries, the reuse and recycling of these batteries have become essential topics to explore in recent years. In terms of reprocessing during the recycling procedure, two methods have been intensively studied and suggested as possible procedures: smelting with a furnace and wet chemical extraction [10]. Due to environmental concerns related to fossil fuel-derived furnaces, instead of conventional smelting in a mineral processing area, stepwise chemical extraction of valuable metals (e.g., Ni, Co, and Mn) from cathode materials recovered from mechanical separation, known as black powder, has been extensively investigated [11]. Currently, commercial reprocessing procedures have been fully established and operated in South Korea to produce Ni, Co, or Mn sulfate precipitates, which provide ingredients for the fabrication of new Li-ion batteries. Although significant progress has been made in recovering metals from spent Li-ion batteries from EVs, no attempts have been made to apply the cathode powder for environmental applications. Using black cathode powder as it is, before the complicated stepwise metal-extraction procedures, could prove beneficial.

Triclosan is an antibacterial agent frequently detected in water environments. Its accumulation in aquatic ecosystems and its human absorption can result in potential toxicity. Therefore, the study of treating waters polluted with triclosan is a crucial subject for protecting the environment. Methods to remove triclosan from the environment include adsorption, advanced oxidation, biodegradation, and combined techniques [12-15]. For adsorption, carbon nanomaterials, notably carbon nanotubes, also exhibit good adsorption for triclosan [16]. Bionic lipophile-activated carbon has high hydrophobicity, whose adsorption capacity of triclosan is 395.2 mg/g, which is much higher than that of activated carbon (71.5 mg/g) [17]. For catalytic oxidation, laccase-catalyzed oxidation is one way to degrade phenolic pollutants in sewage. Maryskova et al. [18] found that after 24 h of catalytic oxidation, the removal rate of triclosan could reach as high as 70%. For photochemical oxidation, Li et al. [19] manufactured Ag/BiVO₄/reduced graphene oxide composite by a hydrothermal strategy, which catalyzed the complete photodegradation of triclosan in a concentration of 2 mg/cm³ in 100 min. For electrochemical oxidation, the removal of triclosan was remarkably high (>95%) via the Fenton reaction of a polarized carbon electrode and cation exchange resin [20]. Recently, when Zhou et al. [21] applied an Mn, Fe-doped porous carbon electrode to the Fenton reaction under a wide applicable pH range, it succeeded at removing triclosan from different types of water, including river water, tap water, and sewage. Some soil organisms may also assist in the removal of triclosan during biodegradation. Peng et al. [22] found that *Limnodrilus hofmeister* could significantly accelerate the reduction of triclosan via methylation and sulfation. For combined methods, Lin et al. [23] reported that green-synthesized Fe-Ni nanoparticles have promising application prospects for removing triclosan/Cu²⁺-mixed pollution through adsorption and reduction. Microbial fuel cells mainly remove triclosan from sewage through adsorption and biodegradation, with high efficiency and low toxicity of the by-products, so they are promising for practical applications [24, 25].

In this study, it was hypothesized that cathode powder from spent Li-ion batteries and Sn-bearing materials may play a role as reductants to remove triclosan through sorption and reduction. The combination of cathode powder and Sn-bearing materials could significantly enhance the reduction of triclosan. The objectives of this study are to characterize the physicochemical and electrochemical properties of black cathode powder and Sn-bearing materials, to determine the kinetics of triclosan removal with cathode powder and Sn-bearing materials, to examine the possible mechanisms through mass balance and product identification, and to evaluate the feasibility of synergistic dosages of SnCl₂ with Sn(0)/SnO and cathode powder to enhance the reduction of triclosan. Triclosan was selected due to its well-known antibiotic properties. The electrochemical properties of cathode powder and Sn-bearing materials were determined. Product identification was conducted via liquid chromatography-mass spectrometry (LC-MS) analysis, and possible reduction mechanisms were suggested and discussed.

2. MATERIALS AND METHODS

Chemicals. Elemental tin powder (Sn(0), 99%), tin oxide (SnO, 95%), and SnCl₂ (99%) were purchased from Aldrich (Milwaukee, WI, USA). 2-[4-(2-hydroxyethyl)piperazin-1-yl] ethanesulfonic acid (HEPES, 99%) was purchased from Sigma-Aldrich (Burlington, MA, USA). The cathode powder was provided by SungEeel Hitech (Gunsan, South Korea). All chemicals were used without further treatment.

Batch experiments. Batch reduction experiments were conducted using sealed 250-cm³ amber borosilicate vials. All preparation procedures were conducted in an anaerobic glove box (Jisico, Seoul, South Korea) under N₂. The dosages of reductants amounted to 0.5, 5.0, or 50 g/dm³, and the initial concentration of triclosan was 21.8 mg/dm³ (0.0753 mM). The solution was deoxygenated by purging it with N₂ for at least 30 min in the glove box. The triclosan solution contained 0.1 M HEPES to maintain a constant pH of 7.4 throughout the experiment. Each vial was sealed with a Mininert valve (VICI, Baton Rouge, LA, USA) and low-permeability vinyl tape (Scotch 471, 3M, St. Paul, MN, USA). All vials were placed horizontally on an orbital shaker at 150 rpm throughout the experiment except during sampling. At various elapsed times, a 1-cm³ aliquot

was withdrawn using a glass syringe through the Mininert valve and immediately passed through a 0.20-µm cellulose syringe filter (Millipore, MA) before chemical analysis.

Chemical analysis.Triclosan was analyzed using an UltiMate[™] 3000 HPLC system (Dionex, Sunnyvale, CA, USA) equipped with an Acclaim[®] 120 guard column (4.3×10 mm, Dionex) and an Acclaim[®] 120 C18 column (4.6×250 mm, 5 µm, Dionex). A mixture of methanol and water (60:40, v/v) was used as the mobile phase at a flow rate of 1.0 cm³/min, and the sample injection volume was 100 μ L. The UV detector's wavelength was set at 224 nm. The retention time of triclosan was 8.2 min. For quantification purposes, a calibration plot was constructed within the range of the experimental concentrations used $(R^2 > 0.99)$. A standard solution of triclosan was used to confirm the accuracy and precision of the triclosan concentration in HPLC analysis. The total organic carbon (TOC) concentration was determined using a TOC analyzer (TOC-L, Shimadzu, Kyoto, Japan). To identify the redox-transformed products, LC-MS analysis (1200 series, Agilent, Santa Clara, CA, USA) was conducted with a Symmetry C18 column (4.6×150 mm, 5 µm, Waters, Milford, MA, USA). A mixture of acetonitrile and deionized water (80:20, v/v) served as an eluent at a flow rate of 0.8 cm³/min, and the UV wavelength was set at 220 nm. For mass spectrometry, both electron spray ionization and atmospheric pressure chemical ionization modes were utilized as ion sources, and the mass range covered 50-3000 (m/z) with a scan speed of 2600 amu/s.

The physicochemical properties of Sn-bearing materials and cathode powder, including pH, point of zero charge, and BET surface area, were determined according to the methods suggested elsewhere [26, 27]. The electrochemical properties of Sn-bearing materials and cathode powder were evaluated in terms of electron-donating capacity (EDC) and electron-accepting capacity (EAC) according to the method described by Aeschbacher et al. [28]. The measuring processes were carried out in a nitrogen-filled anoxic acrylic glove box using an IVIUMSTAT potentiostat (Ivium Technologies, Eindhoven, the Netherlands) with three-electrode configurations. The working electrode was a pure platinum plate (1×1 cm), while a pure Pt strip and a KCI-saturated Ag/AgCl electrode served as the counter and reference electrodes, respectively. Detailed procedures were outlined in our previous paper [29]. The surface chemical forms of the Snbearing material were examined using X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Fischer, Waltham, MA, USA) using an Al K α monochromator (1.487 keV).

3. RESULTS AND DISCUSSION

3.1. PROPERTIES OF Sn-BEARING MATERIALS AND CATHODE POWDER

pH of Sn(0) and SnO solution was slightly acidic and slightly alkaline, measuring 5.6 and 7.3, respectively (Table 1). Consequently, their points of zero charge values were 5.2 and 7.0, respectively. These pH values indicate that increasing pH in the presence

of water may not inhibit the reductive transformation of triclosan by Sn-bearing materials. The pH decrease caused by SnCl₂ was significantly substantial. The solution's pH decreased to 1.4, strongly suggesting that SnCl₂ could be highly favorable for triclosan reduction. However, the insolubility of Sn(0) and SnO, along with their low BET surface areas (0.32 and 2.29 m²/g) might not be conducive to the reductive transformation of triclosan. It appears that acidic pH conditions with strong acid might be necessary to dissolve Sn(0) and SnO in the solution. Consequently, the black cathode powder from spent Li-ion batteries exhibited an extremely high pH (11.5) and a relatively high BET surface area (5.29 m²/g), implying that the solution's pH might hinder the reduction of triclosan due to the formation of OH⁻ in the presence of water.

Table 1

Material	Purity [%]	рН ^а	Point of zero charge ^b	BET surface area [m ² /g] ^c	Water solubility [g/dm ³]
Cathode powder	-	11.5	11.6	5.29	not available
Sn(0)	99	5.6	5.2	0.32	insoluble
SnO	95	7.3	7.0	2.29	insoluble
SnCl ₂	99	1.4	1.3	not available	839

Properties of cathode powder and Sn-bearing materials

^a Determined by the method of Rump and Krist [26].

^b Determined by the method of Faria et al. [27].

^c Analyzed by nanoPOROSITY-XQ (Mirae Scientific Instrument, South Korea).

Table 2

Elemental contents obtained from XRF analysis of cathode powder [wt. %]

Co	Ni	Mn	Fe	Cu	Ba	Cl	Cd
18.17	75.38	1.23	3.01	3.26	1.45	0.29	0.24

According to an elemental analysis by XRF (Table 2), besides Ni, Co, and Mn, the contents of Fe and Cu were 3.01 and 3.26%, respectively, indicating that such transition metals might act as reductants for triclosan's reductive transformation. It was previously reported that the chemical forms of cathode materials may include LiNi_xMn_yCo_zO₂ (lithium nickel manganese cobalt oxide), LiNiCoAlO₂ (lithium nickel cobalt aluminum oxide), LiNi_{0.89}Co_{0.05}Mn_{0.05}Al_{0.01}O₂ (lithium nickel cobalt manganese aluminum oxide), LiMn₂O₄ (lithium manganese oxide), LiFePO₄ (lithium iron phosphate), and LiCoO₂ (lithium cobalt oxide) according to the manufacturing company [30]. To assess their potential as reductants in the water system, the EAC and EDC of Sn(0) and SnO were determined through mediated reduction and oxidation reactions, following the electrochemical methods proposed by previous researchers [28, 29]. As shown in Table 3, EAC values of Sn(0) and SnO were higher than EDC values, indicating that the surfaces of Sn(0) and SnO were oxidized and that electrons might not be easily released from the surface due to the oxidation of Sn(0) and SnO. Conversely, the EDC of cathode powder (0.0812 ± 0.0095 mmol/g) was more than twice as large as the EAC (0.0325 ± 0.0122 mmol/g), suggesting that cathode powder might have a significant potential to act as a reductant for triclosan. The electrochemical properties of Sn-bearing materials and cathode powder revealed that cathode powder could be more favorable as a reductant.

Table 3

Material	EAC	EDC	EEC ^c	
Sn(0)	0.0499 ± 0.0083	0.0066 ± 0.0004	0.0565 ± 0.0087	
SnO	0.0129 ± 0.0014	$0.0085 {\pm} 0.0005$	0.0275±0.0019	
Cathode powder	0.0325±0.0122	0.0812 ± 0.0095	0.1137±0.0217	

Electron donating capacity (EAC), electron accepting capacity (EDC), and electron exchange capacity (EEC) of Sn-bearing materials^a [mmol/g]

^a EAC and EDC according to Aeschbacher et al. [28], EEC is the sum of both.

3.2. REDUCTIVE REMOVAL OF TRICLOSAN BY Sn-BEARING MATERIALS AND CATHODE POWDER

The removal of triclosan in the presence of the Sn-bearing materials and cathode powder is shown in Fig. 1. To minimize the effect of pH, the batch experiments were designed to incorporate HEPES buffer into the solution to maintain a pH of 7.4. However, in the presence of Sn(0), SnO, and SnCl₂, the solution's pH decreased from 6.4 to 6.3, 5.4, and 2.7, respectively.



Fig. 1. Removal of triclosan by cathode powder and Sn-bearing materials. The dosage was 0.5 g/dm^3 . The initial concentration of triclosan (C_0) is 21.8 mg/dm³

It appears that electrons generated from Sn-bearing materials might produce hydrogen ions during the reactions:

$$Sn(0) + 2H_2O \rightarrow SnO_2 + 4H^+ + 4e, \quad E_h = 0.235 V$$
 (1)

$$SnO + H_2O \rightarrow SnO_2 + 2H^+ + 2e, \quad E_h = 0.961 V$$
 (2)

$$Sn^{2+} + 2H_2O \rightarrow SnO_2 + 4H^+ + 2e, \quad E_h = 0.094 V$$
 (3)

Thus the solution's pH was not controlled with HEPES buffer. As shown in Fig. 1, 0.5 g/dm³ of Sn-bearing materials exhibited an abrupt triclosan removal within 1 h. Sn(0) and SnO showed approximately 45% of removal in 1 h. With 0.5 g/dm³ of SnCl₂, 81% of triclosan was removed from the solution in 1 h. After 1 h, triclosan removal slowed significantly until 24 h. The reactivity of Sn(0) and SnO almost completely stopped after 1 h, probably due to surface passivation, which hindered further oxidation of Sn(0) and SnO. Regarding SnCl₂, the dissolved Sn²⁺ was rapidly oxidized to Sn⁴⁺ $(E_h = 0.15 \text{ V})$, which promptly precipitated in the system. The reduction decrease might be attributed to the limited number of electrons generated from 0.1 g of SnCl₂, and the dosage of SnCl₂ might act as a rate-limiting step. Unlike the Sn-bearing materials, pH rapidly increased to 10.6 in the presence of cathode powder, like other elements such as Fe [31]. The addition of cathode powder decreased the concentration of triclosan by 20% in 24 h. Probably triclosan gradually decreased, likely due to the limited amount of cathode powder. Controlling pH at 7.4 using HEPES buffer did not significantly enhance triclosan removal. To decisively determine the reductive removal of triclosan by Sn-bearing materials and cathode powder, increasing the dosage is necessary.



Fig. 2. Impact of dosage (5.0 and 50.0 g/dm³) on triclosan removal by cathode powder and Sn-bearing materials

Increasing the dosage significantly improved triclosan removal under the provided conditions (Fig. 2). Elevating the cathode powder dosage to 50 g/dm³ resulted in complete triclosan removal within 1 h, suggesting that the reductive removal of triclosan with 0.5 g/dm³ of cathode powder may be a surface area-limiting reaction. Concerning Sn(0) and SnO, increasing the dosage did not notably alter the extent of triclosan removal under the given conditions. In the presence of 50 g/dm³ of Sn(0) and SnO, 55–60% of triclosan was removed within 6 h (Fig. 2). The results indicated that the surface area of Snbearing materials was not the primary factor influencing the limited triclosan removal by the Sn-bearing materials and that the surface passivation of the Sn-bearing materials might be responsible halting triclosan removal. To identify SnO₂ formation, XPS analysis was conducted. As shown in Fig. 3, the peaks of Sn⁴⁺ at 495.38 eV and 486.70 eV of binding energy were increased for Sn(0) and SnO, confirming the presence of SnO₂ on the surface of the Sn-bearing materials. It is inferred that additional treatment conditions such as sonication, strong acidic pH, and stepwise dosing might be required to overcome the hindrance of the passivation layer.



Fig. 3. XPS spectra (Sn 3d) of Sn-bearing materials: a) Sn(0) and b) SnO before and after the removal of triclosan

To examine the dechlorination of triclosan by the Sn-bearing materials and cathode powder, the concentration of chloride (Cl⁻) in the solution was determined with 0.5 g/dm³ of the Sn-bearing materials and cathode powder. In the control containing Sn(0) and SnO in the presence of deionized water, no chloride ions were observed, while the control group with cathode powder showed a chloride concentration of 1.2 mg/dm³ in the solution. Considering background chloride concentration and the initial concentration of chlorine (0.2259 mM) corresponding to the initial concentration of triclosan (0.0753 mM), the mass recovery of chlorine as chloride was calculated. The chloride concentration in solution with Sn(0) and SnO in the presence of triclosan remained on the level 3.6–3.8 mg/dm³ over 24 h, representing 44–48% of initial chlorine concentration (Fig. 4).



Fig. 4. The formation of chloride during the removal of triclosan by cathode powder and Sn-bearing materials. The dosage was 0.5 g/dm^3

This chlorine mass recovery was similar to the extent of triclosan removal in the presence of 0.5 g/dm³ of Sn(0) and SnO (Fig. 1). The cathode powder also exhibited mass recovery of 22% as chloride over 24 h, similar to ca. 20% of removal of triclosan. The addition of SnCl₂ resulted in the formation of 6.6 mg/dm³ of chloride over 24 h, corresponding to an 82% mass recovery of chloride (data now shown), which closely matched the extent of triclosan removal (Fig. 1). These results indicate that triclosan was dechlorinated by Sn-bearing materials and cathode powder, and the removal of triclosan primarily resulted from reductive transformation.

3.3. ELUCIDATION OF REDUCTION MECHANISMS AND ENVIRONMENTAL IMPLICATIONS

To confirm the dechlorination of triclosan, an LC-MS analysis was performed. For the Sn-bearing materials and cathode powder, in addition to triclosan (m/z = 288.7), dechlorinated products (m/z = 252.9 and 218.8) were identified in the Sn(0) and SnO

systems, suggesting the release of 1-2 chlorine atoms from triclosan in these systems. However, fully dechlorinated products were not found in the mass spectra, implying that the reductive transformation of triclosan was limited in the presence of Sn(0) and SnO. As shown in Fig. 2, although the dosage of Sn(0) and SnO was increased to 50 g/m³ under the given conditions, the reduction was not greatly promoted, probably due to strong surface passivation. One potential method to overcome this hindrance could involve creating acidic conditions to reduce passivation layer formation. To maintain an acidic pH, 0.5 g of SnCl₂ was added to 0.5 g of Sn(0), SnO, or cathode powder. The combination of SnCl₂ with the Sn-bearing materials or cathode powder reduced the solution's pH to 1.9–2.1 under the given conditions. As expected, the triclosan removal was correspondingly elevated to 75–85% removal within 7 h, suggesting that acidic conditions play a critical role in enhancing the reduction of triclosan by Sn-bearing materials and cathode powder (Fig. 5).



Fig. 5. Removal of triclosan by cathode powder/Sn(0)/SnO in the presence of SnCl₂. The dosage of SnCl₂ and Sn(0)/SnO/cathode powder was 2.5 g/dm³, respectively

Among these conditions, triclosan removal by cathode powder was significantly enhanced by adding SnCl₂, indicating that the removal of the passivation layer on the cathode powder's surface was more effective than that of the Sn-bearing materials. Ultrasound sonication might enhance the removal of the passivation layer on the Sn-bearing materials [7]. Additionally, a stepwise dosage at regular intervals could accelerate the removal of the passivation layer to enhance the reductive transformation by Sn-bearing materials. The effectiveness of these enhancement methods still requires further examination. The effects of solution pH, sonication, and dosage method on the degradation of triclosan by Sn-bearing materials and cathode powder will be reported soon. It should be noted that due to the high values of Ni and Co, their recovery may be essential. Therefore, after applying the cathode powder for the removal of triclosan via sorption and reduction, subsequent recovery processes should be followed. So far, pyrometallurgical and hydrometallurgical processes, which emit large amounts of CO_2 , and are costly and unsafe, were proposed for the recovery process [32, 33]. As a result, much effort has been made to develop safe and cost-effective processes. It is reasonable that these newly developed recovery procedures may be applied after triclosan removal.

4. CONCLUSIONS

Sn-bearing materials and cathode powder recovered from spent Li-ion batteries were examined as reductants for transforming triclosan, a common antibiotic, through batch experiments. The reductive removal of triclosan by Sn(0) and SnO was rapidly observed within 1 h under the given conditions. However, further removal was limited regardless of the dosage of Sn-bearing materials and pH changes. It was revealed that the formation of a passivation layer, primarily composed of tin dioxide (SnO₂), accounted for the halt of reduction reactions at the surface of SnO and Sn(0). Conversely, the removal of triclosan by cathode powder was limited by an increase in pH. A synergistic dosage of SnCl₂ with Sn-bearing materials and cathode powder could significantly enhance the reduction of triclosan by reducing pH levels. Our findings suggest that the application of cathode powder/SnO/Sn(0) with SnCl₂ might present a promising approach for the reductive transformation of triclosan in the environmental remediation of contaminated water and soil.

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