Review of odour control technologies

Introduction

How many times have you been to a site, for example an animal rendering plant, chicken factory, landfill site, or effluent plant and thought that it was about time they found out how to control that distasteful odour? By understanding the problem you can start to identify what odour control products may be helpful in overcoming this problem. It is even rumoured that the Queen of England has the local Windsor effluent plant close when she was in residence at Windsor Castle due to the unpleasant smell.

Over recent years, industrial producers have focused on reducing the quantity and improving the quality of their solid waste. Nevertheless, for odour issues it has long been a forgotten issue within the producers' environmental concerns. Neighbours of the producers have taken legal action against them based on the odour nuisance. To date, odour sources have been subject to nuisance suits based on the unreasonable interference with their neighbours' use of their property. A distinction often is made between a public nuisance (infringement on the rights of a number of people) and a private nuisance. In most cases, action is lodged against an odour source as a public nuisance by a local community seeking relief in the form of administrative orders to cause an abatement of odour, administrative penalties, or injunctive relief. However, the lack of clear regulations leads to more difficult technical assistance for odour control. A private nuisance action consists of a lawsuit between private parties that seeks a court order to cause the operator to abate the odour, an injunction to close the operation, actual damages, punitive damages, or some combination of these. Producers can avoid many of the potential lawsuits that threaten them by being worthy of retention in their local communities. Communities support enterprises that contribute to the overall well-being of the area. When the benefits of an operation in the community outweigh the total cost, that operation become worth keeping. As a result, it can be foreseen that the overall spending by the industrial producers for preventing and reducing odour nuisance has increased substantially.

Controlling odour emission has become a challenge for many industrial production facilities, but what is considered odour nuisance? Odour is a very complex matter to quantify and qualify, so it varies from person what is considered smelly. A malodorous substance called mercaptan can be very pungent at an extremely low concentration of for example 5 ppb (parts per billion). Other bad odours such as H_2S loose their smell at very high concentrations. Research has provided a useful background on how odours are produced and where odours are most likely to be formed. There are basically three elements that cause most foul odours: *nitrogen*, *oxygen* and *sulphur*. The parent compound of the nitrogen is normally ammonia, found in all manner of household and industrial compounds such as glass cleaner and smelling salts. Whilst pungent, ammonia is not normally considered foul unlike organic derivatives of ammonia.

Amines such as dimethylamine and trimethylamine give rise to fishy odours, and higher amines; tetra and penta-methylenes arise from the putrifaction of flesh. Ammonia derivatives are also associated with pet urine. Sulphurous odours are normally associated with rotten eggs and organic derivatives such as butyl mercaptan with animals such as the skunk. Low velocity, constant wind movement favours odour transport because such wind movement minimizes dilution. The following tables show an overview on odour thresholds and concentrations.

Odorous Substances	Formula	Characteristic Odour	Odour Threshold (ppm)	Recognition Threshold	Molecular Weight
Acetaldehyde	$CH_3{\cdot}CHO$	pungent, fruity	0.004	0.21	44.05
Allyl mercaptan	$CH_2{\cdot}CH{\cdot}CH_2{\cdot}SH$	strong garlic, coffee	0.0005	-	74.15
Ammonia	NH_3	sharp, pungent	0.037	46.8	17.03
Amyl mercaptan	$CH_3{\cdot}(CH_2)_3{\cdot}CH_2{\cdot}SH$	unpleasant, putrid	0.0003	-	104.22
Benzyl mercaptan	$C_6H_5{\cdot}CH_2{\cdot}SH$	unpleasant, strong	0.00019	-	124.21
Butylamine	$C_2H_5{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$	sour, ammonia-like	-	0.24	73.14
Cadaverine	$H_2N{\cdot}(CH_2)_5{\cdot}NH_2$	putrid, decaying flesh	-	-	102.18
Chlorine	Cl_2	pungent, suffocating	0.01	0.314	70.91
Chlorophenol	ClC_6H_5O	medicinal, phenolic	0.00018	-	128.55
Crotyl mercaptan	$CH_3{\cdot}CH{:}CH{\cdot}CH_2{\cdot}S$	skunk-like	0.000029	-	90.19
Dibutylamine	$(C_4H_9)_2NH$	fishy	0.016	-	129.25
Diisopropylamine	$(C_3H_7)_2NH$	fishy	0.0035	0.085	101.19
Dimethylamine	$(CH_3)_2NH$	putrid, fishy	0.047	0.047	45.08
Dimethyl sulfide	$(CH_3)_2S$	decayed vegetables	0.001	0.001	62.13
Diphenyl sulfide	$(C_6H_5)_2S$	unpleasant	0.000048	0.0021	186.28
Ethylamine	$C_2H_5{\cdot}NH_2$	ammoniacal	0.83	0.83	45.08
Ethyl mercaptan	$C_2H_5{\cdot}SH$	decayed cabbage	0.00019	0.001	62.1
Hydrogen sulfide	H_2S	rotten eggs	0.00047	0.0047	34.1

Table 1.1 Odour substances and odour thresholds

Odorous Substances	Formula	Characteristic Odour	Odour Threshold (ppm)	Recognition Threshold	Molecular Weight
Indole	$C_2H_6NH_2$	recal, nauseating	-	-	117.15
Methylamine	CH_3NH_2	putrid, fishy	0.021	0.021	31.05
Methyl mercaptan	CH_3SH	decayed cabbage	0.0011	0.0021	48.1
Ozone	O_3	irritating above 2 ppm	0.001	-	48
Propyl mercaptan	$CH_3 \cdot CH_2 \cdot CH_2 \cdot SH$	unpleasant	0.000075	-	76.16
Putrescine	$NH_2(CH_2)_4NH_2$	putrid, nauseating	-	-	88.15
Pyridine	C_6H_5N	disagreeable, irritating	0.0037	-	79.1
Skatole	C_9H_9N	fecal, nauseating	0.0012	0.47	131.2
Sulfur dioxide	SO_2	pungent, irritating	0.009	-	64.07
Tert-butyl	$(CH_3)_3C \cdot SH$	skunk, unpleasant	0.00008	-	90.19
Thiocresol	$CH_3 \cdot C_6 \cdot H_4 \cdot SH$	skunk, rancid	0.0001	-	124.21
Thiophenol	C_6H_5SH	putrid, garlic-like	0.000026	0.28	110.18
Triethylamine	$(S_2H_5)_3N$	ammoniacal, fishy	0.08	-	101.19

Table 1.2 Odour substances and odour thresholds

In general speaking, the major types of odours generated in wastewater treatment facilities are:

1. Amines (fishy odour quality);
2. Ammonia, NH_3 (ammonia odour quality);
3. Diamines (decayed flesh odour quality);
4. Hydrogen sulphide, H_2S (rotten egg odour quality);
5. Mercaptans (skunk odour quality);
6. Organic sulphides (rotten cabbage odour quality);
7. Skatole (fecal odour quality).

Technologies are available that allow prediction of the distances that odours will be transported in identifiable concentrations under various climatic conditions. Engineering solutions have been demonstrated that will solve most of the odour control issues. The design of systems balances the construction and operating cost of the system with the degree of odour control. The challenge is that under current social and regulatory constraints, sites that are close to developed areas, along major highways, or near an adequate feed and labour supply may have more demanding odour control constraints, making them more expensive to develop.

One of the challenges regarding odour control is the difficulty in measuring odours in a way that is meaningful to neighbours or the courts. As most samples of odorous air contain a mixture of smelly substances with each different odour threshold, it is nearly possible to have an on-line analyzer or measuring system which can quantify and differentiate between these components. Nowadays, the standard method for measuring odours is the olfactory method. In order to detect odours the responsible compound needs to be volatile and therefore be dispersed in the air we breathe. Once airborne the compound can stimulate the olfactory glands in the nose and cause a number of complex reactions resulting in what we know as smell. With some compounds only a few molecules may be needed to cause this reaction, whilst others are capable of blocking odours when in high concentrations and become no longer detectable above certain levels. This in fact could be dangerous as it may be a lethal compound such as *hydrogen sulphide*. Many foul smells are formed by dead and decaying matter and during the process of decay the organic material breaks down into other, volatile, compounds giving rise to the smell.

Treatment facility personnel and the consulting engineering community are generally aware of many of technologies available to treat these odours. However, these groups are often hindered in their attempts to make the proper technology selection by the lack of an effective, unbiased means to compare the relative merits of each technology.

This short paper provides unbiased technical information to the industrial community, especially to malodorous substances producers, i.e. wastewater plants, animal breeding, composting plants, landfill sites, etc.. By comparing currently commercially available odour control technologies, producers and engineers can accomplish their needs.

Currently available odour control technologies

There are a wide variety of odour control products available on the market today. The majority can be grouped into four distinct categories:

- Physical
  - Physic adsorption
  - Dilution
  - Coverage
  - Masking

- Chemical
  - Absorption
  - Oxidation

- Biological
  - Biofiltration
  - Bioscrubbing

- Combined technologies

Besides of the above mentioned odour control methods, some other technologies may also be used to reduce the odour generation, for instance: replace the raw material to control of the generation of less odorous emissions; change the production process to reduce the generation of odorous compounds; diet optimization for animals to limit odour produced from livestock.

- ***<u>Physic Adsorption</u>***

Adsorption has been used in odour control at least since the mid of 1970's. Adsorbers commonly used empty activated carbon or alumina pellets impregnated with permanganate. These materials are highly porous and consequently there is a large surface area upon which adsorption of odorous compounds may occur.

Activated carbon is generally considered for organic gases and vapours, some inorganic gases and some metallic vaporous. The mechanism which attracts and attaches the molecules to the surface of the pores is known as Van der Waals forces.

The odorous stream needs to be pretreated before it passes through activated carbon when its temperature is high, moisture content is high or it contains dusts. The odorous stream should be free of dust in order not to clog the surface of activated carbon.

Activated carbon systems generally have the smallest overall footprint of any of the odour control technologies. Moreover, activated carbon systems do not require lots of moving parts. The carbon system itself has no moving parts; the fan and dampers are the only components with moving parts. Carbon systems generally do not require electronic sensors or instruments and generally do not require controls, other than fan motor starters and start-stop buttons. Activated carbon needs to be replaced before it is saturated. This operation requires that the system goes off line for several days. The used activated carbon can be regenerated, otherwise it should be disposed to a landfill.

Activated carbon can exhibit a wide range of *hydrogen sulphide* capacities. It is generally accepted that activated carbon can be economically used to treat H_2S levels as high as 20 to 30 ppm. *Organic sulphur compounds* are the most prevalent in wastewater odour control after hydrogen sulfide. In all cases, these compounds will be removed by activated carbon via physical adsorption. Carbon can economically treat organic sulphur compounds up to the low ppm (1-5) concentration level. Higher concentrations than these will typically exhaust the carbon so frequently that carbon exchanges will represent an unreasonable expense and operator headache. Activated carbon is generally not well suited economically for treatment of high loadings of organic compounds (5 ppm and greater). Carbon, regardless of type, is also not recommended for H2S loadings greater than 200 ppm.

Activated carbon can provide useful capacity for most *amine compounds* found in municipal wastewater. However, if the odorous stream is mixed with organic sulphur compounds, carbon has a limited capacity for such compounds and cannot be regenerated in place. Most activated carbons are ineffective for *ammonia* removal. The ammonia molecule adsorbs very poorly on carbon and breakthrough occurs rapidly. Carbon is not typically recommended for ammonia removal.

- ***<u>Chemical Absorption</u>***

This technology is widely known in the odour industry as chemical wet scrubbing. Chemical scrubber has been shown to be highly effective on H_2S and ammonia odours. Moreover, chemical scrubber becomes economically attractive compared with incineration and adsorption on activated carbon when the volume of odorous gas to be treated is greater than 5000 m^3/hour.

The odour removal is achieved by mass transfer absorption via contact of the air stream with aqueous solution on random packing material in a scrubbing chamber. The liquid is typically water, adjusted to the proper pH and oxidation potential by chemicals. Thus, chemical scrubber needs to be well designed to ensure adequate contact between the gas and liquid phase. Furthermore, the treatment ability should be sufficient enough to treat the odorous gases generated. It is also important to note, when necessary to remove ammonia with sulfuric acid, an additional chamber will be required. Hot moist vapour streams need be cooled before contacting scrubbing solutions.

The most frequently used absorbing solutions are:

- Sodium hydroxide – ideal for absorb hydrogen sulphide and mercaptans;
- Amine – used to trap hydrogen sulphide of hydrocarbon gases from petroleum refinery;
- Chlorine, sodium hypochlorite, potassium permanganate, ozone or hydrogen peroxide – effective to absorb unsaturated organic compounds;
- Diluted sulphuric acid – used to absorb ammonia.

The following simplified equations illustrate the chemical combinations and typical pH/ORP settings for the removal of H_2S and ammonia in conventional chemical scrubbing systems:

- Absorption process

$$NaOH + H_2S \rightarrow Na^+ + HS^- + H_2O$$

- Adsorption with oxidation

$$HS^- + NaOCl \rightarrow SO_4^{2-} + HCl$$

- Absorption of ammonia with acid

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

The principal types of gas absorption equipments include packed towers, plate or tray towers, spray towers, venture and fluidized-bed scrubbers. Chemical scrubbers require numerous and sophisticated controls and instrumentation. Instruments include pH and ORP sensors, metering pumps (linked to and controlled by H_2S monitors), recirculation pumps, level switches (linked to chemical supply tanks and alarms), and fan controls. This makes chemical scrubbers more complex and maintenance intensive. Moreover, chemical scrubbers require periodic replenishment of their chemical supply. Normally, chemicals are replenished every 30 to 60 days.

When configured as a two-stage caustic system, chemical scrubbers can achieve 99% removal of H_2S, and when a third stage (usually the first in line) is added with acid for ammonia removal, ammonia can also be removed in the 99% efficiency range. However, chemical scrubbers are less effective on organic sulphur compounds, with removal efficiencies between 20 to 70%.

- ***<u>Biological Oxidation</u>***

Biological units commonly used for air treatment are based on three different technologies:

- Biofilter;
- Biotrickling filter;
- Bioscrubber.

These technologies can be distinguished either by the mobility of the micro-organisms and the liquid phase (as in bioscrubber) or only the liquid phase (as in trickling filter).

In biofilters and trickling filters, the microorganisms are fixed in a support or packing material. Since the biological technologies work at normal operating conditions of temperature and pressure, therefore, they are relatively cheap with high efficiencies when the waste gases characterised by high flow rates and low concentrations of odorous compounds.

a) Biofilters

For biological odour control, the odour is removed by biological processes – bacterial action. The bacteria grow on inert supports, allowing intimate contact between the odorous gases and the bacteria. The organic odour and VOCs are brought in contact with the natural microorganisms that can use them as a food source. The process is self-sustaining.

In recent years, engineered biofilters have been developed with a variety of advances to increase their efficiency of treatment and reduce their footprint. The contaminated air stream is conditioned to maintain temperature and humidity levels ideal for the metabolism of the microbes. The compost or organic media that supports the microbes is structured to increase the effective surface area and allow treatment throughout the depth of the beds.

All properly design biofilters require fans and dampers to provide and regulate odorous air supply to the biofilters. Additionally, biofilters must be kept hydrated, so an irrigation system is required as well. Normal fan and pump maintenance must be performed. Some biofilters also require the addition of nutrients or buffering chemicals, requiring additional storage tanks and pumps. The bed may have to be replaced regularly because of mechanical failure.
Organic compounds are very effectively treated with biofilters. Sulphur compounds, amines and ammonia are also effectively treated with biofiltration. In contrast with activated carbon, biofilters prefer higher concentrations of organic compounds. Hydrogen sulphide in low to moderate levels (up to 10 ppm) can also be effectively and economically treated by biofilters. However, higher loadings will cause a loss of capacity for the other odorous compounds. Furthermore, biofilters generally operate with contact times between 15 to 60 seconds, with higher contact times resulting in higher efficiencies. Biofilters typically achieve an average odour unit (OU) effluent level between 200 and 400 OU.

b) Bioscrubbers

Bioscrubbers use the combined principles of liquid scrubbing and the biofiltration in order to remove vapours pollutions from waste gases. Bioscrubbers can only be used successfully if the contaminants can be removed from the waste gas by absorption in a water and activated sludge mixture, Furthermore, the contaminants must be biodegradable.

As discussed, Bioscrubber's operate similarly to biotrickling filters and wet packed chemical scrubbers. However, they contain an acid resistant inert high porosity media. Secondary effluent solution, or make up water, containing mineral nutrients and trace elements recirculating solution and media serve as an ecosystem to optimize the growth of thin film sulphur oxidizing bacteria, principally *thiobacilli*.

$$H_2S + 2O_2 \rightarrow H_2SO_4$$

Because the byproduct of biological hydrogen sulphide oxidation is sulphuric acid, the recirculation solution must have adequate blowdown rates to ensure that the acid concentration does not increase to the point that it limits the solubility of hydrogen sulphide in the water. Although the sulphur oxidizing bacteria can survive a pH well below 1, an optimum balance for both the growth of the bacteria and the solubility of hydrogen sulphide is achieved in the range of 2 to 3.

Bioscrubbers require a fan, flow control dampers, and a recirculation pump. Media life is generally 10 years or even longer. Compare with other hydrogen sulphide control technologies, bioscrubber's operational costs are fairly low, microbial oxidation occur at ambient temperatures, no chemicals are consumed, and a minimal amount of labour is required for maintenance.

Bioscrubbers are best used for removal of moderate to high levels of H2S (concentrations from 5 to 1000 ppm). Within this range, bioscrubbers should deliver a minimum of 98% removal capacity, and often the removal capacity is greater than 99%. As the byproduct of H2S consumption is sulphuric acid, this allows the bioscrubbers to effectively function as an acid scrubber for ammonia and amine reduction. Removal efficiencies in the high 90% ranges are typical.