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Odour removal from industrial wastewaters by wet air oxidation

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Industrial wastewater samples were studied by wet air oxidation. The aim was to remove the pungent odour and simultaneously to decrease the high organic load of industrial wastewaters. Further, the effect of enzyme (catalyst) on the oxidation efficiency was studied.

Waste water samples were collected at two different plants (a rendering plant and a slaughterhouse) and oxidized with air for several days at ambient temperature. Simultaneously the odour level was monitored analytically. Quality parameters of waste water (biological oxygen demand, pH, total nitrogen, temperature and conductivity) were determined according to the standards. Chemical composition of the wastewater samples was also determined.

According to the results, wet air oxidation seems to be a suitable method for the odour abatement in wastewaters. A significant decrease in the odour level was observed after a two-day oxidation period, which was also analytically observed as a decrease in the concentrations of odorous gases. Oxidation reduced also the total nitrogen concentration and the concentration of total organic carbon. Instead, the enzyme had no effect on the odour level or on the organic load of wastewater.

Keywords: odour, rendering plant, slaughterhouse, wastewater

1. Introduction

Emissions with the sense of pleasant or unpleasant smell are defined as odorous. Principal characteristics of an odour are perceptibility, intensity, diffusibility, chemical nature and edonic tone (Pistarino *et al.* 2003). Odorous compounds have an odour threshold limit, which typically is very low, often at ppb level. Therefore, odorous air streams must be diluted at least to this limit to eliminate the smell (Mills 1995). Low odour concentrations are also a challenge to reliability of analytics and reproducibility of results.

The nuisance odour is a typical problem at many rendering plants and slaughterhouses in Europe, and it has led to complaints by the neighbouring habitants. The rendering process consists of crushing and heating animal remains to produce products; proteins and animal fats. These fatty acids can further be used e.g. in biodiesel production. Benefits of the rendering process also include reducing total waste material. However, the rendering process can have a negative effect on the environment through the emissions of unpleasant odorous compounds such as hydrogen sulphide, reduced sulphur compounds, ammonia, various fatty acids, ketones and aldehydes. (Defoer *et al.* 2002; Shareefdeen *et al.* 2005) At the slaughterhouses, wastewaters contain high levels of fats and proteins that present low biodegradability (Batstone *et al.* 1997; Martinez *et al.* 1995; Masse *et al.* 2003). However, the concentrations of fats and proteins in wastewaters are not high enough to be economically recovered. Similar to rendering plants wastewaters at a slaughterhouse also emit unpleasant odorous compounds. (Lassi *et al.* 2007).

At rendering plants and slaughterhouses, odour is often present also in the condense waters of a process, and therefore, it should be removed both from the gas and the liquid phases. Wet air oxidation (WAO) seems to be a promising technology in wastewater treatment. In this technology water soluble and suspended compounds are oxidized (by air or oxygen) at high temperatures and pressures to carbon dioxide and water (Kolaczkowski *et al.* 1999). Some intermediates, mostly carboxylic acids, are also formed (Verenich, 2003). Low mass transfer rate between the liquid and the gas phase decreases the efficiency of the process. Oxygen solubility can be increased by increasing the pressure (cost-efficiency decreases). (Levec and Pintar, 2007)

In this study, wet air oxidation was used to study the purification of industrial wastewaters at a rendering plant and at a slaughterhouse. The aim was to remove the pungent odour and simultaneously to decrease the high organic load of industrial wastewater samples. Further, the effect of enzymatic treatment (catalyst) on the oxidation efficiency was studied.

2. Experimental

2.1 General

The wastewater samples were collected at a slaughterhouse (ref 1) and at a rendering plant (ref 2) in 20 l barrels. In both cases, samples were taken prior to the main wastewater treatment process.

The experiments were performed by using a batch reactor (with a height of 1 m and a diameter of 0.6 m) equipped with a fine bubble diffuser (IFU Type D 520–252, with a diameter of 0.52 m and height of 0.11 m) through which air flow was introduced. The fine bubble diffuser was installed at the bottom of the reactor and the bubble size was adjusted to be from 1 to 4 mm. The oxygen transfer efficiency of the fine bubble diffuser was 24 g O_2 Nm^{-3} in one meter of water. The flow rate used in the experiments was 0.24 m^3 air h^{-1}. The experimental set-up is presented in Figure 1.

Wastewater samples were oxidized for several days (1-4 days) at ambient temperature (22°C, constant during the oxidation) and simultaneously the odour level was monitored analytically by an FTIR gas analyzer (Gasmet Dx4000N). The odour level was monitored by an olfactometry-like board of people evaluating the odour with the scale from 1 to 5. Enzymatic solution was added at the beginning of the experiments (when used).

a) b)

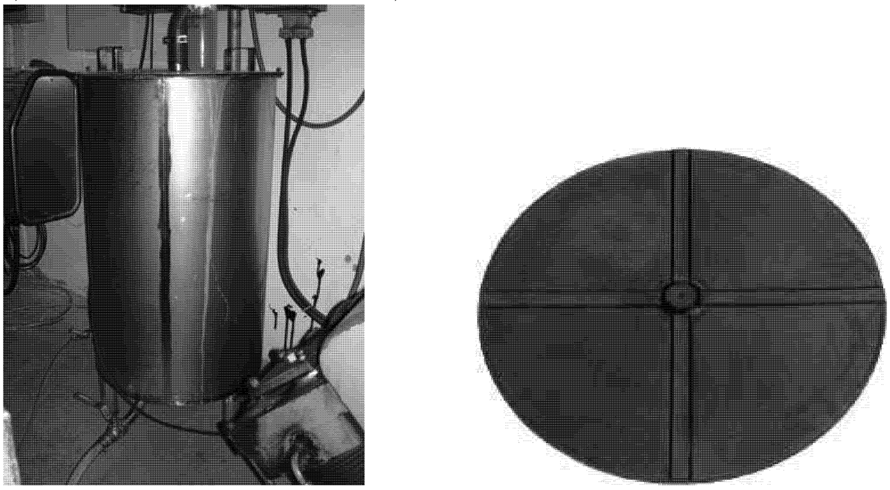

Figure 1. Experimental set-up for the oxidation experiments. a) A pilot-scale absorption-oxidation reactor with a height of 1 m and a diameter of 0.60 m. b) A fine bubble diffuser (IFU Type D 520–252), with a diameter of 0.52 m and height (maximum) of 0.11 m.

2.2 Measurement and analysis of odours

The odour measurements were performed during the oxidation. *In situ* analysis of odorous gas flow was carried out during the oxidation by FTIR, Gasmet Dx 4000N (Gasmet Technologies, 2006). The FTIR spectrometer was equipped with the automatic sampler, with heated sampling lines and sampling probe. It has calibrations for 35 gaseous compounds in the concentration area of 0-500 ppm.

2.3 Analysis of wastewater samples

Quality parameters of waste water (biological oxygen demand BOD, pH, total nitrogen, temperature and conductivity) were determined before and during the oxidation according to the standard procedures (SFS 1979; SFS 1988; SFS 1994; SFS 1998).

Chemical composition of the water samples was determined after filtration by TOF-MS. The wastewater was filtered and the solid contents were determined.

3. Results and discussion

3.1 Effect of air oxidation on the odour level

An olfactometry-like board was used to evaluate the odour level of untreated and treated wastewater samples with the scale from 1 to 5.

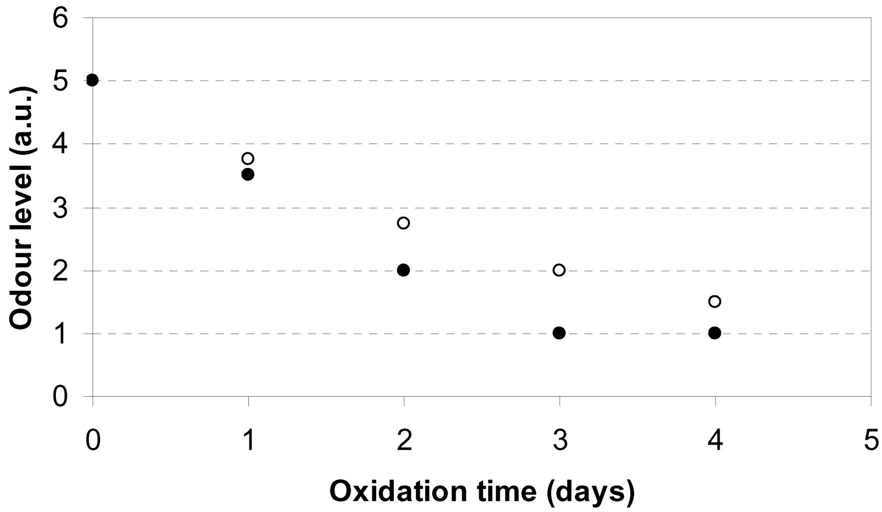

Figure 2. Odour level as a function of oxidation time (days); ● at a slaughterhouse (ref 1) and ○ at a rendering plant (ref 2). In both cases the level of odour in the beginning of the experiment was evaluated to be 5.

A significant decrease in the odour level was observed according to an olfactometry-like board (see Figure 2). After a two-day oxidation period the unpleasant (pungent) odour disappeared. At that time, the odour level (a.u.) has decreased to about 50% from the original level (ref 1 and ref 2). Therefore, based on this fact, this abatement technique was suitable for odour abatement at the rendering plant and at the slaughterhouse.

Based on the analytical measurements, it can be concluded that odour is a mixture of several gas compounds (see Table 1). Analytical results showed also the reduction in the total gas concentrations of odorous compounds during the oxidation.

Table 1. Odorous compounds analytically detected (ref 2).

Compound		
Ammonia	Methylamine	Formic acid
Acetaldehyde	Dimethylamine	Formaldehyde
Methyl mercaptane	Trimethylamine	
Dimethyl sulphide	Triethylamine	

3.2 Effect of oxidation on the wastewater quality

Table 2 presents the average composition of wastewater before and after the oxidation (ref 1). The BOD_7 level of the treated wastewater should be below 500 mg/l.

Table 2. Average composition of wastewater before and after the oxidation (slaughterhouse, ref 1).

Parameter*	**Before the oxidation**	**After the 4 d oxidation**
pH	6,4	7,9
Conductivity (mS/m)	297	245
BOD_7 (mg/l)	2800	970
Total nitrogen (mg/l)	278	239
Temperature (ºC)	21	21

*wastewater contains also some cations and anions

As can be concluded based on the results presented in Table 2, wet air oxidation had a significant effect on the BOD_7 level of the wastewater. A 65% reduction was observed. This is a good result due to the fact that wet oxidation was used as a pre-treatment step in wastewater treatment process (before flotation). Therefore, the reduction requirement in the process is easily achieved. Instead, wet air oxidation affected only a little total nitrogen concentration, and thus, the reduction achieved (14%) was too low. This result was expected, because it is known that aerobic wastewater treatment typically reduces total nitrogen concentration only 10 to 15% (Karttunen, 2004). Further, in an industrial scale the residence times in the reactor are typically shorter, and thus there is still need for the improvements in the system.

Table 3 presents the average composition of wastewater before and after the oxidation (ref 2). In this case, the reduction requirement (optimal) for the BOD_7 is over 95% and for total nitrogen over 80%.

Table 3. Average composition of wastewater before and after the oxidation (rendering plant, ref 2).

Parameter	**Before the oxidation**	**After the 4 d oxidation**
pH	8,5	8,9
Conductivity (mS/m)	390	352
BOD_7 (mg/l)	3200	1700
Total nitrogen (mg/l)	780	670
Temperature (ºC)	21	21

According to the results (Table 3), the oxidations of wastewater samples led to poor removal efficiencies of BOD_7 and total nitrogen (rendering plant). At its best, these removal efficiencies for BOD_7 and nitrogen were at around 47% and 14%, respectively. For nitrogen this was expected, but for BOD_7 removal efficiency was too low.

3.3 Effect of enzyme

The effect of enzyme was evaluated in the case of ref 1 (where higher reductions for BOD_7 were observed). An olfactometry-like board evaluated the odour level of slaughterhouse´s wastewaters in the presence and absence of enzyme (in the scale of 1 to 5). Enzyme solution was added in the ratio of 1.5 ml of enzyme in one litre of wastewater.

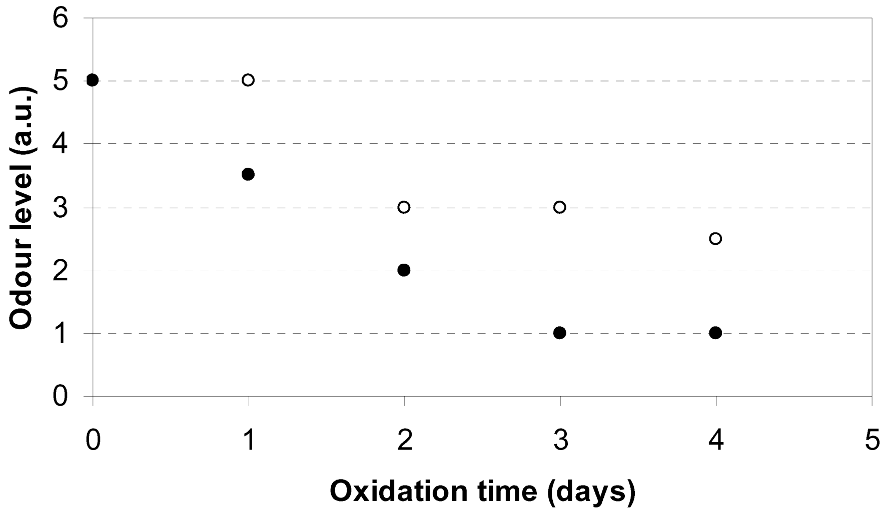

Figure 3. Odour level as a function of oxidation time (days) at a slaughterhouse (ref 1); ● without the enzyme and ○ in the presence of enzyme.

As can be seen in Figure 3, the use of enzyme did not decrease the odour level, which was the original reason for the use of it. The odour level was even higher in the presence of enzyme. Analytically no significant differences were observed in concentrations of odorous compounds.

Table 4 presents the effect of enzyme on the wastewater quality. Wet air oxidation in the presence of enzyme affected only a little BOD_7 level, and it had no effect on the total nitrogen concentration. Better results for BOD_7 and total nitrogen were obtained without the enzyme. The similar results were obtained also in a full-scale wastewater treatment system.

Table 4. Effect of enzyme on wastewater quality after the 4 d oxidation (slaughterhouse wastewater samples).

Parameter	Wastewater (untreated)	Without the enzyme	In the presence of enzyme
pH	6,4	7,9	7,2
Conductivity (mS/m)	297	245	266
BOD_7 (mg/l)	2800	970	2300
Total nitrogen (mg/l)	278	239	278
Temperature (ºC)	21	21	21

4. Conclusions

Animal production facilities, e.g. rendering plants and slaughterhouses as in this case, emit various odorous compounds, such as ammonia and sulphur containing organic compounds. Therefore, treatment technologies are needed to limit nuisance odour in the effluent flows. This study aimed at decreasing the unpleasant odour and simultaneously at removing high organic load in the wastewaters.

According to the results, wet air oxidation as a pre-treatment step seems to be a promising technology for odour abatement in wastewater treatment process at the slaughterhouse and at the rendering plant. In both cases a significant decrease in the odour level was observed and the pungent odour disappeared already after a two-day oxidation period: This was also analytically observed in the concentrations of odorous gases (e.g. methyl mercaptane). At the slaughterhouse, oxidation reduced BOD_7 level significantly, but also a 47% reduction was observed at a rendering plant. In the case of total nitrogen concentrations, only a 14% reduction was obtained. This was expected due to the aerobic treatment process.

Based on the results, it can be concluded that the enzyme used as a catalyst had no effect on the odour level. Further, it had no effect on the reduction of organic load of wastewater neither the nitrogen concentration.

5. References

Batstone, D, Keller, J., Newell, B., Newland, M., 1998, Water Sci. Technol. 36, 423.

Defoer, N., De Bo, I., van Langenhove, H., Dewulf, J. and van Elst, T, 2002, Journal of Chromatography 970, 259.

Finnish Standards Association SFS, 1979, Standard SFS 3021: Determination of pH-value of water.

Finnish Standards Association SFS, 1988, Standard SFS 5505: Determination of inorganic and organic nitrogen in waste water. Modified Kjeldahl method.

Finnish Standards Association SFS, 1994, Standard SFS-EN 27888: Water quality. Determination of electrical conductivity.

Finnish Standards Association SFS, 1998, Standard SFS-EN 1899-1: Water quality. Determination of biochemical oxygen demand after n days (BOD_n).

Gasmet Technologies, 2006, Gasmet Dx4000 technical data. Brochure.

Karttunen, E., 2004, RIL 124-2 Vesihuolto II. Suomen Rakennusinsinöörien Liitto RIL r.y. Vammala: Vammalan Kirjapaino Oy. (in Finnish)

Kolaczkowski, S.T., Plucinski, P., Beltran, F.J., Rivas, F.J., McLurgh, D.B., 1999, Chemical Engineering Journal 73, 143.

Lassi, U., Heikkinen, M. and Perttunen, A-S., 2007, Measurement report, unpublished data (in Finnish).

Levec, J. and Pintar, A., 2007, Catalysis Today 124, 172.

Masse, L, Massé, D.I., Kennedy, K.J, 2003, Process Biochemistry 38, 1365.

Mills, B, 1995, Filtration & Separation, 147-152.

Pistarino, C., Busca, G. and Gerla, R, 2003, Chemical Engineering Transactions vol. 3, 715.

Shareefdeen, Z., Herner, B., Webb, D., Verhaeghe, L. and Wilson, S, 2005, Chemical Engineering Journal 113, 215.

Verenich, S., 2003, Wet Oxidation of Concentrated Wastewaters. Doctoral thesis, Lappeenranta University of Technology.