

Handling of Amine-Based Wastewater Produced During Carbon Capture

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ABSTRACT. The large-scale implementation of amine-based carbon capture processes requires the development of sustainable handling technology of the waste effluents. The generated wastewater contains significant amounts of ammonia and toxic degradation products, nitroamines and nitrosamines. They both pose great threats to the ecological environment and human health. Monoethanolamine (MEA) is one of the most commonly used absorption solvents in the post-combustion carbon capture process. In order to make a better management strategy, the waste components and the pathways of MEA degradation are demonstrated based on different reference papers and case studies. Moreover, the toxicity and environmental impact of the degradation products are evaluated. The goal of this review is to elucidate potential technologies that can either eliminate the hazardous nature of the amine waste or convert it into marketable products. We categorize these technologies as waste disposal, recycle, reuse, and chemical/biological treatment method. Several applications with a focus on biodegradation technique are examined according to their amine removal performance. The results reveal that bioconversion is a promising technique for handling amine-based wastewater at large-scale.

Keywords: Amine-based wastewater, carbon capture, monoethanolamin, solvent degradation, reclamation, biological treatment

1. Introduction

Fossil energy combustion like coal, natural gases, and oil is a significant source of greenhouse gas emission, which is closely associated with climate change. To reduce the concentration of carbon dioxide in the atmosphere is of great concern considering its importance in contributing to global warming. It is indicated that about 40% of global carbon emissions are presently from the coal combustion industry, and this trend will reach a peak around 2030 (Harris and Roach, 2016). The carbon foot-print reduction of related industries is urgent as the world's energy demand continues increasing and fossil fuels remain a reliable source of energy in the foreseeable future (Liu et al., 2018). Carbon capture and storage (CCS) technology has been developed towards achieving this goal.

There are three key technologies for CO₂ capture: pre-combustion, oxyfuel combustion and post-combustion (MacDowell et al., 2010). In post-combustion capture (PCC), CO₂ is absorbed by the solvent and separated from other flue gas mixtures after complete combustion with air. The oxyfuel combustion process is performed under high purity oxygen, producing a flue gas of CO₂/H₂O steam, which is ready for sequestration. Pre-combustion CO₂ capture process converts the fossil fuel

into the syngas through gasification or reforming, which can remove CO₂ before combustion is completed. Depending on the process, different technologies can be applied to capture and separate CO₂ from the flue gas stream, including absorption, adsorption, chemical looping combustion and membrane separation (Zhang et al., 2013; Leung et al., 2014; Gwak et al., 2019). Among these technologies, amine-based post-combustion capture (PCC) is regarded as the most mature technology to mitigate CO₂ emission due to its full commercial availability, high absorption capability and relatively simple operation (Wang et al., 2015). Two examples of existing large-scale power plants with amine-based post-combustion capture (PCC) unit are the Petra Nova project in the United States (1.6 million tonnes of CO₂ captured annually) and the SaskPower's Boundary Dam power station in Canada (1.3 million tonnes of CO₂ captured annually) (Liang et al., 2015; Mazari et al., 2019).

Among various amine solvents in PCC technology, monoethanolamine (MEA) is widely used and regarded as a benchmark solvent, due to its high chemical reactivity, fast adsorption rate and high water solubility (Puxty et al., 2009). However, the high energy penalty, solvent degradation and ecotoxicity problem present enormous challenges for large scale deployment of PCC (Kumar et al., 2014; Dutcher et al., 2015). Therefore, significant research efforts have been directed to the development of optimizing solvent with good thermal stability, low cost and toxicity, as well as a high absorption performance (Abu-Zahra et al., 2013).

CO₂ flue gas passes through the aqueous amine solution

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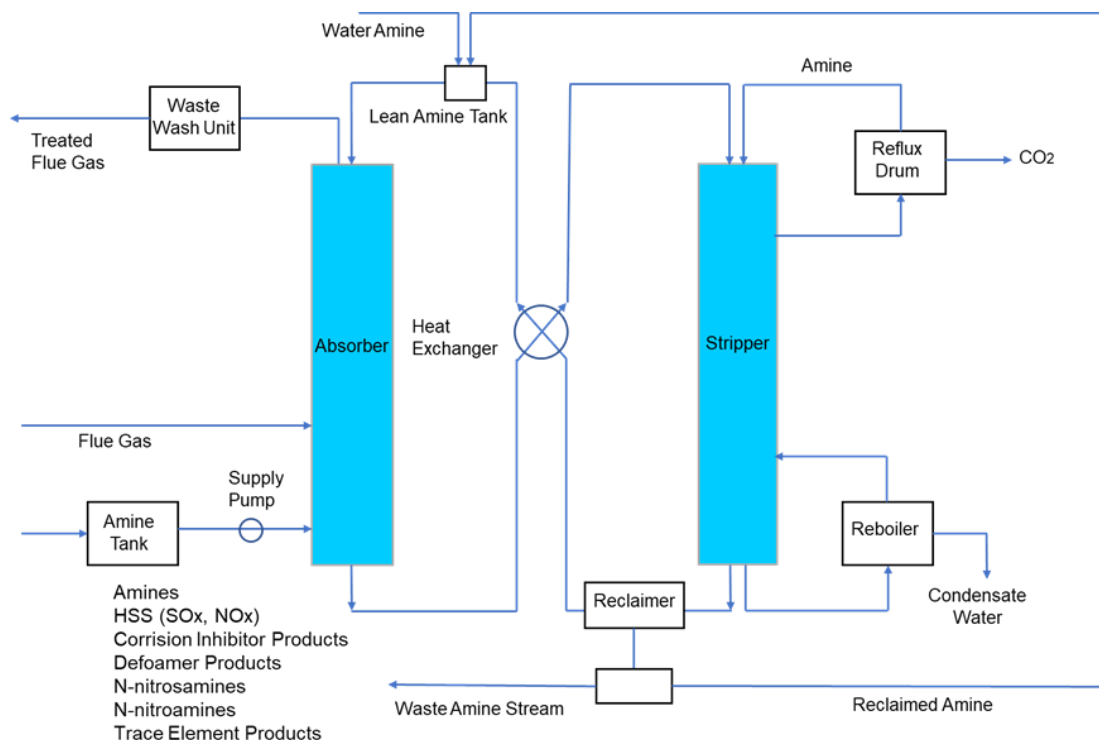


Figure 1. Typical schematic diagram of amine-based PCC process.

creating neutralization reactions and producing degradation products by high thermal exposure. Simultaneously, heat-stable salts are generated from the side reaction between amine-based solvent and reactive species contained in the exhaust gas or the impurities in makeup water (Haws et al, 2001). The reclamation of amine waste, including its degradation products and heat-stable salts, are vital to maintain the efficiency of the process and avoid potential corrosion problems. Also, these degradation products and heat stable salts may induce potential risk to human health and the environment. A comprehensive environmental, health and safety hazard assessment framework of the PCC system has been studied by many researchers to mitigate these impacts (Gjernes et al., 2013; Badr et al., 2017; Kimura et al., 2017; Guan et al., 2019). The majority of the amine waste in the carbon capture process comes from the wastewater of the reclaimer. A slipstream is taken out from the desorber column to remove the amine degradation products and heat-stable salts via commercial reclamation technologies (Shao and Stangeland, 2009). A recent study has estimated that about 1.17 ~ 3.94 kg reclaimer waste is produced with one tonne of CO₂ captured using the thermal reclaiming process (Nurrokhmah et al., 2013). The composition and toxicity of amine waste heavily dependent upon the type of amine solution at use, as well as the contaminants in the flue gases and other process conditions (Thitakamol et al., 2007). In general, this waste amine stream contains ammonia, carbamate polymers, heat-stable salts, organic acids, nitrosamines, nitramines and other degradation products. Thus, handling and reuse of this large quantity of hazardous amine waste have become a major issue concerning the

strict enforcement of environmental regulations.

In this review, we will give a comprehensive introduction to the amine-based PCC carbon capture process, and the amine degradation pathways, chemical components and their potential toxicities will be analyzed. Three reclaiming technologies are compared and assessed to purify the amine solvent and drive down the system cost. Different techniques for managing the amine waste are investigated on the basis of existing findings. Waste disposal, recycle, reuse and biological treatment methods are discussed, and their corresponding research gaps are identified. Among these approaches, the feasibility of biodegradation/bioconversion and biological treatment design are presented under various conditions. These information are essential to developing an environmentally safe and cost-effective nitrogen removal system for large-scale implementation of carbon capture technology.

2. Amine-Based PCC Capture Process

A typical schematic diagram of amine-based PPC process is illustrated in Figure 1. Absorber and stripper column are two major units in this system. CO₂ in the gas mixture reacts with the liquid amine solvent in the absorption section, forming carbamate salts while the absorbed CO₂ can be released by thermally decomposing the enriched amine in the stripping column. The raw gas containing CO₂ passes through the bottom of the absorber, encountering the fresh amine solution coming from the top of the column. Under certain temperature and loading, most CO₂ will be removed by chemical absorption. The other

treated gases will proceed to the washwater unit to reduce amine solvent loss before finally being emitted out. The CO₂ loaded solution leaves the absorber from the bottom and gets heated in a cross heat exchanger. It then flows downwards into the stripper and comes upon the hot water vapor generated from the stripper, leading to the release of captured CO₂ from the loaded solvent. Finally, the regenerated lean amine solvent is recycled back to the absorber by cooling down through the cross heat exchanger. According to Mazari et al. (2019), a majority of the operating cost involved in the system are amine regeneration and amine solvent cost.

2.1. Amine-Based Solvent for CO₂ Capture

It is crucial to understand the solvent chemistry in order to develop a reliable and reactive solvent in the PCC system with outstanding absorbent performance. The selection of amine solvents should be addressed based on many criteria, including its thermodynamics, kinetics, absorption solubility, mass transfer, regeneration and solvent stability (Liang et al., 2015). At present, there are a number of amine-based solutions for CO₂ capture, which can be classified as primary amine (monoethanolamine, MEA), secondary amine (diethanolamine, DEA), and tertiary amine (N-methyldiethanolamine, MDEA) depending on the number of replaced hydrogen atoms in ammonia (Shao and Stangeland, 2009). Sterically hindered amine (2-amino-2-methyl-1-propanol, AMP) has also emerged as a novel solution with considerable reactivity. During PCC process, CO₂ reacts with primary/secondary amine to form a carbamate and protonated amine, consuming 2 mol amine/mol CO₂ absorbed, as shown in the following path (McCann et al., 2009; Feron et al., 2010):

Primary amines:

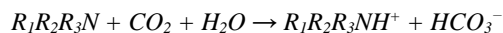


Secondary amines:

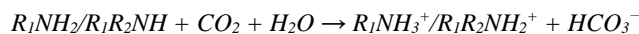


Tertiary and sterically hindered amines may react with CO₂ and form bicarbonate by consuming only 1 mol amine/mol CO₂ absorbed. The reaction path is shown to be (Reynolds et al., 2012):

Tertiary amines:



Sterically hindered primary or secondary amine:



Henni et al. (2013) determined the CO₂ loading ability in a variety of aqueous amines solvents and concluded that the increased hindrance in amino groups might lead to higher loading capacity, and the trend is primary amines < hindered amines

< secondary amines < tertiary amines < diamines. Although the primary and secondary amines have lower CO₂ capacity, they are more generally used for pilot scale PCC due to their rapid reaction speed. For MEA, DEA and MDEA, CO₂ absorption rate can be ranked as MEA > DEA > MDEA. Singh et al. (2007) also point out the structural effect of amine solvent on carbon capture performance: (1) alkyl and amine groups play important roles in enhancing the absorption capacity and rate of amine solvents; (2) substitution of hydroxyl groups can improve absorption capacity of the solution but slow down its absorption rate.

Monoethanolamine (MEA) has been commercially employed in the carbon capture industry for a long time. However, it still faces several limitations, such as high energy consumption, low adsorption capacity, and poor thermal stability. Obviously, there is no single solvent that can possess all advanced features in carbon capture. Recently, the blending of amine solvent has shown improved performance in this application. A mixture of 4 mol·L⁻¹ MEA/1 mol·L⁻¹ MDEA amine solvent is carried out at a test plant and the result reveals that this blended solution maintains good chemical stability and consumes less heat-duty than single MEA solvent.

We may recognize that most amine used in CO₂ capture can be recycled within the PCC system. However, there is still a portion of amines waste emitted into the atmosphere or degraded to some hazardous and toxic substances that may cause a risk of cancer to animals and humans in the environment. A reclaiming attached to the hot stream stripper is used to collect and treat these amine waste and degradation products.

2.2. Amine Degradation Products in PCC

Degradation of amine solution during the PCC process can result in reduced energy efficiency, heavier corrosion problem, increased operation cost, and unwanted environmental emissions (Strazisar et al., 2003; Reynolds et al., 2016). It is estimated that solvent degradation accounts for about 10% of the total cost in the carbon capture process (Rao and Rubin, 2002). Therefore, it is crucial to understand the degradation mechanisms and the composition of the degradation products. Comprehensive reviews have identified the type of degradations involved in the PCC process. There are two main degradation mechanisms that occur in the system: oxidative amine degradation during CO₂ absorption with the presence enough O₂ in flue gases and the thermal degradation due to high thermal exposure in the stripper. The type and amount of degradation products inevitably depend on the type of amine used and the quality of flue gas, as well as the combustion process and operation condition (Nurrokhmah et al., 2013). MEA, as the most commonly used amine solvent, has been studied by many articles focusing on its degradation products and degradation pathway. Here we list the oxidation and thermal degradation information of MEA solvent.

2.2.1. Oxidation Degradation of MEA

Bello and Idem (2005) have identified an extensive list of

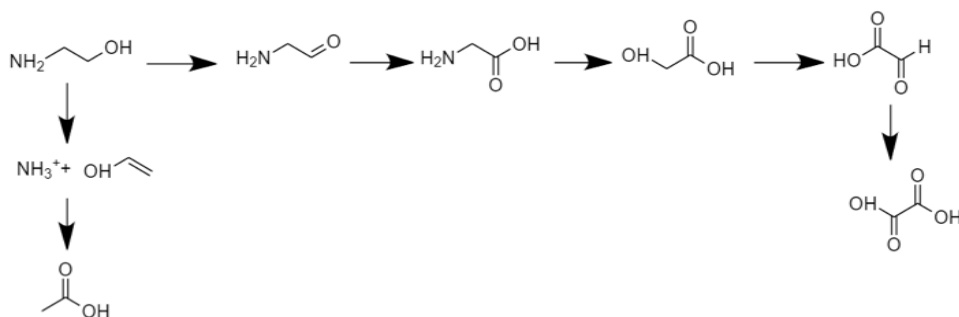


Figure 2. Oxidation degradation of MEA.

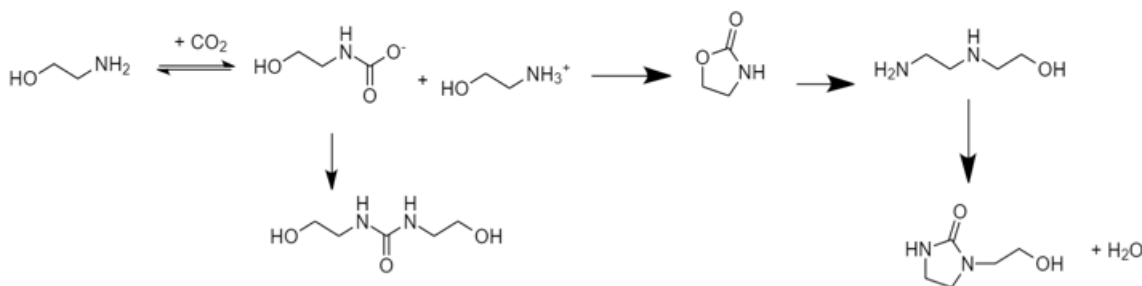


Figure 3. Thermal degradation of MEA.

degradation products at a laboratory scale. The reaction is induced by O_2 and produce the oxidized products of amine solvent such as ammonia, organic acid, and aldehydes. The oxidative degradation mechanism is very complex, and it has not been fully understood yet. The most likely amine oxidative degradation reactions are provided in Figure 2. More extensive degradation pathways and unexplained degradation products have been reported by Lawal et al. (2005) and Gouedard et al. (2012). The final oxidative degradation products will mainly be ammonia, formic acids, and some intermediate products like formaldehyde (HCHO) and hydroxyacetaldehyde (HOCH₂-CHO). The dissolved metal ions (Fe, Mn, Cr, Ni, and Mo) in the anti-corrosion additives and makeup water can also act as catalysts in the oxidation process. These products are a dominant contributor to solvent degradation, and they have also been detected by the CASTOR pilot plants at Esbjergværket, Denmark (Knudsen et al., 2009). The presence of transition metals can accelerate the oxidative degradation rate of MEA due to the generation of oxide radicals, indicating that metal catalysis is closely related to the oxidation degradation pathway (Goff and Rochelle, 2004). The oxidative degradation is determined by the concentration of CO_2 , oxygen, and metal ion. Under specific conditions, this process is controlled by the rate of oxygen mass transfer instead of the kinetics of the degradation reactions (Chi and Rochelle, 2002).

2.2.2. Thermal Degradation of MEA

Thermal degradation (carbamate polymerization) primarily occurs during MEA- CO_2 desorption process. The high pressure of CO_2 and high temperature in the stripper provide suitable conditions to break down the chemical bonds of amines.

Thermal degradation with CO_2 can be summarized into four steps: demethylation reactions, oxazolidinones formation, additions, and ring closures (Lepaumier et al., 2009). Figure 3 summarizes the most commonly reported thermal reactions of MEA. In the initial step, MEA reacts with CO_2 in the flue gas and undergoes carbamate formation. Then, this carbamate is supposed to condense and transform into 2-oxazolidone (Gouedard et al., 2012). 2-Oxazolidone successively interacts with another molecule of MEA and forms 1-(2-hydroxyethyl)-2-imidazolidinone (HEIA) (Nurrokhmah et al., 2013). Finally, the cyclic compound N-(2-hydroxyethyl) ethylenediamine (HEEDA) is obtained by intramolecular cyclisation of HEIA (Davis et al., 2009). These degradations include HEIA, HEEDA, MEA-urea, and other polymerization products, making up around 20 ~ 30% of the total amine solution loss. The rate of thermal degradation is also strongly influenced by CO_2 loading, temperature, and amine concentration. Increasing temperature and pressure will increase the amine degradation rate, leading to more degradation byproducts and amine solvent loss.

Besides these two degradation processes, another concern exists in the reclaimer waste is the presence of nitrosamine and nitramines, which is mainly induced by the chemical reaction between NO_x and primary/secondary/tertiary amine solvent (Chen et al., 2018). Nitrosodiethanolamine (NDELA) and nitrosodimethylamine (NDMA) are two well-known nitrosamines that usually detected as the byproduct of MEA (Fostås et al., 2011). In addition, trace elements from the impurities of coal such as Cu, Zn, As, and Se can also be present in the bottom of the reclaimer but with negligible amount. Based on the information from lab-scale degradation experiments (Lepaumier et al., 2011; Nurrokhmah et al., 2013; Thompson et al., 2017),

Table 1. Composition of MEA Reclaimer Waste

Compound & Quantity	Source	Biodegradability	Hazard classification
Water (20 ~ 33.9%)			-
Total nitrogen (14%)			-
NH ₄ ⁺ (0.04%)	Amine solvent	Yes	-
MEA (25 wt%)			Danger
1-(2-hydroxyethyl)-2- imidazolidinone (HEIA)	Thermal degradation		Warning
N-(2-hydroxyethyl)-ethylenediamine (HEEDA)	& carbamate	Yes	Danger
N,N-bis(2-hydroxyethyl) urea (UREA)	polymerization		-
Formic acid/formate (HCOOH/HCOO ⁻)			Danger
Acetic acid/acetate (CH ₃ COOH/CH ₃ COO ⁻)			Danger
Oxalic acid/Oxalate (HOCOCOOH/HOCOCOO ⁻)			Danger
Ammonia/ammonium (NH ₃ /NH ₄ ⁺)			Danger
Formaldehyde	Oxidation degradation	Yes	Danger
Acetaldehyde			Danger
Hydroxyethyl formamide (HEF)			Warning
Hydroxyethyl imidazole (HEI)			Warning
Hydroxyethyl glycine (HEGly)			-
Nitrosodiethanolamine (NDELA) (10 ng/kg)	Reaction with NO _x	Considered to be biodegradable	Danger
Nitrosodimethylamine (NDMA) (5 ng/kg)			Danger

the commonly recognized degradation products in MEA-based PCC process are shown in Table 1. Different pilots and processing conditions may lead to difference in both the type and the quantity of specific compound. However, the major degradation products of MEA are HEIA, acetic acid, MEA urea, ammonia, and HEEDA. Other contaminants are all at low concentrations in the solvent. However, the reported MEA degradation products in the lab-scale experiment cannot represent real data from the PCC pilot plant. A validate model or simulation at the lab-scale is desired by incorporating proper sampling and analytical regimes into the current amine-based pilot-scale PCC process (Xie et al., 2018).

2.3. Composition and Toxicity of Amine Waste

2.3.1. Amine Waste Composition

The waste amine stream from the reclaimer contains liquid, solid, and semi-solid fractions. Their composition, toxicity, and volumes are highly dependent on the amine type, flue gas ingredients, and PCC operations. Nurrokhmsah et al. (2013) estimate the components of amine waste sample based on a real case of Fluor's Econamine FGSM coal-fired plant. The flue gas in this plant contains 12.21% CO₂, and 13,123.2 tonnes of CO₂ is captured per day. 1.6 kg of MEA is required per tonne of CO₂ captured, and the expected waste quantity is 39.37 m³/day on a flow rate basis. The analytical tests on the amine wastewater from pilot-scale plants are inconsistent with the results conducted on the laboratory scale. Table 1 illustrates the main composition of the reclaimer amine waste. The common materials found in the reclaimer bottom are HEIA, 2-oxazolidone, ammonia, acetic acid, and MEA (Strazisar et al., 2001). Thermal degradation products, including HEIA, HEEDA, and DHU have the largest quantity in the amine wastewater. Besides, organic compound (NH₄)₂SO₄ dominates a great proportion (~87%) in oxidative degradation products. In addition, another study reports that the formation of nitramines and nitrosamines through NO_x nitrosation are up to 5 ~ 47 ng/Nm³ under MEA-

based pilot plant conditions (da Silva et al., 2013). From the table, we can see most of the components are biodegradable.

2.3.2. Toxicity of Amine Wastes

Amine wastewater from the reclaimer is the primary source of amine emissions from PCC. Amine waste produced from carbon capture poses a moderate to severe threat to the human health and ecological system. According to a projected MEA emission rate of 79 tonnes/year, the waste amine can increase the toxicity to freshwater ecosystems by ten times (Veltman et al., 2010). However, amine itself does not pose a great risk to the environment, its wide range of degradation products included nitramines, nitrosamines, carbonyls, amine dimers, heterocyclics, carboxylic acids, and amides are toxic and hazardous (Rohr et al., 2013; Xin et al., 2018). Many researchers have proved that nitramines and nitrosamines are carcinogenic and mutagenic at extremely low levels (Låg et al., 1984; Fjellsbø et al., 2014; Chen et al., 2018). The average genotoxic risk estimation for nitramine/nitrosamine is about 0.45 ng/m³ (Ravnum et al., 2014). Nitrosamines are more carcinogenic but less stable than nitramines, which are 15 times more mutagenic than their nitramines analogues. The Integrated Risk Information System database of USEPA indicates the concentrations (low ng/L) of several nitrosamines in drinking water that are associated with excess lifelong cancer risk (Wagner et al., 2014).

Eide-Haugmo et al. (2012) test the biodegradability and acute toxicity of different amines compounds on marine phytoplankton. The results display a large variation, even when the structure of the compound is similar. Rohr et al. (2013) find significantly increased toxicity in the mice cells, neutrophils, and lymphocytes when exposed to degrade MEA. Liuzinas et al. (2007) evaluate the toxicity of amine contaminated soil on the growth of plants. It is found that phytoremediation can be used for detoxification of waste amine at low concentrations. They also observed the toxicity sensitivity of amine wastes on

Table 2. Characterization of Raw Waste Amine from the Reference Case

Raw waste amine	Concentration	Drinking water standard	Concentration
COD (mg/L)	1050 ~ 1870	COD (mg/L)	< 10
BOD ₅ (mg/L)	392 ~ 698	BOD ₅ (mg/L)	< 10
Ammonium	14320	TSS (mg/L)	< 10
Sulfate (mg/L)	< 144	Turbidity (NTU)	< 0.3
Ammonia	-	TN (mg/L)	< 3
Nitrate (mg/L)	186	TDN (mg/L)	< 500
N-Kjeldahl (mg/L)	40000	<i>E. coli</i> (CFU/100ml)	< 200
pH	6.5 ~ 7.8	Coliforms (CFU/100ml)	< 200
Temperature (°C)	43	pH	7.0 ~ 8.5
Alkalinity (mg/L)	1450 ~ 1752	Temperature (°C)	< 15

Table 3. Comparison of Commercially Available Amine Waste Reclamation Technologies

	Distillation	Electrodialysis	Ion exchange
Applicability	Removal of solids and non-volatile species	Removal of ionic contaminants	Removal of ionic contaminants
Waste type	Hazardous, non-aqueous	Non-hazardous, aqueous	Aqueous
Volume	Low	Moderate	High
Chemical usage	Stoichiometric NaOH	Stoichiometric NaOH	NaOH and H ₂ SO ₄
Energy demand	High	Moderate	Low
Total cost	High	Moderate	Moderate
Requirements	Fuel gas or high temp.	DC power	Regeneration chemicals
Advantages	Highly concentrated waste	Efficient for charged species; lower chemical consumption	Low energy consumption
Limitations	High cost, low amine recovery; energy intensive; most amines need vacuum	Cannot remove non-ionic contaminants; membrane selection and durability	Cannot remove non-ionic contaminants; high salt levels lead to bed exhaustion

different microorganisms. Due to the hazardous nature of the amine degradation products, the appropriate treatments and disposal schemes are necessary to reduce these substances to acceptable emission levels and ensure the safe operation of the plant. Biological treatment as an efficient and cost effective method, is becoming a potential trend for waste amine handling at industrial-scale.

2.3.3. Biodegradability and Characteristic of Amine Waste

There is extensive research indicating the biodegradability of MEA solvent, including aerobic biodegradation in seawater and soil, biogas production under anaerobic condition, and anoxic nitrogen removal (Henry et al., 2017). Most alkanolamines have a toxicity level of 10 ~ 1000 mg/L, and some of them are biodegradable under aerobic and anaerobic conditions. It is indicated that the degradation rate of MEA-based amine waste is 1.64 g/dm³·h, suggesting a strong possibility to treat the carbon capture waste with biological technology (Ohtaguchi et al., 1995). Ammonium is the decomposition product of aerobic digestion, and ammonium, acetic acid, acetaldehyde, formic acid, and ethanol are formed under anaerobic conditions. A syringe batch experiment examines the biodegradability of waste amine under aerobic, micro-aerobic, and anaerobic conditions (Li et al., 2008). It shows that more than 90% of amine COD is removed, and the highest BOD reaction rate is 1.08/day with an initial BOD of 125 mg/L. BOD and COD are important indicators for the biodegradation process, representing the oxygen required for oxidizing the organic compound. From the analysis

of wastewater composition, we know there is a lot of sulfate in the degradation products. It may be generated from SO₂ captured from the amine solvent and converted to (NH₄)₂SO₄. Sulfate will biologically break down into sulfide under anaerobic conditions, which can then form hydrogen sulfide (H₂S) by hydrogen combination. Total nitrogen (TN) is composed of organic nitrogen, ammonia, nitrite, and nitrate. The organic nitrogen can be readily converted to ammonium through the action of microorganisms in the reactor. Phosphorus is essential to the growth of biological organisms, and the orthophosphates (e.g., HPO₄²⁻) form are directly available for biological metabolism. Amine wastewater is very acidic with a pH around 4, so it must be adjusted by adding alkalinity and maintained at neutral for better biodegradation performance. Although several reports have documented the biological treatment of MEA wastewater, few people list the biological characterization of the real industry reclaimer waste components. Table 2 shows the raw waste amine sample tested in Aker Kvaerner pilot plant at Kårstø (Norway) (Li et al., 2008), compared with the standard of Canadian drinking water. These waste compositions, biodegradability, and characterization information are useful for (1) investigations of waste amine reuse and recycling activities, (2) design of biological treatment, and (3) evaluation of capital and operation cost derived from the system.

3. Amine Reclamation Technologies

Waste reclamation is one of the MEA waste handling practices in the carbon capture process. Waste reclaimer is the unit

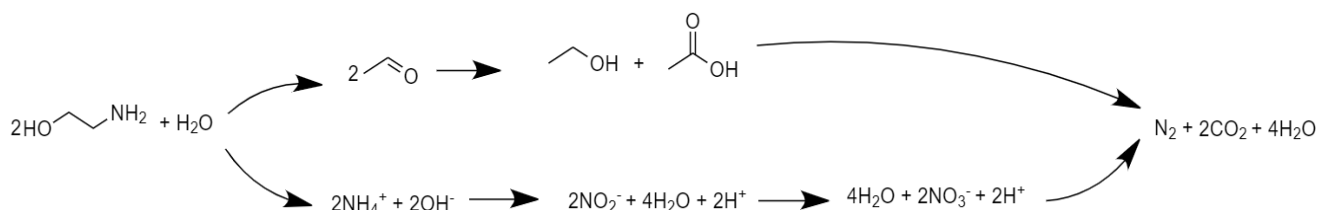


Figure 4. Biodegradation of MEA.

to remove the degradation components from amine solvents, then recycling back the useable amine. Reclaiming the contaminated amine solvent is considered as an ecological friendly technique from the long-term perspective. Amine waste may contain both toxic degradation products and other hazardous heavy metals corrosion inhibitors, including vanadium, antimony, and cyanide compounds. (Thitakamol et al., 2007). The existence of these contaminants leads to reduced carbon adsorption capacity, foaming, fouling, and increased viscosity in operation (Ciferio et al., 2009). In order to purify the amine solvent, three reclaiming technologies have been widely used for the separation process, namely thermal reclaiming (distillation), electrodialysis, and ion exchange. Some advantages and disadvantages are compared in Table 3 (Wang et al., 2015).

Thermal reclamation uses heat energy to recover amine solvent via evaporation, leaving behind the degradation products, heat stable salts, and non-volatile impurities with high-boiling points. Canadian Chemical Reclaiming Ltd. reported an amine recovery rate of 90 ~ 95% from the contaminated solution. However, it is assumed that elevated temperature can result in further solvent and corrosion inhibitors degradations. Also, the thermal reclamation process requires considerable heat consumption, which is approximately 3.0 ~ 3.7 GJ/tonne CO₂ captured (Romeo et al., 2008). To overcome these disadvantages, the vacuum thermal reclamation is designed to improve the amine purification efficiency and reduce the operating cost (ElMoudir et al., 2012). Another case study points out that potassium hydroxide can be used to remove sulfate in amine waste by crystallization of K₂SO₄ (Xu and Rochelle, 2009). Small amounts of waste are generated compared with the process without solvent reclaiming. Ion exchange and electrodialysis reclamation technologies do not need heat input and thus avoid the thermal degradation problem. However, these two options are insufficient in the removal of uncharged components from contaminated amine solvent.

Ion exchange can only separate ionic degradation products and impurities accumulated in the amine system. It consumes fewer chemicals and energy to remove heat stable salts, and the amine recovery rate is up to 99%, especially when the concentration of heat stable salts is low. However, the practice of ion exchange still meets some technical challenges. For example, the loading and regeneration steps involved in the ion exchange process needs large amounts of water for rinsing. Hence, large quantities of diluted waste are produced, which requires further disposal. Additionally, transition metals are likely to cause fouling on the exchange resin (Dumée et al., 2012). Therefore,

ion exchange alone may not be satisfactory for CO₂ capture applications. The development of a new ion exchange process is needed to purify amine solutions in the system.

Electrodialysis (ED) uses appropriate current and selective-ion membranes to separate charged degradation products between two chambers (Cummings et al., 2007) and can remove 86 ~ 97% heat stable salts. ED also requires less water usage than ion exchange technology. However, the presence of a small quantity of CO₂ in amine solutions can lead to decreased effectiveness and increased energy consumptions (Volkov et al., 2013). Besides, the ion-permeable membrane is temperature sensitive, which means additional cooling is needed to reduce the input temperature of the lean solvent. The high manufacture costs of membranes and fouling problems on the surface also limit the application of ED. Electrodialysis is not capable of removing non-ionic impurities from the system, such as the nitrosamines. Thus, very little information is available for using ED technology to reclaim amine waste in the PCC plant. More work is desired on the membrane modification in accordance with the characteristic of the amine solution.

4. Waste Amine Treatment Technologies

4.1. Waste Disposal, Recycle, and Reuse

The options used to treat amine wastes could be disposal, recycle, reuse, and biological treatment. Table 4 lists the current application and feasibility for treating MEA wastes. A large amount of amine wastes is generated owing to the degradation of solvents during flue gas scrubbing. Many studies have focused on looking for an economical and environmentally sustainable approach to handle these amine wastes. Landfilling and incineration are two common disposal methods regarding small quantities such liquid wastes. The waste stream could be fed directly to a waste incinerator to destroy amines. However, it is not a cost-effective solution because of the presence of water, resulting in a negative net calorific value (Botheju et al., 2011). In addition, incineration is an additional emission source of NO_x, and the poorly treated amine wastes may release into the environment and harm the local ecosystems.

Co-firing can avoid the potential release of toxic waste amines into the environment employing simultaneous combustion of coal and recycled amine waste into a coal burner (Woods et al., 2006). This option can be considered as an option for recycling reclaimer waste. The calorific value of amine wastes (16.3 MJ/kg) has a good match with the value of coal (14 ~ 30

MJ/kg), indicating a suitable characteristic for co-combustion. However, the practical evaluation of this waste recycling method still needs further investigation.

Table 4. Overview of Amine Wastes Handling

Handling activity	Purpose/technique
Disposal	Landfill and incineration
Recycle	Co-combustion in coal burner
Reuse	NO _x scrubbing agent
Treatment	Peroxidation, UV treatment, photolysis, activated carbon, biodegradation/bioconversion

Ammonia generated from the deposition of amine wastes can be reused to reduce NO_x emission in incinerators (Botheju et al., 2012; Wang et al., 2014). NH₃ and other amino compounds present in wastewater are commonly regarded as the scrubbing agents to transform NO_x into N₂ and water. It has been observed that spraying amines in the combustion process can effectively reduce the formation of harmful nitrogen oxides (NO and NO₂). Botheju et al. (2012) investigate the possibility of using amine rich wastewater for the selective non-catalytic reduction (SNCR) of NO_x. The results indicate that a 96% reduction is achieved when TN/NO (total N to nitric oxide ratio) increases to 8.5 under the optimum temperature of 950 °C. It is noted that this chemical reduction route is only applicable for thermal reclaimed waste, but not an ideal treatment for ED/ion exchange waste due to the low amine concentration in the generated aqueous solution (Ghayur et al., 2019). Using NO_x as a scrubbing agent at a laboratory scale has been proven to be feasible, but its economic potential still needs to be evaluated.

There are several treatments available for mitigating the toxic degradation products of amine wastes, including nitrosamines and nitramines. Peroxidation, UV treatment, photolysis, biodegradation/bioconversion, adsorption by activated carbon have all been proven as effective methods for the destruction of nitrosamines and nitramines. Among these techniques, UV treatment with oxidants and photolysis are the mainstream in the large-scale continues degradation application. Although biological treatment is time-consuming, its environmental and social benefits cannot be neglected. Based on previous studies, there are some successful biodegradation experiments in handling the amine wastes. A combination of biological treatment and physical adsorption using active carbon is thought to be a promising removal method (Liao et al., 2015). About 90% of several precursors of N-nitrosamine are removed through this biological activated carbon (BAC) techniques.

4.2. Biological Treatment

Biological treatment is an up-and-coming technique in handling wastewater due to the fact that organic waste is rich in carbon and nitrogen, which can be catabolized by the microorganisms as food and energy source. The aerobic condition has the potential to mineralize amines while anaerobic approach can utilize waste amine as a nitrogen source by converting the biomass into chemical fuels (Ghayur et al., 2019). This method has many environmental benefits and economic feasi-

bility. Therefore, potential biological treatments are investigated as a sustainable solution to deal with the amine wastewater generated in carbon capture facilities (Lai and Shieh, 1996; Ohtaguchi and Yokoyama, 1997; Strazisar et al., 2003; Mrklas et al., 2004; Ndegwa et al., 2004; Kim et al., 2010; Botheju et al., 2011; Brakstad et al., 2012; Eide-Haugmo et al., 2012; Hauser et al., 2013; Wang et al., 2014; Song et al., 2019).

4.2.1. Biodegradation/Bioconversion of Amines Waste

The biodegradability of amines used during carbon capture is extensively assessed under aerobic conditions. Ohtaguchi and Yokoyama (1997) verified that MEA is biodegradable through aerobic process by utilizing the *Escherichia coli K12* microbes. The final degradation products will be ammonium ion (NH₄⁺) and acetaldehyde (CH₃CHO). They recognize co-enzyme B12 is the major factor initiating this decomposition. Interestingly, it is also found the amine waste solution has a higher degradation rate than pure MEA solution. Under aerobic conditions, ammonium (NH₄⁺) can be oxidized into nitrite (NO₂⁻)/nitrate (NO₃⁻) and denitrified into nitrogen (N₂). While the acetaldehyde (CH₃CHO) then hydrolyzes into ethanol and acetic acid (CH₃COOH), which can be uptake by bacteria and turned into CO₂ (Zhu et al., 2008). It is known that the degradation rate is related to the degree of adaption to the microbial culture medium (Botheju et al., 2011). By using a readily degradable substrate combined with amine wastes can prevent ammonia and pH inhibition. And increasing C/N ratio may enhance the degradation. Kim et al. (2010) study the adaption time and antimicrobial effects of MEA on biodegradation in wastewater treatment with activated sludge. An aerobic sequencing batch reactor (SBR) is used to test the biodegradation. The results indicate that eight weeks of adaptation is needed for nitrifying ammonium. The removal efficiency reaches 92% with 9,000 mg/L MEA at the hydraulic retention time (HRT) of 10.5 days. Another research proves that fresh MEA is fully biological degraded within 21 days after phosphate addition in aerobic condition (Mrklas et al., 2004). The degradation products of amine waste, N-nitrosodimethylamine (NDMA), can also be biologically decomposed by axenic strain bacteria under aerobic conditions (Sharp et al., 2005).

The second option to treat amine waste is to use the amines as a nutrient source for microbes in the production of biofuels or chemical fuel under anaerobic conditions. MEA is a typical nitrogen source for hydrogen production (Seifert et al., 2012). Unicellular *synechococcus leopoliensis* are able to grow in the MEA solution sparged by CO₂, which is thought to be suitable for the sequestration of CO₂ (Ohtaguchi and Wijanarko, 2002). Different bacterial can convert various amines into a number of products, including ethanol, ammonium, and acetic acid. Wang et al. (2013) successfully run an anaerobic bioreactor over a year for converting waste MEA to methane. By running this MEA-based PCC coal power plant for two years, they observe the formation of ammonia in addition to methane (Wang et al., 2014). Also, the toxicity of MEA wastes decrease by 10 ~ 126 folds through anaerobic degradation. It means that ammonia removal, together with anaerobic digestion of MEA

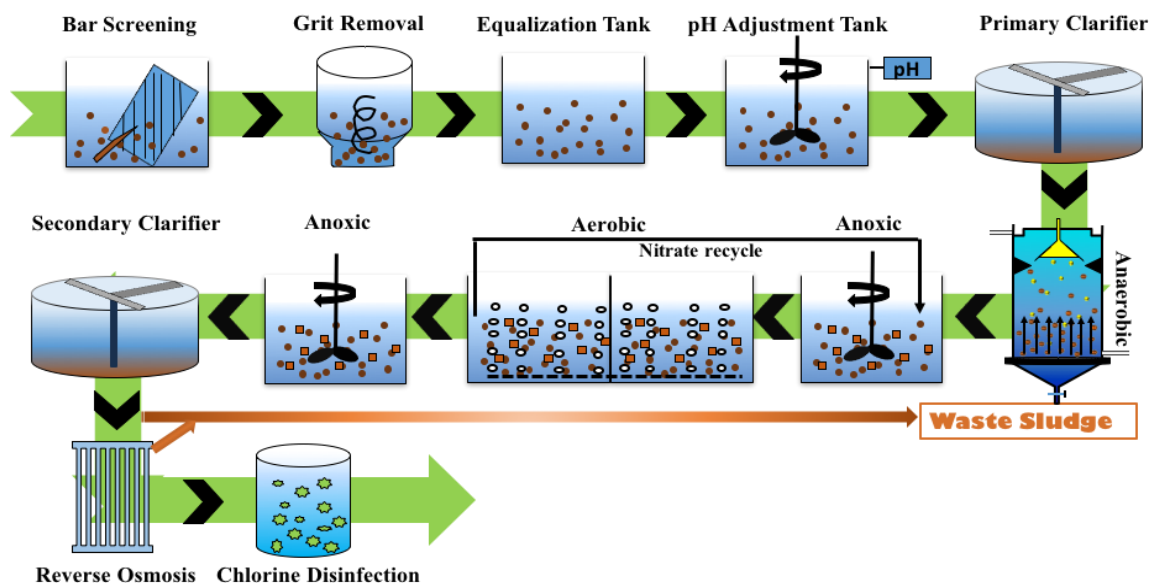


Figure 5. MBBR system with pre-anoxic and post-anoxic reactors.

wastes, can be achieved. This approach has the potential to reduce the toxicity of the contaminants and enable safe discharge of effluent. Under oxygen limiting conditions, microbes will switch to nitrate respiration and produce chemical fuels (Lu et al., 2014, 2015). According to Lai and Shieh (1996), under anoxic conditions in a batch experiment, MEA is highly degraded into ammonia by using NO_3^- as an electron acceptor, and the end product is ammonia and ethanol. More than 70% of total organic carbon (TOC) in the mixed liquor can be removed within 4 h after the introduction of the MEA solvent.

Ndegwa et al. (2004) tested the biodegradation performance and pathways in the MEA contaminated soil under various environmental conditions. Even when the concentration of MEA is above 1,500 mg/kg, the degradation rate is not impacted and microbial growth is not inhibited. Figure 4 shows the biodegradation of MEA under aerobic and anaerobic conditions. This process involves hydrolysis of MEA to ammonium and acetaldehyde. Ammonium can be further oxidized to nitrite and nitrate, then finally denitrified to N_2 . Acetaldehyde is degraded to ethanol and acetic acid through a hydrolysis reaction. The presence of acetic acid and ethanol can also act as an electron donor for the denitrification of nitrate. The limited oxygen in anoxic zones of soil enables the simultaneous nitrification and denitrification. The degradation rate is reduced with the decreased temperature in soil. Generally, aerobic condition provides higher biodegradation rates, whereas more energy efficient is acquired during anaerobic treatment (Botheju et al., 2011). It is a promising solution to combine aerobic, anaerobic, and anoxic treatment together.

4.2.2. Biological Treatment Design

Biological treatment can be carried out using various process configurations. The income wastewater requires pretreatment with bar screening, grit removal and equalization tank,

then adjust pH values between 7.0 and 8.5 by adding alkalinity like calcium carbonate. Also, it is important to remove of toxic materials like heavy metals from the wastewater and considerate waste biodegradability, dissolved oxygen, food to microbe ratio (F/M in the range of 0.2 ~ 1.0, and adequate buffering (alkalinity in the range of 50 ~ 100 mg/L). These conditions will favor the removal of total nitrogen, sulfate, and organic matter in the wastewater. Treatment requirements and process selection can be categorized according to effluent discharge water quality needs, which may range from secondary treatment for BOD removal, nitrification to achieve low effluent ammonia concentration, anoxic-aerobic processes to provide nitrogen removal, and anaerobic-anoxic-aerobic processes to provide nitrogen and sulfate removal. No matter what kind of treatment process is and how many stages are used, they all require an anaerobic zone to reduce sulfate, an aerobic zone for nitrification and an anoxic zone for denitrification and hydrolysis MEA.

Plug-flow aeration tank is suitable for aerobic nitrification with high dissolved oxygen (DO) level ($> 1\text{ mg/L}$), long solid retention time, high microorganism number, and alkaline condition. In contrast, denitrification can only happen in anoxic condition with DO level $< 0.5\text{ mg/L}$. Krauss et al. (2009) report that nitrification/denitrification combined with additional sand filtration is able to reduce up to 90% nitrosamine in the wastewater.

Three biological designs covering Complete-Mix Activated Sludge (CMAS), oxidation ditch, and trickling filter are presented by Nurrokhmah et al. (2013) to treat the amine reclaimer wastewater. In order to meet the landscape irrigation water standard in the United Arab Emirates (UAE), some critical parameters are tested, such as the food to microbe ratio (F/M) and volumetric loading. The results indicate that 90% of nitrogen and organic compound are removed in trickling filter

design, and this process is defined as the most economically feasible method among these three biological designs.

Hauser et al. (2013) are the first to demonstrate the feasibility of pre-anoxic denitrification in the MBBR system. It achieves nitrogen removal of real amine waste from a PCC carbon capture facility without external carbon source apply. The biofilm system delivers 98% removal of MEA and up to 88% removal of total nitrogen. The pre-denitrification treatment system contains an anoxic reactor and then followed by an aerobic nitrification reactor. COD, MEA, and total nitrogen are efficiently removed with a hydraulic retention time (HRT) of 7 h. This research clearly demonstrates the advantage of pre-anoxic denitrification over post-anoxic denitrification in treating MEA contaminated effluents. Pre-anoxic can utilize available organic substances derived from MEA degradation, avoiding the use of additional carbon sources to the denitrifying step. Also, pre-anoxic process is more robust towards toxic loads. Figure 5 shows the flow diagram of MBBR system with pre- and post-denitrification set up.

It is identified that avoiding the overloading of amines or other organics is curtail in the biofilm nitrogen removal of amine-based wastewater (Henry et al., 2016). However, there are other challenges hindered the commercialization of waste amine biodegradation during the carbon capture process. For instance, the microbial species can only selectively degrade the component in mixed amine waste. Nevertheless, a combination of different amine solvent may be used in the real CO₂ capture plant. Besides, most of the degradation products of amine exhibit microbial toxicity. Therefore, a reliable and flexible biological treatment design is required to reduce these toxins and generate marketable chemical fuel products.

5. Conclusions

MEA is the most favorable solvent for chemical absorption of CO₂ during the post-combustion capture process. Compared with other amine solutions, MEA has higher CO₂ absorptivity and a faster reaction rate. These advantages make MEA a good candidate for large-scale industrial applications. However, the reported MEA degradation products in the laboratory experiment level cannot represent real data from the PCC pilot plant. A validate laboratory-scale model and simulation is desired by incorporating proper operations and analytical regimes into the pilot-scale carbon capture program. The heat stable salts and degradation products generated during carbon capture cause lots of troubles in the reclamation of MEA waste. It is essential to purify the solvent to maintain the capture efficiency and to reduce the environmental concerns. In the current stage, all reclamation technologies consume high energy and many limitations hinder its full applications. The extraction method developed by Karnwiboon et al. (2017) achieved HSSs removal from contaminated solvent under atmospheric pressure and relatively low temperatures. Integration of the current process or new reclaiming techniques is expected to be developed to reduce the PCC cost and improve the amine solvent recovery rate.

Amine-based waste handling difficulties substantially inhibit the commercial implementation of carbon capture tech-

nologies. It is not wise to substitute the nontoxic CO₂ emission with more toxic chemical compounds pollutions. In this perspective, different amine waste disposal, recycle, reuse, and chemical/biological treatments are reviewed. Of all these techniques, NO_x scrubbing is a very attractive method for reusing amine wastewater due to its cost-effective and easy to operate features. Further study should address the commercialization of this technology and the impact of the accumulated impurities on the PCC plant operation. The biodegradation method is technical and economically viable at laboratory scales under various environmental conditions. However, the slow biodegradation rate is its biggest shortcoming. Thus, the primary focus should put on optimizing operational parameters and discovering the microbial strains that can destruct amine waste in a practicable degradation time range. A combination of biological treatment with the added catalyst may accelerate the bioreaction speed, which is a promising amine removal technique. Utilization of waste amine for biofuel conversion or biomass pretreatment has a growing potential in the waste handling of these toxic compounds. Its commercial availability and technical maturity make it a sustainable option for treating waste amines. More research attention should be addressed on increasing the product yields and the choice of microbial species according to different amine wastes. Biological treatment of amine-based wastewater is still on laboratory-scale, more detailed biological designs and economic analysis need to be integrated into the development of the cost-effective treatment at the industrial scale.

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