Categorization of Chemical Additives to Food Processor Wastewater

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Additives are used in the food processing industry to facilitate plant operations and provide sanitation. These chemicals often pass through the plant and may interfere with the disposal of process waste. In addition, chemicals are used to preserve food, control moisture, control texture, enhance flavor, decrease cooking/preparation time and enhance nutritional value. The vast majority of these chemicals remain in the product and are not found in the waste streams in significant concentrations. This manuscript reports on a study with the following goals.

- Divide commonly used chemicals that facilitate food processing plant operation into categories relating to their role in plant operations.
- Identify chemicals in each category and provide selected structures.
- Identify potential wastewater treatment problems associated with chemicals in each category and environmental impacts if treatment pass through occurs.

Four categories of chemicals that are of importance to wastewater treatment and disposal are commonly used at food processing plants to facilitate operations.

- Ligands
- Pesticides
- Sanitizers
- Surfactants

For each category, its use in the food processing industry is explained, chemicals within the category are listed and their significance relating to treatment and the environment are discussed. Several chemicals may be categorized in more than one way. These are discussed under the division that is most applicable.

Ligands

Ligands are also called complexing or sequestering agents. Their primary use is to reduce scaling. Scaling can build up rapidly and leads to clogged pipes, inefficient heat exchange and uneven temperatures. Scale that flakes off can enter machinery and cause premature wear (Summers, 2006).

A ligand is an ion with a bonding site that can donate an electron pair in order to form a bond with a metal ion. Chelating agents are ligands with two or more bonding sites.

When two of the sites bond to the same metal a very stable ring structure is formed (Rathke, 2006).

Ligands are sorted into three categories, organic acids, phosphates and phosphonates. Organic acids are the strongest. Included within this category are aminopolycarboxylic acids. These surfactants form stable salts that are soluble in water (Bucheli-Witschel and Egli, 2001). The two aminopolycarboxylic acids most widely used for industrial application are EDTA and NTA. (Bucheli-Witschel and Egli, 2001). Both EDTA and NTA are synthetic and neither is toxic to humans at typical concentrations (Schwuger, 1997).

Ligands commonly used for industrial applications in the USA and Western Europe are listed below (Bucheli-Witschel and Egli, 2001). Structures for selected ligands are shown in Figures 1-3.

- Organic Acids
    - Aminopolycarboxylic acids (ACPAs)
    - Ethylenediaminetetraacetate (EDTA)
    - Nitrilotriacetate (NTA)
    - Diethylene-triaminepentaacetate (DTPA)
    - Hydroxyethylenediaminetriacetate (HEDTA)
    - Hydroxycarboxylic acids - Citric acid

- Phosphates - Sodium polyphosphates
- Phosphonates - Organophosphonates

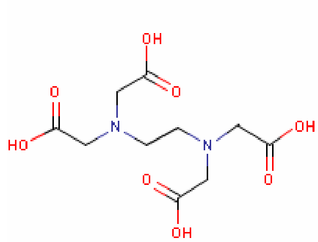

Figure 1. EDTA

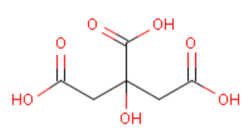

Figure 2. Citric Acid

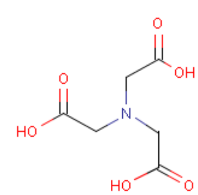

Figure 1. NTA

<u>Treatment Potential and Environmental Fate</u>

EDTA is not removed by conventional wastewater treatment plants (Thomas, 1998). However, Willett and Rittman, 2003, found certain aerobic bacteria capable of dissociating EDTA complexes formed with calcium or magnesium. Further, EDTA biodegradation has been demonstrated by specific cultures in a continuous-flow immobilized biofilm system (Schwuger, 1997, Thomas, 1998). EDTA can be oxidized by ozone and UV radiation.

Salts and metal complexes of NTA are extremely soluble in water (Schwuger, 1997), and consequently very mobile. NTA is also biodegradable in both aerobic and anaerobic conditions (Bucheli-Witschel and Egli, 2001). Degradation is faster and more complete in aerobic conditions (European Amino-carboxylates Producers Committee, 2003). In conventional wastewater treatment plants, NTA removals are generally in the range of seventy to ninety percent (Bucheli-Witschel and Egli, 2001).

Problems with chelators arise because they mobilize metals found naturally in the soil. One of the most problematic is EDTA as it does not readily degrade in the soil profile and groundwater (Sartorius and Zundel, 2005). However, EDTA is photochemically oxidizable in surface water. (Schwuger, 1997).

Pesticides

Pesticides reduce pests in the food processing plant such as rodents, insects and fungi. Large quantities may be used in facilities that handle fresh produce. Additionally, residual pesticides on the commodity may enter the waste stream during washing. Pesticides are sorted into three categories, insecticides, herbicides and fungicides. Categories are further divided up into classes of chemicals with common examples listed, with the exception of fungicides which are not widely used food processing industry (Büyüksönmez, et. al., 1999; Stringer and Johnston, 2001). Figures 4 – 8 show structures for selected pesticides.

- Insecticides
    - Carbamates
        - Aldicarb
        - Carbaryl
        - Carbofuran
    - Organochlorines
        - Methoxychlor
        - Endosulfan
        - Lindane
    - Organophosphates
        - Chlorpyrifos
        - Diazinon
        - Malathion
    - Pyrethroids
        - Cypermethrin
        - Cyfluthrin
        - Esfenvalerate

- Permethrin

- Herbicides

  - Benzoic acids
  - Paraquat
  - Phenoxy acids
  - Substituted ureas
  - Triazines

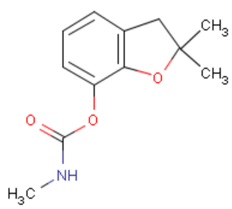

Figure 4. Carbofuran

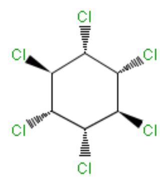

Figure 2. Lindane

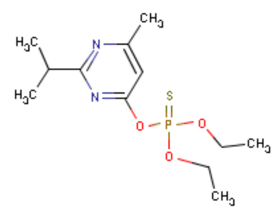

Figure 6. Diazinon

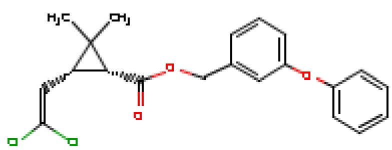

Figure 7. Permethrin

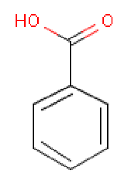

Figure 8. Benzoic Acid

<u>Treatment Potential and Environmental Fate</u>

Modern pesticides are formulated to be biodegradable and there is a large body of research on the fate of pesticides in the environment and mechanisms of controlling pests (Rathke, 2006). A detailed description is beyond the scope of this paper however, below are a few significant highlights.

Insecticides are generally more toxic than herbicides and fungicides. Organochlorines are the most toxic (Büyüksönmez, et. al., 1999). They tend to bioaccumulate and are recalcitrant to biological and chemical degradation (Büyüksönmez, et. al., 1999). Due to this toxicity, most (such as chlordane, dieldrin and DDT) have been banned in the US. The three previously listed however, are still used. Organophosphates are also toxic but do not bioaccumulate. Carbamates are generally considered to be non-persistent however, toxicity varies by compound (Büyüksönmez, et. al., 1999). Except for Paraquat, herbicides generally have a short half life and are less toxic.

Several pesticides are biodegradable in small concentrations. Higher concentrations may also be treated provided the biological system has time to acclimate to the presence of pesticides in small concentrations. Organophosphates, carbamates and herbicides degrade relatively quickly, while organochlorines and many currently banned pesticides degrade at a significantly slower rate (Büyüksönmez, et. al., 2000).

Sanitizers

Sanitizers are used to deactivate bacteria on food contact surfaces. The US government and state governments have many regulations enforcing the use of sanitizers for food safety purposes. The more concentrated the sanitizer is, the more damaging it is to microbial populations. The mechanisms vary but are generally the physical destruction of the cells and/or inactivation of cell function at the genetic level.

Sanitizers can be divided into two categories, oxidizing agents and non-oxidizers (Diversey Lever and Echolab, 2007). Oxidizing sanitizers may be further categorized as either halogen or peroxygen (Diversey Lever and Echolab, 2007). Organic bromine compounds work synergistically with many chlorine compounds and are rarely used alone, and are not examined in this report.

Non-oxidizing sanitizers include acid sanitizers, acid anionic sanitizers, acid-quat sanitizers and quaternary ammonium compounds (Marriott and Gravani, 2006). Acid anionic sanitizers consist of anionic surfactants combined with acids such as phosphoric acid or organic acids. Acid-quat sanitizers consist of a combination of organic acid sanitizers and quaternary ammonium compounds. Quaternary ammonium compounds are compounds with a nitrogen center with 4 alkyl substitutes. These three categories are also surfactants.

Below is a list of common sanitizers used in the food processing industry (Marriott and Gravani, 2006). Figures 9 – 11 are structures are common sanitizers.

- Oxidizing Sanitizers
    - Halogen
        - Organic bromine compounds
        - Common chlorine compounds

            - Liquid chlorine
            - Hypochlorites
            - Inorganic chloramines
            - Organic chloramines
            - Chloride dioxide

        - Common iodine compounds

            - Iodophors
            - Alcohol-iodine solutions
            - Aqueous iodine solutions

    - Peroxygen Sanitizers

        - Hydrogen peroxide
        - Mixed peroxy acid/organic acid sanitizers
        - Peroxyacetic acid
        - Peroxy acid sanitizers

- Non-oxidizing Sanitizers

    - Acid sanitizers – organic acids

        - Acetic acid
        - Lactic acid
        - Propionic acid
        - Fatty acids
        - Formic acid

    - Acid anionic sanitizers
    - Acid-quat sanitizers
    - Quaternary ammonium compounds

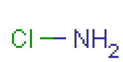

Figure 9. Chloramine

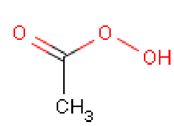

Figure 40. Peroxyacetic Acid

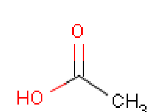

Figure 4. Acetic Acid

Treatment Potential and Environmental Fate

Halogenated sanitizers are strong biocides and therefore, not readily degradable. Many undergo phase changes and are volatile.

Organohalogens are moderately degradable by many aerobic bacteria (Janssen, *et. al.*, 2000). Several specific anaerobic bacteria strains have been found to dehalogenate organohalogens, at a much slower rate than that of aerobic populations (Janssen, *et. al.*, 2000). However, in general, organohalogen compounds can strongly sorb to soil resulting in persistency (Stringer and Johnston, 2001). Most chlorine compounds will degrade when exposed to light or temperatures above 60°C (Marriott and Gravani, 2006).

The organic acid sanitizers are biodegradable and are precursors for methanogens. Excessive quantities lower the pH inhibiting the process. However, the environment and concentrations greatly influence their fate.

Surfactants

Surfactants lower the surface tension of a solvent, such as water. This allows other cleaning compounds to penetrate a water film surrounding a dirt particle so that bonds can be formed (Schmitt, 2001).

There are four types of surfactants: anionic, cationic, nonionic and amphoteric. Anionic surfactants account for 50% of surfactant use in Europe and 60% in the United States. The balance, roughly 40%, is nonionic surfactants (Schmitt, 2001). Consequently these are the focus of this review. Several classes are listed below (Schmitt, 2001) and selected structures for specific surfactants are presented in Figures 12 and 13.

- Anionic surfactants
    - Alkyl sulfates
    - Ether carboxylates
    - Ether sulfates
    - Isethionate esters
    - n-Acylated amino acids
    - Phosphate esters
    - Sulfonates
    - Sulfosuccinate esters

- Nonionic surfactants:
    - Alkyl polyglycosides
    - Amine oxides
    - Esters of polyhydroxy compounds
    - Ethoxylated compounds
    - Fatty acid alkanolamides

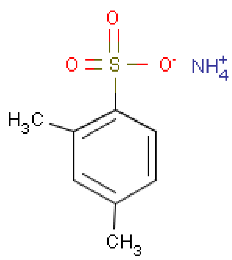

Figure 6. Ammonium Xylene Sulfonate

Figure 6. Dimethyldodecanamine oxide

<u>Treatment Potential and Environmental Fate</u>
Surfactants are generally organic and are only slightly soluble in organic solvents and water. Cationic surfactants are toxic (Schwuger, 1997). The escape of surfactants into surface water may result in foaming (Schwuger, 1997). In soils, surfactants degrade slowly and can alter soil microorganism and plant activity, although the interaction is complex and not well understood (Schwuger, 1997). Surfactants can also drastically increase the solubility of normally insoluble hydrophobic organic compounds.

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