Application of Ionic Nano Particles in Fish Processing Wastewater by using Biochemical Treatment: A Short Review

Mohamad Anuar Kamaruddin$^{1,2,a}$, Lim Ewe Teik$^{3,b}$ and Muhd Nazmi Ismail$^{4,c}$

$^{1,3}$Environmental Technology Division, School of Industrial Technology, Universiti Sains Malaysia, 11800, Penang, Malaysia
$^{2}$Center of Excellence Geopolymer and Green Technology (CEGeoGTech), School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
$^{4}$Civil Engineering Department, Politeknik Sultan Abdul Halim Mu'adzam Shah (POLIMAS), Bandar Darulaman, 06000 Jitra, Kedah, Malaysia

Email: $^a$anuarkamaruddin@usm.my, $^b$anuar197@gmail.com, $^c$nazmiphd@gmail.com

Abstract: Concerns of microorganisms growth in fish processing plants are crucial to the operation of the fish processing facilities. The presence of toxic microorganisms in the effluent could bring detrimental effects to the environmental and public health as several disease outbreaks could possibly take place with the release of infectious wastewater from the facilities. Environmental Quality (Industrial Effluent) Regulations 2009 published by Department of Environment Malaysia has clearly stated that the discharge limit of total coliform into water bodies that are safe for marine life, fisheries and human consumption must be not exceeded 600MPN/100 mL while for $E$.coli is not more than 400MPN/100mL. To cope with the laws and regulations, the industry has practiced several methods on disinfecting the effluent such as chlorination or ultraviolet treatment. However, the excessive use of such methods can cause deterioration to the environment as the by-products get released from the effluent are usually harmful to the natural systems of the environment. This paper aims to summarize recent progress on disinfectant methods that have been reported and published in the literature.

1. Introduction

Malaysia fish processing industry is considered as one of the important contributor to the national gross development. Based on the data recorded by Department of Fisheries Malaysia, fish processing industries alone, which includes the making of fish fillets, fresh, chilled or frozen products contributed about 14 thousand tonnes of yield which equal to USD 44 million. A trend of large industry development for these purposes are being supported by the present Malaysian government. The trend is expected to continue with the growing numbers of small and medium enterprises for fish processing plant coming out in the coming years.

Fish processing activity in Malaysia has been established like other manufacturing industry that releases large volume of wastewater. Fish processing industry produces a high volume of wastewater daily. In order for this industry to be recognized and well accepted by the authority, there are several stringent regulations to be adhered with. For example, operation license from the authority must be obtained prior operating the facility. Meanwhile, strict requirement by Department of Fishery Malaysia has been imposed for fish processing activity and its products need to follow enacted regulations and complying to international standards. The discharge from processing facility is regarded as industrial has wastewater needs. The discharge needs to adhere to Environmental Quality (1974) Industrial
Effluent (Regulations) 2009 for various parameters that covers physical, chemical and biological parameters.

1.1 Wastewater Generation
In general, there are a few fragmented procedures involves during fish processing activity. Typical activity and their byproduct is shown in Fig. 1. The wastewater generated for whole activity can be as much as 30 m$^3$ per batch. Throughout the process, water is commonly used for cleaning, beheading and washing generate large amount of wastewater. The constituents in the wastewater typically with oil and grease, chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS) and

![Fish processing and its byproducts](image)

**Figure 1.** Fish processing and its byproducts (Source: (Chowdhury et al., 2010)).

1.2 Fish Processing and its Wastewater
Typically, large volume of water during processing of fish is needed as the manufacturer required to cleanse the fish product for every process of scaling, washing, beheading, gutting and filleting [1]. Those downstream processing industries and fish processing carries wastewater laden with various kind of organic contaminants, salts and oils (proteins, lipids and enzymes) which are quite difficult to treat. In fact, large volume of wastewater is also produced after the canning process as they usually contain the raw leftover materials that constitutes large portion of the organic contaminants [2]. The major issue associates with the fish processing industry is due to excessive organic loading discharge to the receiving water body without effective treatment in place. Albeit, there have been significant progress of efficient treatment of the wastewater by selected promising method, however, the excessive use of such methods can cause deterioration to the environment as the by-products get released from the effluent and carries harmful substances to the natural systems of the environment.

The COD of effluent are commonly found to be higher than BOD for fish processing wastewater due to high organic load production which leads to a higher amount of bacteria coliform produced [2]. It is important to find a sustainable treatment method for fish-processing wastewater that allows treating
of wastewater that fulfills the discharge limit or available for reuse in other sectors. Typical wastewater treatment can be ranging from physical, chemical and combination of physico-chemical treatment. Each of the treatment has their advantages and drawbacks depending to the extent of discharge limit allowable by the authority. One of many methods is known as disinfection which is considered as important procedure in a wastewater treatment system which serves as a preventive method that ensuring biological strains which causes severe diseases are not present prior to release as effluent [3]. The disinfectant particles commonly interact with bacteria cells by interrupting the transmission of electron or causes damage to the DNA of the bacteria by disrupting its cell membrane [4]. According to Lee et al. [3], the low operation cost of chlorination method is the main cause for chlorine overuse in industrial sectors.

2. Disinfectant Technology

There have been a lot of chemical agents that have been synthesized and commercialized in the recent years. These chemicals include chlorine dioxide, ozone, organic acids, peroxyacetic acid, electrolyzed oxidizing water and hydrogen peroxide [5]. The properties of these disinfectants are listed in Table 1 as summarized by [6]. Accordingly, there have been a substantial evidence of disinfectant agents application due to their inactivation capabilities against various pathogenic and spoilage microorganisms.

Table 1. List of disinfectant chemicals and their properties [7].

| Parameters                  | Chlorine   | Chlorine dioxide | Ozone     | Peroxyacetic acid | H$_2$O$_2$ |
|-----------------------------|------------|------------------|-----------|-------------------|------------|
| Boiling point, °C           | -34.04     | 11               | -112      | 107               | -0.43      |
| Melting point, °C           | -101.5     | -59              | -192      | -                 | 150.2      |
| Solubility in water         | 0.007 g/mL | 8 g/L (at 20 °C) | 0.570 g/L (at 20 °C) | Completely soluble | Miscible |
| Density                     | 3.2 g/L (at 0 °C) | 2.757 g/L | 2.144 g/L (at 0 °C) | 1.0375 g/mL | 1.450 g/cm$^3$ |
| Acidity                     | 11.7       | 3.0              | 7/5       | 8.2               | 11.75      |
| Oxidation potential (eV)    | 1.36       | 1.57             | 2.1       | 1.81              | 1.8        |

2.1 Chlorination

The use of chlorine is a very well known method to disinfect effluent before discharging them into any streams, river or ocean [5, 8]. The ability of chlorine to breakdown nucleic acids and also the cell membranes of microorganisms makes it a very good choice of disinfectant for treating the wastewater in industrial sector [7]. It is commonly known for its ease of application, disinfecting effectiveness and low costing in the treatment of municipal sewage [6]. However, the formation of carcinogenic chloramine are one of the main problem from overdosing chlorine in wastewater disinfection [9]. Chloramine are formed by mixing chlorine with ammonia as shown in equation, which is very toxic to fishes and could decimate certain fish species [10].

\[ \text{NH}_3 + \text{HOCl} \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O} \quad \text{Monochloramine} \]

\[ \text{NH}_2\text{Cl} + \text{HOCl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O} \quad \text{Dichloramine} \]

The current emphasis on stricter enforcement in effluent standards causes exponential growth in the use of chlorination for disinfecting effluent [11]. In contrast, not much have been done by those who proposed and supported such methods to find out the subsequent effect of the increased usage of chlorine [12].
2.2 Ozonation
Ozone may act as a primary disinfectant which provides an alternative to the use of chlorine acting as powerful oxidizing agent. Ozonation provides a higher efficiency in removing several types of organic micropollutants especially pesticides in downstream water system [13]. The residual time for ozone in water bodies are shorter than the other type of disinfectants as ozone decays rapidly compared to other chemical additives. Besides that, ozonation will also be able to improve the removal rate of algae in water bodies and eliminate other micropollutants that gives out bad smell and color.

2.3 Ultraviolet
Another popular choice for industrial application in deactivating pathogens contained in wastewater is the Ultraviolet (UV) disinfection [14]. Compared to conventional methods like chlorination and ozonation, ultraviolet disinfection does not require any addition of chemicals and no toxic by-products are produced from the use of it [15]. It is found that the use of ultraviolet disinfection will not lead to generation of disinfectant-resistant bacteria as the rays does not have direct contact with the water bodies and pathogens, but the disadvantage of this method will have much higher implementing cost [14]. Fig. 2 shows typical ultraviolet and ozone set up for fish processing wastewater.

![UV and ozone set up](image_url)

**Figure 2.** UV and ozone set up.

2.4 Environmental Concerns of Disinfectant Application
Although several popular disinfection methods for fish processing wastewater such as the use of chlorine, ozone and ultraviolet may be able to reduce bacteria growth in the effluent, with the exception that all of them does in fact have side effects that may just transferred the pollution from water to another medium without solving the root problems. Table 1 summarizes the disadvantages and limitations of the few common disinfection methods obtained by some researchers in disinfecting industrial wastewater.

| Type of disinfectant | Limitation                                      | Source |
|----------------------|-------------------------------------------------|--------|
| Chlorine             | Toxic by-products                                | [16]   |
|                      | Promotes growth of disinfectant-resistant bacteria| [9]    |
| Ozone                | Toxic by-products                                | [5]    |
|                      | High cost in industrial scale                    | [17]   |
|                      | Toxic gas and corrosive upon in contact with moisture | [3] |
| Ultraviolet          | Very high cost in industrial scale               | [13]   |
|                      | May be radioactive to human                      | [14]   |
3. Biochemical Treatment

There are various processes available for the treatment of wastewater with the most common method such as chemical destabilization and membrane processes [18]. Compliance with the discharge limits might not be achieved completely even when some of these techniques are used. The major economic advantage is the main reason that most industry treat their effluent with biochemical treatment system as it is cheaper, produces a cleaner effluent that fulfill the discharge limit and emit lesser toxic by-products. Biochemical treatment uses natural processes which relies on the help of bacteria in the decomposition of organic complex substances. The method is also more environmental friendly comparing to physical or chemical treatment [2].

Some researchers conducted studies and found that the copper(II) ions was affecting the cell metabolism of the microorganisms present in wastewater [19]. Therefore, copper compounds are usually present in pesticides and algae-killing solution in swimming pools or natural lakes. The ability of copper ions in interfering the microbe’s cell metabolism shows the antimicrobial effect clearly. A study done by European researchers stated that the removal of copper ions from biological wastewater treatment systems can be easily done by adsorption and precipitation of copper ions [20]. The potential impact of the copper ions towards the environment are also much lower compared to the chlorine ions. A review paper in the same journal showed that about 33 to 98% copper ions can be removed from activated sludge treatment which are definitely easier to remove compared to E.coli and Salmonella sp. removal or even the toxic compounds formed from chlorine overdosing. Thus, we can opt to use copper ions in treating wastewater instead of using the costly ultraviolet treatment or chlorination which may cause detrimental effect to the environment and hard to remove the excess ions.

Quality of wastewater effluents can be monitored by relying on the indicator bacteria namely the coliforms, E.coli and Pseudomonas [21]. Thus, several bacteriological tests such as enumeration of E.coli and coliforms are developed in modern world to cater for the needs of industries in monitoring the microbiological quality of their wastewater effluents. Solid medium plating method are commonly used to test the presence of coliforms and E.coli due to its low costing and quick analysis [12].

One of the main issues with membrane filtering application in wastewater treatment are the formation of biofilm [16]. It would cost a lot to change the membrane filter periodically so it is important to control biofouling on the membrane surfaces [22]. It is found that having copper ions on the membrane surface would show a significant anti-biofouling activity and extends the periodic changing of membrane filters by 30% [19].

4. Conclusion

Although many efforts concerted on disinfectant technology have been devoted especially in the materials science field, there is growing interest for the application of antimicrobial products for diverse field in the recent times. Albeit, knowledge of the frontier of the bacterial.

Acknowledgement

Authors gratefully acknowledge the grant received from Universiti Sains Malaysia under Innovation Seed Fund Project (AUP100248).

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