Catalytic ozonation for odour removal of high temperature alumina refinery condensate
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ABSTRACT

Odour emissions from aluminium processing can cause an impact on local communities surrounding such facilities. Of particular concern is fugitive odours emitted from the handling and use of refinery condensate streams, particularly the digestion condensate. This study evaluated the application of using catalytic ozonation to treat alumina refinery condensate in order to remove the potential emission of odourous compounds from the industrial wastewater. The technical challenges in treating the alumina refinery condensate are the high pH and temperatures of the wastewater effluent (over 80 °C and pH above 10) due to the industrial process. The odour removal efficiencies for different catalysts (FeCl₃, MnO, and MnSO₄) under experimental conditions in terms of controlled pH, temperature and ozone dosage were determined before and after ozone treatment using dynamic olfactometry. The result demonstrated that the addition of both FeCl₃ and MnO catalysts improved odour removal efficiencies during the ozonation of alumina condensates at similar pH and temperature conditions. FeCl₃ and MnO had similar enhancement for odour removal, however MnO was determined to be more appropriate than MnSO₄ for odour removal due to the colouration of the treated condensate.

Key words | condensate, odours, odourous emission, odour treatment, ozonation

INTRODUCTION

Odour emissions from alumina processes can be highly pervasive and cause significant concern to local communities surrounding such facilities in terms of odourous impact (Coffey 2002; Graham et al. 2002; Coffey & Ioppolo-Armanios 2004). Of particular concern are fugitive odours emitted from the handling and use of refinery condensate streams, particularly the digestion condensate. Digestion of humic substances from bauxite leads to the formation of volatile low molecular weight organics. These condensates contain a large number of volatile organic compounds (VOCs) including phenols, amines, pyrroles, ammonia, alcohols, aldehydes, ketones, sulfides and thiols, as well as low concentrations of less soluble VOCs such as toluene and C5–C7 hydrocarbons. Many of these substances have low odour thresholds (Muñoz et al. 2010), which provide the characteristic odour obtained from evaporation of condensates (Coffey & Ioppolo-Armanios 2004).

Ozonation has been successfully applied to the treatment of drinking water and wastewater. Examples include its application to reduce the tastes and odour of drinking water (Hargesheimer & Watson 2006; Meunier et al. 2006), treatment of wastewater to remove colour (Oguz et al. 2006; Hsing et al. 2007; Kreetachat et al. 2007), chemical oxygen demand reduction (Beltrán et al., 1997, 2001; Selçuk et al. 2006) and total organic carbon and dissolved organic carbon reduction (Beltrán et al. 2001; Fahmi et al. 2003; Coelho et al. 2006). However limited studies have focused on treating the wastewater itself to reduce the emission potential of the sources to emit odours. Hwang et al. (1994) demonstrated some preliminary application of using ozonation to treat wastewater in order to remove odourous compounds but the study only related to odourants treatment and did not include odour measurements using dilution olfactometry to estimate odour removal efficiency by ozonation. More recently, Wang et al. (2008) demonstrated the application of using ozonation to treat high temperature and high pH alumina refinery condensate from the Bayer process. The study showed odour removal efficiency to be greater than 80% when both the condensate and ozonation conditions were optimised. The optimised batch ozonation

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Conditions were determined to be 60 °C at pH 10 using an ozone dosage of 0.31 g/L for 30 min. The study suggested that further investigations are needed to better understand the odour characteristics before and after ozone treatment.

The aim of this paper is to evaluate the possibility of applying catalytic ozonation to the treatment of an alumina refinery condensate in order to remove the potential emission of odourous compounds from the industrial wastewater. The odour removal efficiencies for ozonation with the addition of catalysts (FeCl₃, MnO, and MnSO₄) was evaluated at previous optimised experimental conditions (Wang et al. 2008) in terms of pH, temperature, and ozone dosage, with dynamic olfactometry results being used to determine the removal potential for the wastewater before and after ozone treatment.

Material and Methods

Experimental Conditions

Alumina refinery condensate samples (Queensland Alumina Ltd) with production conditions of temperatures over 80 °C and pH above 10 were used as the test wastewater.

Ozonation experiments were conducted in a 90 cm tall bubble column reactor filled with 3.5 L condensate. The column reactor was seated within a temperature controlled water jacket with ozone being bubbled from the bottom of the column reactor through a glass fibre distributor at a flow rate of 1 L/min. Ozone was supplied by an ozone generator (Wedeco Ozomatic SWO 30) equipped with a PSA oxygen generator. The residual ozone was destroyed by venting the exhaust initially through a potassium iodide buffer solution and then venting through an activated carbon filter. An ozone detector set at 0.1 and 0.5 ppm respectively for warning and alarming concentration was used to detect for any ozone leaks during operation.

The experiments were performed at 80 °C and with 0.31 g/L ozone dosing for 30 minutes with the addition of catalysts (FeCl₃, MnO, and MnSO₄, Sigma-Aldrich) at the start of each trial. Catalyst dose for both FeCl₃ and MnO (or MnSO₄) was 80 mg/L. The pH was adjusted to maintain the original pH condition of the condensates by adding 5 mol/L NaOH solution during the reaction. This was measured manually after liquid samples were collected during the tests.

Odour Measurements

The Odour Emission Ability (OEA) before and after ozone treatment was tested to determine treatment efficiency. Raw condensate and ozone-treated samples were collected in sealed vials after 30 min reaction times. To prepare a sample for OEA determination, a volume of raw condensate or treated condensate (200 μL) was injected into a Tedlar bag filled with 12 L of high purity nitrogen gas (supplied by BOC) using a gas-tight syringe. The samples were equilibrated for at least 30 mins to ensure the complete evaporation of the liquid sample (i.e. no visible liquid droplets left in the bags) and the evaporated gases were well-mixed with the nitrogen before dilution olfactometry assessment. No pH adjustment was made to the treated samples to match the untreated condensate for the olfactometry tests. Odour concentrations were determined by a dynamic olfactometer following the Australian and New Zealand standard: Air Quality – Determination of odour concentration by dynamic olfactometry (AS/NZS 4323.3 2001). All odour samples collected and prepared in one batch of experiment were measured on the same day as the experimental tests.

Calculation of Odour Emission Ability (OEA)

OEA was used to assess odour evaporation of a condensate sample. OEA represents the total odour emission when a unit volume (1 L) of condensate evaporates. The OEA of the test samples were calculated using the equation:

\[ OEA = \frac{C \cdot V_N}{V_i} \]  

where: OEA: odour emission ability, OU/L; C: odour concentration, OU/m³; Vₙ: volume of nitrogen gas filled into a sample bag, m³; Vᵢ: volume of condensate injected into the sample bag, L.

Results and Discussion

The colour of the alumina refinery condensates were observed to change after ozonation with different catalysts (Figure 1). MnO ozonation removed the original light pink colour of the condensate and generated a white colouration of the liquid, whereas after FeCl₃ ozonation, the colour become orange, most likely due to the formation of...
Fe(OH)$_3$, whereas with MnSO$_4$ catalytic ozonation, the solution became black (D), however the dark black colour disappeared after the treated condensate was filtered (C).

The OEA (total odour emission per litre liquid sample, OU/L) was used to compare the odour emissions before and after ozone treatment with different catalysts. Odour removal efficiencies for the different catalytic ozonation conditions are plotted for iron (Fe$^{3+}$) and manganese (Mn$^{2+}$) catalysts in Figures 2 and 3.

Figures 2 and 3 show that catalytic ozonation performed better than the addition catalysts with oxygen bubbling only for both FeCl$_3$ and MnO catalysts. This indicates that the primary mechanism for odour treatment is the ozonation reaction, which is causing the destruction of the odourous compounds in the condensates and that the catalyst alone has a limited effect on odour treatment but aids in the mechanistic degradation of the condensate by ozone.

FeCl$_3$ ozonation and MnO ozonation had similar odour removal efficiency (81–91% and 80–92%, respectively), suggesting that both catalytic enhanced processes are effective for odour removal. The variations in the experimental results may be caused by slightly different pH adjustment due to the manual techniques employed during these trials. It was observed that higher removal efficiencies were achieved when more 5 mol/L NaOH was added or added earlier during the experimental trials. For FeCl$_3$ ozonation, 91–92% odour removals were observed when 5 mL 5 mol/L NaOH was added at 11 min, whereas odour removals dropped to 80–84% when 4.5 mL 5 mol/L NaOH was added at 11 min and 0.5 mL added at 22 min. Similarly for MnO ozonation, 91% odour removal efficiency was obtained when 2 mL 5 mol/L NaOH were added at 11 min; whereas the odour removal efficiencies dropped to 81–87% when 1 mL 5 mol/L NaOH was added at 10 min and subsequently 0.5 mL added at 16 and 28 min, separately. These observations confirm that the pH level during the ozonation process is a critical parameter that determines the ozonation reaction rates for the decomposition of odourous compounds in the condensates. This conclusion is also reflected somewhat by the relationship between odour removal and final pH value at the end of the tests (Figures 4 and 5).

Figure 5 showed that MnO ozonation had a higher odour removal capacity than MnSO$_4$ ozonation. This suggests that MnO and MnSO$_4$ function differently in the ozonation trials although Mn has the same valency in the
two inorganic manganese compounds. MnO is insoluble and therefore it may absorb organic compounds onto its surface resulting in improved decomposition by the ozonation. MnSO₄ is a deliquescent solid and based on the colour changes observed (Figure 1) in the MnSO₄ ozonation trials, it was assumed that one or both of the following two reactions took place:

$$\text{Mn}^{2+} + \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{H}^+ + \text{O}_2$$  \hspace{1cm} (2)

$$2\text{Mn}^{2+} + 2\text{O}_3 + 4\text{H}_2\text{O} \rightarrow 2\text{MnO(OH)}_2 + 2\text{O}_2 + 4\text{H}^+$$  \hspace{1cm} (3)

The black coloured sediment generated in the MnSO₄ ozonation trials may be MnO₂/MnO(OH)₂. Further chemical analysis is needed to determine the composition of the sediment.

During the ozonation tests, the pH dropped sharply from about 10 to as low as 2.6 after 4 minutes of reaction. These pH shifts are similar to the findings of previous studies (Karkmaz et al. 2004; Khadhraoui et al. 2009; Lucas et al. 2009). Khadhraoui et al. (2009) observed that the pH of a Congo red dye solution decreased rapidly from 8.7 to 3.8 after 2 min of ozonation and suggested that this decrease is most likely due to formation of H₂SO₄, aliphatic acids and NH₄⁺ as by-products of ozonation of Congo red dye. Lucas et al. (2009) also observed similar pH decreases from an initial pH of 7 and 10 in ozonation of winery wastewater due to the formation of dicarboxylic acids, small molecule organic acids, as well as CO₂ and carbonic acid from total mineralization. The formation of aliphatic acid compounds is usually encountered during the ozonation of benzene derivatives (Karkmaz et al. 2004; Zhao et al. 2004). It is the intermediates of weak acids generated during the reactions that lowered the pH value of the solution (Zhao et al. 2004). In this study, significant pH drops observed in the FeCl₃ catalytic ozonation trials may be caused by the formation of HCl during the reaction:

$$2\text{FeCl}_3 + 3\text{H}_2\text{O} + \text{O}_3 \rightarrow \text{Fe(OH)}_3 + 6\text{HCl}$$  \hspace{1cm} (4)

The formation of some acidic by-products may also cause pH reduction during ozonation but the formation of such products would need to be confirmed experimentally. The studies however, showed that pH adjustment does play an important role in the ozonation efficiencies of alumina refinery condensates.

Catalytic ozonation involves several processes such as diffusion, adsorption, electron transfer, and desorption, which may be occurring simultaneously during the condensate oxidation. The efficiency of the processes also depends on pH and organic substrates present in the solutions. As the composition of the condensate is largely unknown it is difficult to suggest the mechanistic degradation of the condensate. However, some general degradation approaches can be suggested for: (i) Fe catalysts; the process most likely leads to complete organics mineralization, which are developed through metal–organic complexes and not through hydroxyl radicals at least at low pH, and (ii) Mn type catalysts; like MnO, organic pollutants might be adsorbed and further decomposed on the surface of this catalyst.

Previous studies have shown that ozonation treatment of different compounds may take place at different pH conditions. For example, acidic pH has been found to be effective for ozonation and/or catalytic ozonation of sulfosalicylic acid (Tong et al. 2003), pyruvic acid (Andreozzi et al. 2001), oxalic acid (Andreozzi et al. 1996), and...
polyphenols (Lucas et al. 2009), whereas in basic pH ozonation and/or catalytic reaction conditions, nitrobenzene (Zhao et al. 2008), phenol (Yogeswary et al. 2007), and di-2-ethyl hexyl-phthalate (Khan & Jung 2008) have achieved better degradation. Legube & Leitner (1999) suggest that some inorganics (such as sulfate, sulfide, nitrite ions) are very reactive whatever the pH, whereas others exhibit a low rate constant in acidic medium and a significant increase of their reactivity as the pH increases (as observed by hypochlorous acid, hypobromous acid, ammonia).

The results in this study also indicated that the rate of pH adjustment is a key control aspect that determined odour removal efficiency for catalytic ozonation. The results support the previous study by Wang et al. (2008) and confirmed that higher pH catalytic ozonation can achieve higher odour removal. However, it is still not clear what pH condition results in the greater degradation of odourant forming compounds for different condensates and what is the optimum pH adjustment strategy.

**CONCLUSIONS**

The study demonstrated that the treatment of alumina refinery condensate using ozone in order to reduce the potential emission for odours at high pH and high temperature is enhanced by the addition of catalysts during the ozonation process as catalysts only with oxygen bubbling had limited odour removal. The ability to treat the refinery condensate at these near operational conditions will reduce the need to lower the condensate in terms of temperature and pH prior to treatment. pH adjustment during ozonation studies was important and necessary if high odour removal was required, however different pH conditions are most likely degrading different compounds within the condensate due to the mechanism of degradation. Further studies are needed to optimise the catalytic ozonation processes for removing odour from the alumina refinery condensates.

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