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Selective Organic Removal from the Alumina Industrial Liquor: Wet Oxidation and Catalytic Wet Oxidation of Disodium Malonate

Sharon Eyer,[†] Suresh Bhargava,^{*,‡} James Tardio,[‡] and Deepak B. Akolekar[‡]

Department of Applied Chemistry, RMIT University, Melbourne, Australia 3001,
and Technology Delivery Group, Alcoa World Alumina, P.O. Box 161, Kwinana, Australia 6167

The wet oxidation and catalytic wet oxidation of a key organic component, particularly disodium malonate (the salt of propanedioic acid) found in the alumina industrial liquor have been investigated. The wet oxidation and catalytic wet oxidation of the disodium malonate in highly alkaline media was carried out at 165 °C in a high-pressure reaction system. The main carbon-containing species detected as products from disodium malonate oxidation were sodium carbonate and sodium oxalate produced in similar quantities during wet oxidation and catalyzed wet oxidation. The amounts of ketomalonic acid hydrate detected during disodium malonate oxidation were up to 20 mg/L. Mechanisms for both wet oxidation and copper-catalyzed wet oxidation of disodium malonate are proposed, with ketomalonic acid (hydrate) as a key intermediate organic species.

1. Introduction

The main aim of industrial-scale wet oxidation (WO) and catalytic wet oxidation (CWO) is to decompose organic species to relatively harmless materials such as water and carbon dioxide or carbonate in alkaline systems.^{1–4} In particular, alkaline wastewaters and process liquors are being targeted in order to meet environmental standards for discharge streams. Some industries, including paper pulp production and alumina refining, have the dual interest of environmental targets and potential for process improvements. Many of these process streams contain the sodium salts of mono- and dicarboxylic acids. However, there is little information in the literature regarding the decomposition of dicarboxylic acids and their corresponding salts in the highly basic media.^{5–10} The literature on the behavior of these species during WO and CWO in highly alkaline solutions is scarce. The present investigation is concerned with the less widely studied disodium malonate conversion (the salt of propanedioic acid) to sodium oxalate intermediates during the WO and the CWO treatments. The current investigation also proposes various mechanisms for the formation of organic species in WO and copper-catalyzed WO.

2. Experimental Section

The WO and CWO experiments were carried out in a continuously stirred, 3.75 L, nickel (Inconel) autoclave (Parr Autoclave) which included attachments for gas addition into the liquid phase and kinetic subsampling of the liquid phase. The sodium hydroxide and sodium carbonate concentrations were measured using an automated, potentiometric titration system. Total organic carbon and carbonate concentrations were obtained

using a Dohrmann total carbon analyzer. Gas chromatography (GC) was used for disodium malonate and disodium oxalate analyses (as methyl esters).^{4,11–13} Ketomalonic analyses involved acidification, solvent extraction, derivatization, and subsequent quantification of the trimethylsilated ester by semiautomated GC/mass spectrometry (GC/MS).

In this study, five different types of highly alkaline solutions were used. The compositions of these solutions are given in Table 1. The chemicals NaOH, Na₂CO₃, Al(OH)₃, NaCl, Na₂SO₄, CH₃COONa (sodium acetate), and CH₂(COONa)₂ (disodium malonate) were used to prepare the alkaline solutions (ALK1–ALK3) given in Table 1. The industrial process liquor (LIQ) was collected from an Alcoa alumina refinery located in Western Australia and used without further purification. The “bauxite extract” solution (BES) was prepared by digesting bauxite (a mineral ore), obtained from a bauxite mine in Western Australia, into an alkaline solution (Table 1). Commercial copper(II) oxide (CuO; 99+%, <5 μm) was used as purchased from Sigma–Aldrich [CAS 1317-38-0].

In the standard test, the liquor (2 L) and 5 g/L CuO (catalyst, only in the CWO reaction) were placed into the autoclave, and the headspace area was evacuated to –0.9 bar. In the WO reaction, no catalyst was used. The vessel and contents were heated to the target temperature (165 °C), and a subsample was collected from the autoclave (time zero sample). Oxygen was then added at a partial pressure (*P*_{O₂}) of 500 kPa, which was maintained throughout the test. Additional subsamples of the liquid phase were taken over a period of 3–4 h, with each subsample being approximately 50 mL.

3. Results and Discussion

Relevance to the LIQ. Figure 1 shows the change in concentration of disodium malonate in various highly alkaline solutions [ALK1–ALK3 and LIQ (Table 1)] studied versus the oxidation period. In the different alkaline solutions, the oxidation of disodium malonate

* To whom correspondence should be addressed. E-mail: Suresh.Bhargava@rmit.edu.au. Tel.: +61 3 9925 3365. Fax: +61 3 96391321.

[†] Alcoa World Alumina.

[‡] RMIT University.

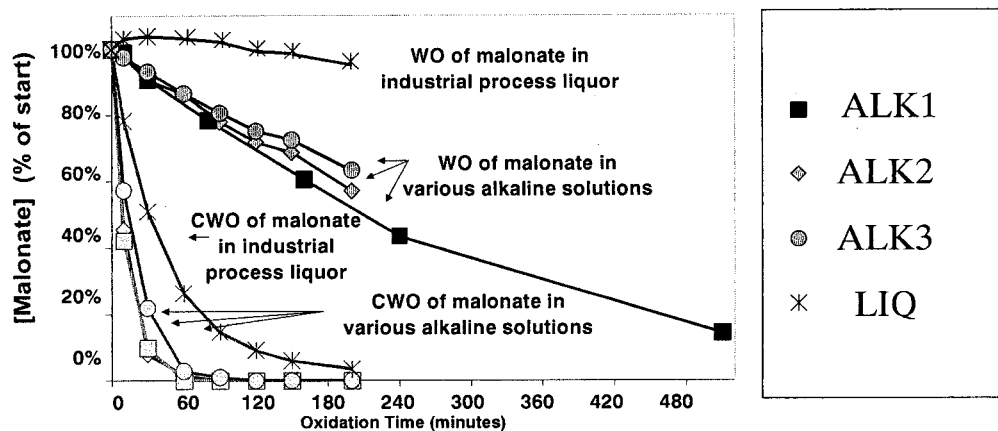


Figure 1. Influence of WO and CWO on malonate conversion in (a) an alkaline solution, (b) an alkaline solution plus acetate, (c) an alkaline solution plus aluminate, and (d) LIQ.

Table 1. Compositions (M) of Different Highly Alkaline Solutions Used To Study the WO and CuO-Catalyzed WO of Disodium Malonate

liquor type	NaOH	Na ₂ CO ₃	NaCl	Na ₂ SO ₄	CH ₂ (COONa) ₂	CH ₃ COONa	Al ₂ O ₃
alkaline (ALK1)	4.4	0.4	0.3	0.2	0.08	×	×
alkaline with Al (ALK2)	4.4	0.4	0.3	0.2	0.08	×	1.0
alkaline with acetate (ALK3)	4.4	0.4	0.3	0.2	0.08	0.1	×
industrial process liquor (LIQ)	4.4	0.4	0.3	0.2	0.08	0.2	1.0
bauxite extract solution (BES)	4.4	0.1	0.06	0.01		nd	1.0

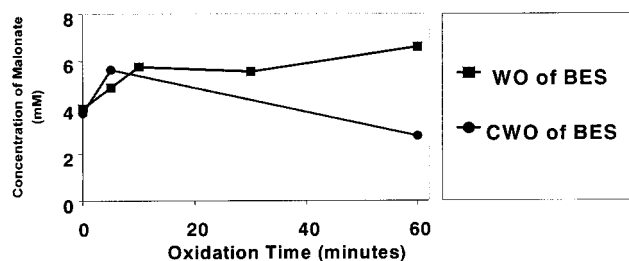


Figure 2. Changes in the malonate concentration observed as an intermediate during WO and CWO treatment of BES (165 °C and 500 kPa P_{O_2}).

was catalyzed by CuO. Comparison of the malonate oxidation results indicates that the CWO conversion of malonate to oxalate and carbonate is more rapid than the WO process. In alkaline solutions and LIQ, the oxidation of sodium malonate was enhanced by the presence of copper-based catalysts (Figure 1). The presence of soluble aluminate species $[Al(OH)_4^-]$ appeared to have a slight negative impact on the catalyzed rate in simple alkaline solutions. Presumably, this is due to a lower free hydroxide concentration with aluminate present.

An apparent slower rate was observed for the oxidation of disodium malonate in the LIQ compared to the simple alkaline solutions (Figure 1). This is most likely due to disodium malonate being formed from the oxidation of some high molecular weight (HMW) compounds that are present in the LIQ. The LIQ contained high concentrations (10–15 g/L) of HMW organic compounds.¹³ To confirm this hypothesis, simulated LIQ was prepared by digesting bauxite ore into a sodium hydroxide solution and collecting the filtrate (Table 1). The BES contained many of the HMW organic species that are found in the LIQ, some at concentrated levels. However, unlike the process liquor, the BES initially contained negligible disodium malonate. Figure 2 shows that trace amounts (up to 7 mmol) of disodium malonate were detected as a reaction intermediate during WO of the BES. In the absence of CuO, the formation rate was

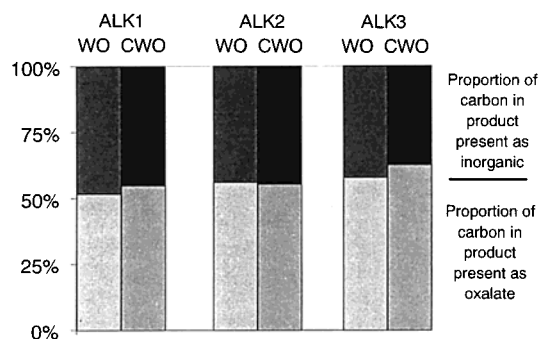


Figure 3. Distribution of carbonate and oxalate: WO (left) of malonate in simple alkaline solutions produces inorganic carbon (top) and oxalate (bottom) in about the same ratio as CWO (right).

slightly faster than the oxidation rate and there was a net increase in the disodium malonate concentration (Figure 2). This confirms that disodium malonate is an oxidation intermediate for some higher molecular weight species.

Oxidation Products. The main carbon-containing species detected as products from disodium malonate oxidation were sodium carbonate and sodium oxalate. Sodium carbonate and oxalate were produced in similar quantities during WO and catalyzed WO (Figure 3). This implies that the product-determining step could be the same in each case. Traces (up to 20 mg/L) of ketomalonic acid hydrate were detected during disodium malonate oxidation. Ketomalonic was also detected during oxidation of the BES and has been found to increase in concentration when the LIQs are oxidized.¹³

A mass balance for selected samples from WO and CWO of disodium malonate in the alkaline solution (ALK1) is shown in Table 2. Essentially all of the carbon in the system is accounted for by the three species: malonate, oxalate, and carbonate. The slight variations in the net results are due to analytical uncertainty and the presence of trace amounts of one or more intermediates (such as ketomalonic acid hydrate). The mass

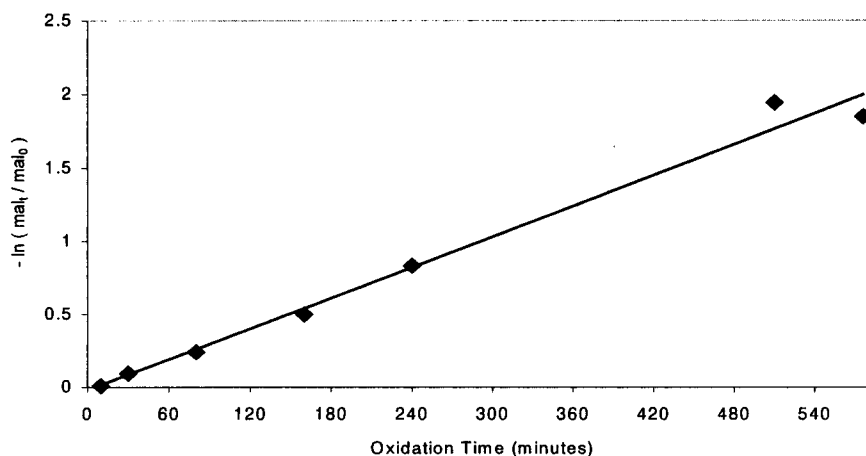


Figure 4. Plot of $-\ln(\text{mal}_t/\text{mal}_0)$ versus oxidation time in simple alkaline solution (ALK) of WO of malonate.

Table 2. Data on the Mass Balance for the Wet Oxidized and Catalytic Wet Oxidized Samples^a

type	oxidation time (min)	malonate oxidation (g of C)	oxalate formation (g of C)	carbonate formation (g of C)	net (g of C)
WO	10	-0.024	0.041	0.003	0.02
WO	30	-0.246	0.114	0.136	0.004
WO	80	-0.586	0.302	0.313	0.029
WO	160	-1.073	0.567	0.567	0.062
WO	510	-2.337	1.267	1.126	0.056
CWO	10	-1.598	0.956	0.618	-0.024
CWO	60	-2.769	1.584	1.14	-0.045
CWO	90	-2.769	1.606	1.192	0.030

^a The starting concentration of malonate was 2.77 g as carbon.

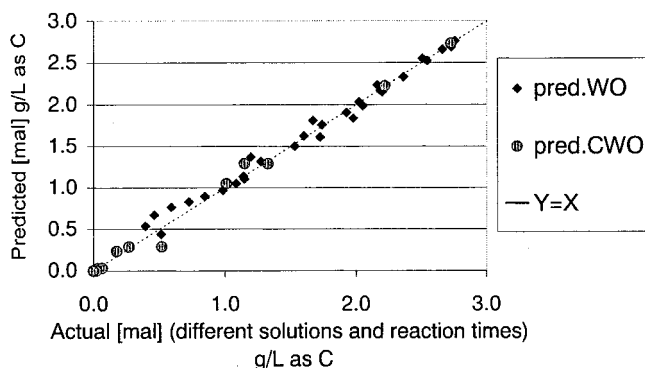


Figure 5. Prediction of malonate concentrations in the alkaline solutions using malonate oxidation models.

balance shows that if any intermediates other than ketomalonic acid hydrate were formed during oxidation, then they were present in extremely small quantities or were highly unstable.

Catalysis of Disodium Malonate Oxidation. Figure 4 shows the first-order plot of $-\ln(\text{mal}_t/\text{mal}_0)$ versus the oxidation time. The straight line shows that in a simple alkaline solution (ALK) the WO of malonate is a first-order reaction. In the presence of excess oxygen, the oxidation of disodium malonate is first-order (Figure 4). Simple exponential models^{4,9} were derived to describe the changing disodium malonate concentration (Figure 5) for alkaline solutions of the type shown in Figures 1 and 3 (i.e., ALK1–ALK3 and LIQ). The reaction rate constants shown in eqs 1 and 2 have been averaged from 40 points each (CWO and WO) using different four alkaline solutions (of type ALK1–ALK3) and different reaction times, with nominally constant temperature (165 °C) and oxidant pressure (500 kPa). On the basis

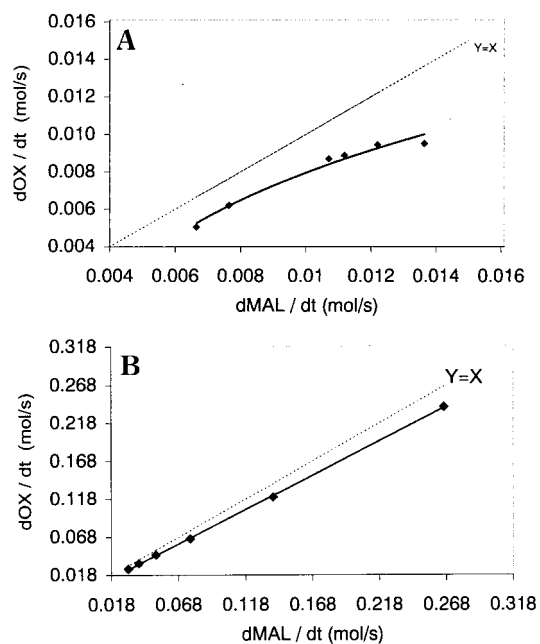


Figure 6. (A) WO rate for malonate with the formation rate of oxalate (mol/s). (B) Copper-catalyzed WO rate for malonate with the formation rate of oxalate (mol/s).

of these equations, it is clear that the CWO rate is about 28 times faster than the WO rate.

$$\text{mal}_t(\text{WO}) = \text{mal}_0 \exp(-0.0027t) \quad (1)$$

$$\text{mal}_t(\text{CWO}) = \text{mal}_0 \exp(-0.0748t) \quad (2)$$

Oxalate Formation. The WO (A) and copper-catalyzed WO (B) rates for malonate along with the formation rate of oxalate (mol/s) are presented in Figure 6 and Table 3. If malonate is oxidized directly to oxalate, then the oxalate formation rate should be comparable to the malonate oxidation rate (on a mole basis). However, the formation of oxalate occurs at a slower rate than the WO of malonate. Some of the apparent decreases in the oxalate formation rate will be due to the simultaneous slow oxidation of oxalate. However, in isolation, the fastest oxidation rate observed for oxalate was 0.0002 mol/s. When this amount of bias is allowed, the oxalate formation rate is still much slower than the malonate oxidation rate. Therefore, at least one intermediate is formed during oxidation or the

Table 3. Data on the Oxidation and Carbonate Formation Rates (mol/s) Observed for the Three Main Carbon Species (Malonate, Oxalate, and Carbonate)

starting material	test	malonate oxidation	oxalate formation	oxalate oxidation ^a	carbonate formation
malonate	WO	0.012	0.012	0.004	0.020
malonate	CWO	0.077	0.077	0.009	0.095
oxalate	WO			~0.000	~0.000
oxalate	CWO			0.0002	0.0002

^a This is the calculated rate of oxalate formation if malonate is oxidized directly to oxalate.

oxidation rate for oxalate increases while malonate is being oxidized, and given the mass balance obtained above, a reaction intermediate would have to be unstable and form carbonate as well as, or instead of, oxalate. It is likely that the oxalate decomposition is accompanied by the formation of formate, which is eventually decarboxylated to CO₂/CO₃²⁻; however, it occurs to a very small extent.

Mechanistic Considerations. The oxidation of malonate to oxalate and carbonate involves at least two distinct steps with at least one intermediate species:



From the observations of previous researchers^{9,10} and the results obtained in this study, it is reasonable to

assume that ketomalonic acid (hydrate) is formed as a "transient" intermediate during disodium malonate oxidation. Schuchmann et al.⁹ used pulse radiolysis to examine the alkaline oxidation of hydroxymalonic acid and reported that ketomalonic acid and oxalic monoperacid [HO-O-C(COOH)=O] were detected as intermediates. Their suggested mechanism proposes a superoxide anion (O₂^{•-}) as the oxidizing species under conditions of high pH.

By analogy with Schuchmann's work, the first step in the malonate oxidation reaction during WO and CWO could be replacement of the acidic hydrogen from the central carbon atom with a superoxide group (Figure 7, reaction 1). This would lead to the formation of a transient peroxy malonate intermediate (Figure 7, species II), which could disproportionate into the salt of ketomalonic acid (Figure 7, species III), a compound which was detected during this study. Further attack of O₂^{•-} on the carbonyl carbon of the salt of ketomalonic acid would most likely follow (Figure 7, reaction 3), resulting in the formation of oxalic monoperacid (Figure 7, species IV) and a peroxy anion radical (Figure 7, species V). The species other than malonate, oxalate, carbonate, and ketomalonic acid (hydrate) are thought to be transitional. Two possible reaction pathways are proposed for both oxalic monoperacid (Figure 7, reaction

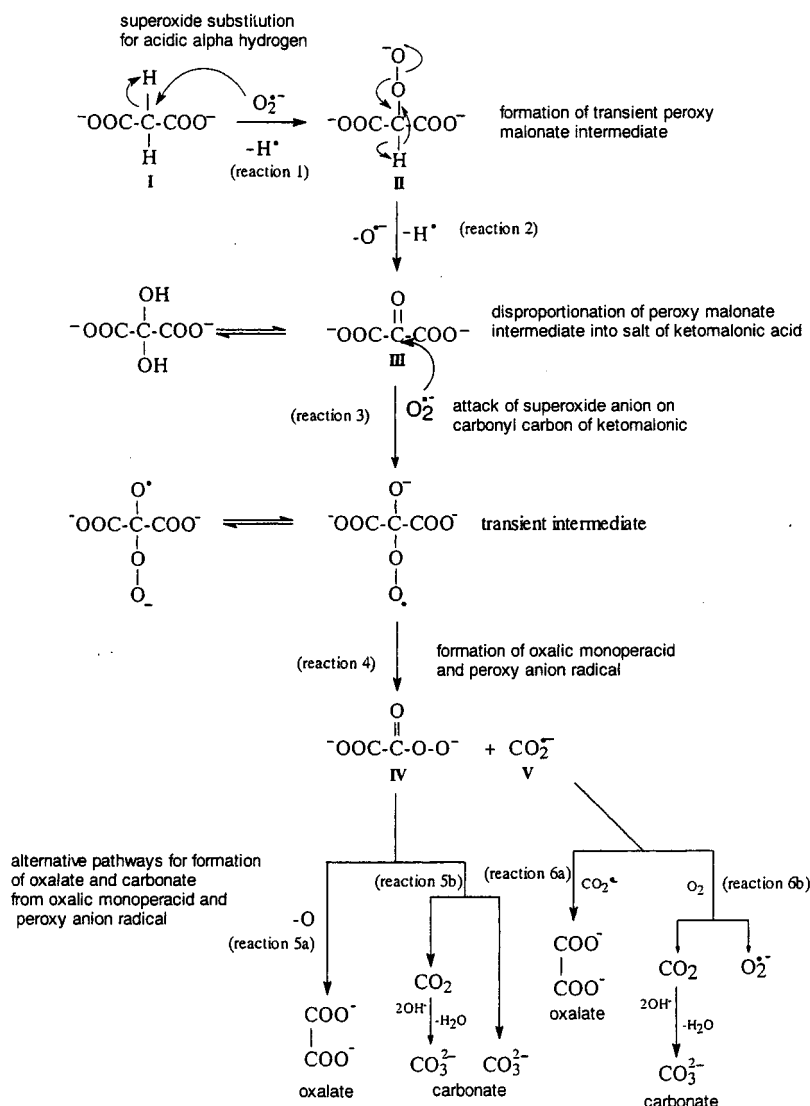


Figure 7. Proposed schemes for WO using O₂^{•-} and for CWO using XO₂[•] showing single and paired electron transfers.

5a,b) and the peroxy anion radical (Figure 7, reaction 6a,b), each leading to the formation of the two main reaction products observed, oxalate and carbonate. On the basis of the oxalate to carbonate production ratio observed and the difference in the malonate oxidation rate and the oxalate formation rate, it is proposed that the reactions leading to carbonate formation (Figure 7, reactions 5b and 6b) are more dominant.

Role of the Catalyst. In water, $O_2^{\cdot-}$ is a relatively weak radical and a weak nucleophile.¹⁰ The potential for symmetrical delocalization is high for the superoxide anion, which stabilizes the radical and makes it less reactive. One possible role for a catalyst is that an oxidizable copper species reacts directly with superoxide or peroxide to increase the formation rate for a more reactive species. A second possibility is that the rate of superoxide formation is increased, with the same end result (reactions 1 and 2).



That is, at 165 °C oxygen (O_2) reacts with water or hydroxide ions to produce superoxide, and the presence of a reduced form of copper (ions or Cu_2O) either enhances this reaction or takes it one step further to produce a more active oxygen species. Copper ions could conceivably catalyze both steps. However, the hypothesis is that the dominant reaction leads to increased formation of superoxide, with an overall increase in the formation rate (and therefore availability) of the active species for organic oxidation.

4. Summary

WO and CWO (165 °C and 500 kPa P_{O_2}) of disodium malonate to disodium oxalate and sodium carbonate are discussed. The detailed studies on the oxidation of disodium malonate lead to the conclusion that at least two distinct steps with at least one intermediate species are involved in the reaction. In the oxidation reaction of malonate to oxalate and carbonate, ketomalonic acid (hydrate) was detected as a key intermediate organic species. The mechanisms have been proposed for the formation of oxalate from malonate via this ketomalonic intermediate as well as for an explanation of the observed oxalate to carbonate product ratio. In regards to the subsequent removal of oxidation products in the Bayer process, one implication of these findings (i.e., that both carbonate and oxalate are formed by WO of malonate) is that complete organics removal would require downstream processing to remove oxalate and carbonate. The former should not be a serious issue for the WA Alumina refineries, who already incorporate oxalate removal processes in their current systems. The sodium associated with malonate that is converted to sodium carbonate could be used to generate sodium hydroxide by reaction with calcium hydroxide (causticization). Thus, the process enables recovery of a key reagent used within the Bayer process.

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Literature Cited

- (1) Mishra, V. S.; Mahajani, V. V.; Joshi, J. B. Wet air oxidation. *Ind. Eng. Chem. Res.* **1995**, *34* (1), 2.
- (2) Alexander, M. Nonbiodegradable and other recalcitrant molecules. *Biotechnol. Bioeng.* **1973**, *15*, 611.
- (3) Zimmermann, F. J. Waste disposal. U.S. Patent 2665249, 1950.
- (4) Bhargava, S. K.; Eyer, S. Removal of Organics from Bayer Liquor—A Scientific Challenge. Proceedings of the 12th International Symposium of ICSOBA, Delphi, Greece, Sept 1998.
- (5) Armellini, F. J.; Tester, J. W. Salt separation during supercritical water oxidation of human metabolic waste: fundamental studies of salt nucleation and growth. *20th Int. Conf. Environ. Syst.* **1990**, 827–841.
- (6) Bhargava, S. K.; Eyer, S.; Sumich, M.; Akolekar, D. B. Heterogeneous catalyst for wet oxidation, method for preparation of same and method for use of same in Bayer process solutions. Australian Patent Application 17606/00, 2000.
- (7) Bhargava, S. K.; Eyer, S.; Sumich, M.; Akolekar, D. B. Homogeneous catalyst for wet oxidation, method for preparation of same and method for use of same in Bayer process solutions. Australian Patent Application 71796/00, 2000.
- (8) Bhargava, S. K.; Eyer, S.; Sumich, M.; Tardio, J.; Akolekar, D. B.; Nyboer, H. Removal of organics from Bayer liquor and wet oxidation. *Light Met.* **2000**, 43–50.
- (9) Schuchmann, M. N.; Schuchmann, H.; Von Sonntag, C. Oxidation of Hydroxymalonic Acid by OH Radicals in the Presence of and the Absence of Molecular Oxygen. *J. Phys. Chem.* **1995**, *99*, 9122–9129.
- (10) Schuchmann, M. N.; Schuchmann, H.; Von Sonntag, C. Addition to Ketomalonic Leads to Decarboxylation. *J. Am. Chem. Soc.* **1991**, *113*, 6934.
- (11) Hind, A. R.; Bhargava, S. K.; Grocott, S. C. ATR FTIR Spectroscopy Investigation of the Solid/Aqueous Interface of Low Surface Area, Water-Soluble Solids in High Ionic Strength, Highly Alkaline Media. *Langmuir* **1997**, *13* (13), 3483.
- (12) Hind, A. R.; Bhargava, S. K.; Grocott, S. C. The Adsorption of Quaternary Ammonium Compounds on the Surface of Sodium Oxalate: a FTIR/ATR Investigation under High Ionic Strength, Highly Alkaline Conditions. *Langmuir* **1997**, *13* (23), 6255.
- (13) Eyer, S. Investigation of Catalytic Wet Oxidation in Bayer Liquor. Ph.D. Thesis, RMIT University, Melbourne, Australia, 2000.

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