Biological treatment of amine wastes generated in post combustion CO$_2$ capture

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Abstract

The wastes generation by amine degradation is an important issue to be addressed when considering CCS schemes. Biological treatment of amine wastes can be a strategy with reasonable economy and environmental sustainability. Both the aerobic and anaerobic wastewater treatment techniques can be used for amine wastes treatment, providing culture adaptation and maintaining suitable operating conditions. Aerobic treatment can, generally, provide higher biodegradation rates while anaerobic processes can be much more energy efficient. A combination of aerobic and anaerobic treatment is promising. Addition of a supplementary organic feed may facilitate the anaerobic digestion of amine wastes and this opens the possibility of using common industrial or municipal waste digesters for amine wastes treatment.

Keywords: Amine wastes, Anaerobic digestion, Biological treatment, Monoethanolamine (MEA)

1. Amine absorption

Amines are organic compounds with active N atoms which can be used to react rapidly with CO$_2$ selectively and reversibly. Several types of amines (including recently introduced hindered amines) and also amine blends are being used in gas purification. The high reactivity, water solubility and cost effectiveness of monoethanolamine (MEA) allow it to be used successfully against low partial pressure diluted CO$_2$ streams like flue gases (0.1 - 0.2 atm. CO$_2$). This predicts that MEA will continue as one of the major solvents to be used in large scale CCS (carbon capture and sequestration) projects in years to come.

2. Waste generation

Disadvantages of using MEA as a CO$_2$ scrubbing agent are the high desorption heat duty and the relatively fast degradation of MEA. This solvent degradation leads to the need of supplementing the solvent system with fresh MEA regularly and also removing the degraded solvent.

Amine reclaimer wastes can contain liquid, semi-solid or solid fractions of wastes generated by amine degradation and by other additives. Exact compositions, toxicity and volumes of these wastes are still under research. MEA itself represents a larger fraction of the composition in amine wastes [1, 2]. Generally, the disposal regulations on these types of reclaimer bottom wastes are stringent [3].

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3. Toxicity of amine wastes

Amine wastes can pose a moderate to a severe threat to the living species and eco-systems. Animal toxicity and health impacts of some of the commonly recognized amine degradation products are presented by Thitakamol et al. [4]. Toxicity on plant growth by amine wastes contaminated soil is evaluated by Liuzinas et al. [5]. It is found that MEA wastes can have a significant toxicity, but at lower concentrations (below 1%, i.e. 1:100 proportion of MEA and soil, respectively) the germination percentages are quite high and that suggests it is possible to use phytoremediation for the detoxification of amine wastes at lower concentrations and that diffuse pollution can be naturally degraded by the vegetation. Eide-Haugmo et al. [6] reported the aquatic toxicity of different amines on marine planktonic unicellular algae.

Liuzinas et al. [5] studied the toxicity of spent amine wastes on microorganisms observing different sensitivities for different species. Microorganisms can grow at high waste concentrations in soil and they also documented MEA degradation. Some microbial toxicity data are reported in IUCLID (International Uniform Chemical Information Database) data sheets [7], showing large variations in MEA tolerance under different conditions.

4. Treatment and disposal options

NH_3 resulting from the decomposition of amine /amine wastes can be used as a way of reducing NO_x emissions in incinerators and kilns. NH_3 is commonly used as an agent to transform NO_x into nitrogen gas [8-10]. It is likely that other amino compounds present in amine wastes can also serve the same purpose. Further it has been observed that spraying amines in incinerators can effectively reduce the formation of dangerous and persistent air pollutants of polychlorinated dibenzo–p–dioxins and dibenzofurans (PCDDs and PCDFs) [11]. According to the above findings, incinerating the solid or semi-solids fractions of amine wastes in an incinerator or a kiln (e.g. cement plants) can be considered advantageous. Incineration of the amine wastes generated as a liquid stream, nevertheless, may not be a cost-effective solution due to the presence of water which results in a negative net calorific value. Potentials of biological treatment are, therefore, investigated as a sustainable solution. It is also investigated to better understand the fate of such matter inadvertently spread in nature.

5. Biological Treatment

The treatment of amine wastes generated in CO_2 capture facilities has been investigated in some studies [12-14]. Data from companies producing MEA, published by IUCLID [7], show considerable variations in the results reported, seemingly due to different experimental conditions.

5.1. Aerobic biodegradation of amines

5.1.1. Earlier studies
Ohtaguchi et al. [12] demonstrated aerobic cleaving of monoethanolamine into ammonium ion and acetaldehyde by *Escherichia coli K 12*. The generated acetaldehyde was further transformed into acetic acid while most of the ammonium was assimilated as a nitrogen source for the microorganisms. A maximum degradation rate of 1.64 g/L.h was detected. Aerobic biodegradation of MEA is considered to start with the cleavage of the amine group and may proceed through the formation of CH_3CHO and CH_3COOH. The evolution of NH_3 can be taken as a measure of the extent of degradation.

According to Lai and Shieh [13] and Ohtaguchi et al. [12], MEA can be catabolised by microorganisms for their nitrogen needs (as ammonium) and as a food carbon and energy source. Lai and Shieh [13] further observed that MEA is highly bio-degradable under anoxic conditions (using NO_3^- as an electron acceptor). Ohtaguchi and Yokoyama [14], Wang et al. [15] and Greene et al. [16] documented different amine degradations, bacterial strains and conditions to enhance aerobic biodegradation. Bio-degradations of about 42 different amines were tested by Eide-Haugmo et al. [6] under natural marine conditions, while the real degradation potential with an adapted biomass can be higher.

5.1.2. Biodegradation rates

The biodegradation rates of MEA under different initial concentrations in four experimental series are presented in Figure 1. Test Series 3 and 4 conducted with the non-adopted inoculum gave a low degradation rate of 0.54 d^{-1} for the initial MEA concentration of 500 mg/L (Figure 1c). But when repeated with an adopted inoculum (series 5 and 6), the degradation rate was significantly increased to 0.78 d^{-1} (Figure 1b).
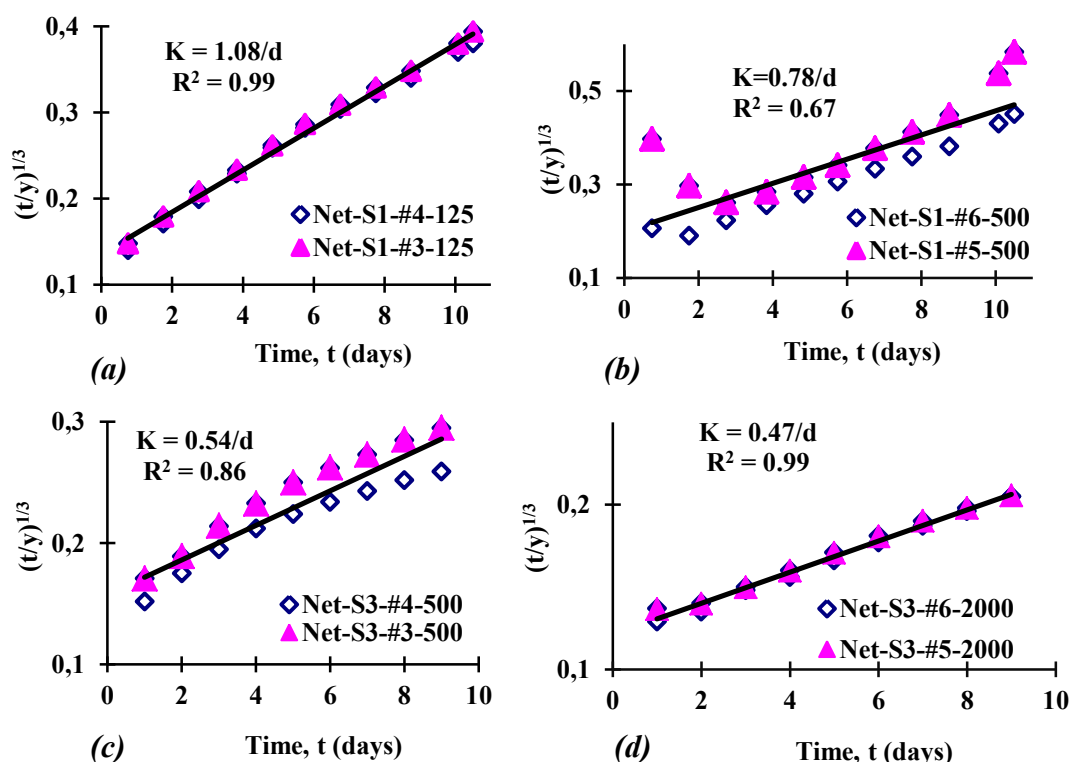

Figure 1(*a-d*): First order bio-degradation rates (*K*) obtained for MEA under different initial concentrations (125, 500 and 2000 mg/L) using adopted and non-adopted inoculums (*y* stands for the BOD exerted at time *t*).

Further, the adopted inoculum was able to tolerate the considerably higher initial MEA concentration of 2000 mg/L (Figure 1d). Fürhacker et al. [17] similarly observed no degradation of a methyldiethanolamine (MDEA) solution in a standard BOD test, but later achieved 96 % degradation using an adapted inoculum. Generally this shows that amines can inhibit degradation but adaptation can overcome this limitation, as for other recalcitrant substrates.

BOD tests of several other amines used in CO_2 capture; piperazine, aminomethylpropanol (AMP), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA) (Figure 2) show that; piperazine and AMP has lower BOD values compared to the blank (inoculum only), indicating their inhibitory

effects. DIPA shows the highest bio-degradation potential out of these 4 amines under the tested conditions using a non-adopted culture.
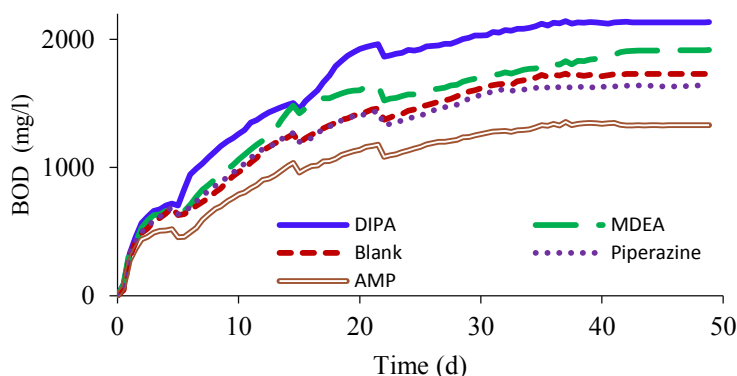

Figure 2: Aerobic bio-degradation of DIPA, MDEA, AMP and piperazine.

5.2. Anaerobic biodegradation of amines

Anaerobic biodegradation studies on amines are relatively rare but a few studies suggest that significant anaerobic bio-degradation should be possible. Bae et al. [18] reported that pyrrolidine and piperidine were completely degraded in 15 days under denitrifying conditions while piperazine, morpholine and thiomorpholine were not degraded at all. No sign of degradation in a 6 month experimental test of sulfate reducing or methanogenic conditions was found. Accordingly: *1.* nitrate respiration conditions can be more favourable for degrading secondary amines compared to sulfate reduction or methanogenesis; *2.* piperazine seems more recalcitrant compared to the other secondary amines tested in this study. Secondary amines are more susceptible to convert chemically or biologically into carcinogenic N-nitrosamines [19]. The easier biodegradation of pyrrolidine and piperidine can be due to their wider presence in natural plant and animal tissues, which could have led to evolutionary selection of degradation pathways for these chemicals. This emphasizes the importance of adaptation in biodegradation of such recalcitrant chemicals.

Hongwei et al. [20] related the anaerobic biodegradability of nitrogenous compounds to their molecular structure descriptors, defining a numerically integrated assessment index (IAI) as a measure of the anaerobic degradability: IAI > 1 - the compound is readily biodegradable; 0.3 < IAI <1 - partially biodegradable; IAI < 0.3 - poorly biodegradable. According to these criteria, MEA is found to be a readily biodegradable compound under anaerobic conditions. This method can be a valuable screening method using a molecular modelling database.

Speranza et al. [21] summarized four mechanisms suggested for anaerobic biodegradation of alkanolamines (primarily MEA, DEA and TEA) with acetaldehyde and ammonia as products. Acetaldehyde can be readily degraded to methane under methanogenic conditions. Speranza et al. [21] further noticed a strictly anaerobic bacterium (*Acetobacterium* sp., from sewage sludge) converting triethanolamine (TEA) into acetate and ammonia, and suggested it can biodegrade all three types of ethanolamines (MEA, DEA and TEA). *Adenosylcobalamin* (coenzyme B_{12}) is recognized to be a major co-factor initiating this kind of eliminase reactions [21], so adding vitamin B_{12} to the nutrient media can have positive impacts on amine degradation. *Ethanolamine ammonia-lyase* is recognized to catalyze the biodegradation of ethanolamines and many microbes can produce this enzyme [22]. Abend et al. [22] further reported that several bacterial groups can use ethanolamines as the sole source of carbon and nitrogen. Anaerobic biodegradation of concentrated

amine contaminated wastewater from a chemical company has been documented by Chen et al. [23]. Accumulation of inhibitory ammonia concentrations due to the degradation of amine compounds can inhibit anaerobic treatment of such wastes [24], but Chen et al.'s [23] study further revealed that a biofilm type reactor is less vulnerable to ammonia inhibition compared to a fully suspended type configuration.

5.2.1 Co-substrate / co-digestion approach

Botheju et al. [24] pointed out benefits of co-digesting amine wastes with readily degradable acidic substrates like acetic acid or fruit wastes, due to the necessity of bringing pH down to neutral levels. Figure 3 displays an extended data set obtained from a continuation of the experimental study described in Botheju et al. [24], obtained by feeding the reactor real MEA reclaimer bottom wastes (obtained from a full scale CO_2 capture facility based on coal combustion). The waste gradually replaced the pure MEA solution being fed before (during < 240 d period). The biogas production data (Figure 3) shows no significant inhibitory impact due to the addition of amine wastes. The chemical analysis of the reactor feed and effluent (Table 1) indicates a complete biodegradation of the MEA fraction in the feed. Further, the observed gas production (during > 245 d period) is quite close to the theoretically expected gas generation from apple juice (which was fed as the readily degradable C source) plus MEA fraction of the amine waste. A non-biodegradable fraction of the waste was also noted under the experimental conditions tested. This might be MEA degradation products and need further studies to identify their composition and specific nature.
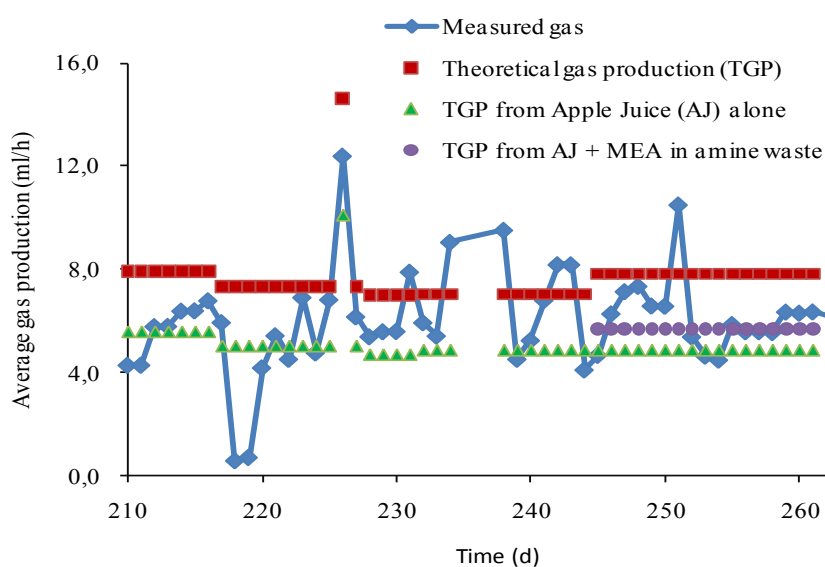

Figure 3: Measured biogas production of the amine wastes fed semi-continuous bioreactor compared to the theoretical productions (up to 216 d, AJ + pure MEA was fed; during 216 - 243 d, pure MEA was gradually replaced by amine waste; from 244 d, AJ + amine waste was fed).

The very low C/N ratios typically found in these wastes calls for co-digestion in anaerobic treatment since the recommended range of C/N ratios for optimum digester performance is 20 - 30 [25] while MEA, piperazine, AMP, MDEA and DIPA have C/N ratios of 1.71, 1.71, 2.42, 4.28 and 5.13, respectively. These low C/N ratios, when used in anaerobic digestion, lead to process inhibition by high ammonia and high pH [24]. This suggests co-digesting amine wastes together with other industrial or municipal wastes, but with attention to heavy metal contamination that may limit the possibility of using digestate as a soil amendment or a fertilizer [26].

Table 1: Feed and effluent analysis of amine wastes fed semi-continuous bioreactor.

Component	Feed (g/kg)	Effluent (g/kg)
MEA	2.5	0.01
Acetic	0.5	< 0.05
NH_4^+	0.1	0.7

5.2.2 Partially aerated anaerobic approach

Advantages of aerobic treatment include faster degradation and the ability to handle higher loads with lesser inhibition effects (mainly due to the higher biomass yields under aerobic conditions). Proposed degradation mechanisms suggest that aerobic biodegradation of MEA goes mainly through CH_3COOH. Instead of allowing further degradation of acetic acid aerobically, anaerobic digestion can strategically be introduced at this point to convert acetic to methane; the conventional methanogenesis process. Other possible end products like ethanol, acetaldehyde, amino acids, H_2 [14] are also candidates for further anaerobic degradation to methane, suggesting partial-aeration assisted anaerobic digestion for conversion of amine wastes into energy (methane) and nitrogen fertilizer [24, 27]. According to this study, biodegradation of the amine wastes was better with partial aeration ("micro-aeration") than with no aeration and surplus oxygen (Figure 4a,b). All cases had > 80 % removal. The waste amine solution used in this particular experiment was collected while emptying the Aker Kvaerner pilot facility at Kårstø, Norway. This waste contains very little degradation products, and is mostly MEA and water.
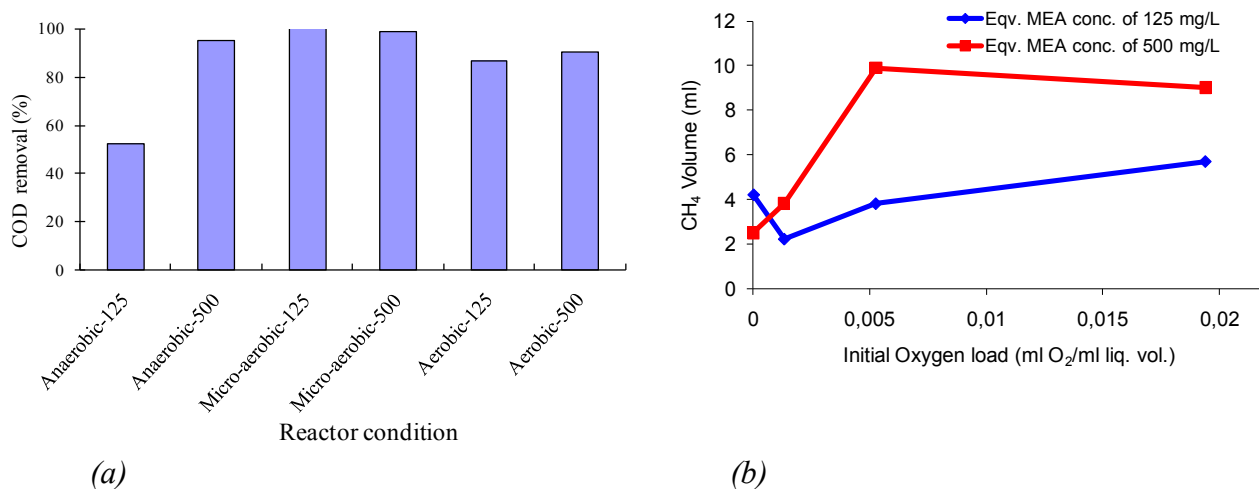

(a)   *(b)*

Figure 4: (*a*) Waste (as COD) removal after 20 days batch test with 3 aeration levels (zero, partial and full aeration) for 2 waste levels (125 and 500 mg/L as MEA); (*b*) Methane from amine wastes at different initial O_2 feeds.

The observed full COD removal (Figure 4a) under partially aerated conditions was followed up by methane (CH_4) generation measurements under different initial oxygenation levels (Figure 4b). At zero initial oxygen loading (strict anaerobic condition), 500 mg/L waste shows less methane production compared to 125 mg/L waste, due to higher inhibition effect by accumulated MEA or related compounds. The observed increased methane generation with partial aeration can be explained by enhanced degradation and reduced inhibition. Too high aeration will give complete aerobic degradation of MEA to CO_2, implying that an optimum oxygen load can yield a maximum

methane potential from this waste. The positive influence of oxygen increases with waste concentration (Figure 4b).

6. Conclusions

Experimental and theoretical studies show that both aerobic and anaerobic amine /amine wastes biodegradation is possible. A combination of aerobic and anaerobic treatment can be the most efficient solution with high rates and low energy costs. Further work is needed on the degradation of products from carbamate reactions of MEA, and on the degradation products of other amines.

The degradation depends on the degree of adaptation of the microbial culture used. Use of a readily degradable substrate together with amine wastes can be used to prevent ammonia and pH inhibition and increase the C/N ratio for enhanced degradation.

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