Nano zero valent iron and ozonation for selected recalcitrant wastewater: Review

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Abstract. This research reviews application of nano zero valent oxidation and ozone for degradation of selected recalcitrant wastewater. Recalcitrant organics refers to non-biodegradable compounds which are of industrial waste source. It is highly pollutant to the environment due to its non-biodegradable properties which can be caused by various factors including lacking of necessary genetic information on the organisms, compound being too large to enter the cell, or non-existence of transport system across the membrane. Examples of recalcitrant wastewater includes palm oil mill effluent, pesticide wastewater, wastewater from paper production, aromatic organic compounds and polycyclic hydrocarbon. These are the wastewater being reviewed to inform about the effectiveness of nano zero valent iron oxidation and/or ozonation. The chosen method aims to be an effective alternative from the traditional method, with simple and easy to handle mechanism. In the treatment of recalcitrant organics, several factors affect the process and are normally investigated. These includes the pH value, the contact time, dosage of treating agent as well as amount of competing cations. Recalcitrant wastewater treated with the suggested method are analyzed before and after the treatment. In addition, XRD, FTIR, SEM and BET maybe used to observe produced catalyst morphology and intrinsic elements prior and after treatment. This review provides scientific information from 2010 until 2019, concerning findings of effective and sustainable treatment of recalcitrant wastewater.

1. Introduction
Recalcitrant organic pollutants refer to the natural organic molecules that is non-biodegradable due to its capabilities of resisting microbial decomposition [1]. Recalcitrant wastewater refers to wastewater that exist in a large amount, with a considerably lower concentration of pollutants, normally found from industries such as palm oil mill, textiles, dyes and so on. Many compounds of the effluent from these industries are considered recalcitrant and therefore can cause hazardous effects to the ecosystem if released to the environment without proper treatment due to its non-biodegradable properties [2], [3]. Nano zero valent iron oxidation, an advanced oxidation water remediation method with rising fame in recent years has been studied for its effectiveness in treating recalcitrant wastewater. The method has been
chosen due to its simplicity of synthesizing the oxidants as well as the effectiveness in treatment non-biodegradable pollutants [4].

2. Methods

2.1 Treatment Methods

The treatment methods involved in this study are oxidation with nano zero valent iron (nZVI) and also ozonation, both considered advanced oxidation processes (AOPs) that is capable of breaking the complex structure of recalcitrant compound and hence making them easier to be biodegraded. During AOPs, highly reactive hydroxyl radicals (·OH) are generated which oxidizes or degrade the recalcitrant compounds and converting them into less harmful products [5, 6].

2.1.1 Nano Zero Valent Iron

Nano particles are commonly used for water remediation in recent years, with various particles from metal oxides, carbon materials, metals or bimetallic particles and so on. Among all the nano particles involved, nano zero valent iron (nZVI) is the most substantially used. The reason is that nZVI has shown high effectiveness in pollutants removing while at the same time being cost effective on production [4].

There are a couple of methods for production of nZVI. The more traditional one being the physical method, where production is achieved through process such as grinding, abrasion or even lithography. Physical production method has evolved over the years and in the present exist through nucleation from homogenous solutions or gas, phases separation as well as annealing at elevated temperatures [7].

Other than physical method, a method more commonly used nowadays is chemical method. nZVI can be synthesized through the following equation:

$$Fe(H_2O)_6^{3+} + 3BH_4^+ + 3H_2O \rightarrow Fe^0 + 3B(OH)_3 + 10.5 H_2$$

The synthesis is done with sodium borohydride (NaBH₄) as the reducing agent [8]. The most extensively used method for synthesizing nZVI is through chemical reduction. This is because of the simplicity of the method, as well as the characteristic of product obtained which is a homogenous structure which translates to high reactivity [9].

Even though nZVI has proven its effectiveness in water remediation, there is also a risk of hazard to be considered due to the minimally explained toxicity of nZVI on living organisms [4]. Most studies conducted regarding nano materials are based on carbon and oxides [10], [11]. Research has identified that nZVI can be harmful on microorganisms, animals, plants and even human due to its toxicity properties. Therefore, precautions should be made during its applications. Fortunately, in most of the cases studies shown that toxicity of nZVI is significantly lower compared to other nanoparticles [12]. Reason for the overall lower toxicity can be explained by iron being the common element in soil necessary for the development of most organisms [13].

2.1.2 Ozonation

Ozone is a strong oxidant which earned the status of GRAS (Generally recognized as safe) [14]. Due to its powerful oxidation properties and high availability, ozone is commonly adopted as the more preferable technologies used for treatment [15]. Ozone (O₃) is formed by 3 oxygen atoms and can be produced by various methods. It can be produced through electrical discharges, or the incidence of high-energy electromagnetic radiation in the air. Another advantage of adopting ozone in treatment is that it is very unstable and therefore decays quickly to diatomic oxygen. This means that after the treatment, there will be no residue left in the water [16].
2.2  Selected Recalcitrant Wastewater
Four different recalcitrant wastewater are studied in this paper, namely palm oil mill effluent (POME), pesticide wastewater, and also textile wastewater. These are the few common recalcitrant wastewater which are difficult to be treated with traditional method. Therefore, the effectiveness of nZVI and ozonation in treating these wastewaters has been studied and reviewed.

2.2.1  Palm Oil Mill Effluent (POME)
Palm oil mill effluent (POME) refers to the large amount of liquid waste produced during the extraction and clarification processes in milling oil palm. The raw effluent contains almost 90-95% water and includes residual oil, soil particles and suspended solids. POME is a highly pollutant material due to its high biological oxygen demand (BOD), and therefore needs to be treated before discharging [17].

Table 1. Characteristics of Palm Oil Mill Effluent (POME)

| Author Characteristics | (Wong et al., 2009) [18] | (Chin et al., 2013) [19] | (O. Edewor, 2007) [20] |
|------------------------|--------------------------|--------------------------|------------------------|
| COD (mg/L)             | 45,500-65,000            | 44,300-102,696           | 42,000-81,300          |
| BOD (mg/L)             | 21,500-30,150            | 25,000-65,714            | 22,500-38,000          |
| pH                     | 4-4.5                    | 4-5                      | 3-4.5                  |
| TSS (mg/L)             | -                        | 18,000-46,011            | 12,700-51,000          |
| Oil and Grease (mg/L)  | -                        | 4,000-9,341              | 18,000-52,000          |

2.2.2  Pesticide Wastewater
Pesticide industry generates concerning amount of effluents which is hazardous to the environment due to its high chemical oxygen demand (COD) which restrains the growth of microorganisms and therefore is difficult to biodegrade [21]. Even at low concentrations, pesticide compounds are generally highly toxic and harmful to the ecosystem [22]. Due to its recalcitrant properties, traditional biological treatment method is not very effective against pesticide wastewater and hence advanced oxidation process are needed.

Table 2. Characteristics of Pesticide Wastewater

| Author Characteristics | (Raut-Jadhav et al., 2016) [22] | (Xiong et al., 2011) [23] | (Chen et al., 2007) [21] |
|------------------------|---------------------------------|---------------------------|------------------------|
| COD (mg/L)             | 17,000-18,000                   | 21,000-23,000             | 31,600-35,800          |
| BOD (mg/L)             | 2,100-2,200                     | 650                       | 5,400-6,800            |
| pH                     | 3-5                             | 13-14                     | 1.5-2.5                |
| TSS (mg/L)             | 106                             | -                         | -                      |

2.2.3  Textile Wastewater
Textile industry has been considered to be among the biggest manufacturing industrial chains due to its extremely wide variety of related products and functions [24]. Unfortunately, the industry comes with a big flaw which is its impact on the environment, specifically on water pollution. Effluents from textile industries are very difficult to be treated due to its non-biodegradable chemical properties which list them under recalcitrant compound which resist degradation [25]. Therefore, traditional water treatment method, namely biological treatment, is not capable of effectively treating the textile wastewater effluent which
requires the removal of color and also the recalcitrant compound. Hence, alternative remediation such as ozonation has been studied and included into conventional treatment for enhanced performance [26].

Table 3. Characteristics of Typical Textile Wastewater

| Author Characteristics | (Kalra et al., 2011) [27] | (Paździór et al., 2016) [28] | (Buthiyappan et al., 2015) [29] |
|------------------------|---------------------------|-----------------------------|---------------------------------|
| COD (mg/L)             | 150-10,000                | 800-1,100                   | 150-12,000                      |
| BOD (mg/L)             | 100-4,000                 | 200-270                     | 80-6,000                        |
| pH                     | 6-10                      | 9-10                        | -                               |
| TSS (mg/L)             | 100-5,000                 | 200-500                     | 2,900-3,100                     |
| Colour (Pt-Co)         | 50-2,500                  | -                           | -                               |

3. Treatment Effectiveness

Researches for the treatment of each of the three wastewaters with either nano zero valent iron oxidation (nZVI) or ozonation are studied and compared to observe the effectiveness of each method in the enhancement of treatment process for the recalcitrant compound. The main responding parameter observed from each treatment is the removal of chemical oxygen demand (COD) which is the main cause of the wastewater being classified as recalcitrant.

3.1 Treatment of Palm Oil Mill Effluent

From the studies reviewed, oxidation of nZVI is very effective in COD removal for POME, with the disadvantage being the long duration of treatment of up to 20 hours. Fortunately, the treatment can be enhanced by either introducing air into the water during the treatment, or an even more effective method of introducing ultrasound which functions to disperse the particles more uniformly which results in more reactions to occur. The introduction of ultrasound into the solution promotes the production of Fe$^{2+}$ ions which reacts with the recalcitrant compound in POME [30, 31]. For ozonation, it has been observed that ozonation serve more as an assistant for traditional biological treatment, where ozonated POME yields significantly better COD removal compared to raw POME due to the enhanced efficiency of hydrogen production [32].

Table 4. COD Removal of POME from Different Treatment Methods

| Treatment Method                  | COD Removal (%) | Source                          |
|----------------------------------|-----------------|---------------------------------|
| Aerated nZVI                     | 75              | (Taha et al., 2014) [30]        |
| nZVI with Ultrasound             | 80              | (Taha et al., 2014) [31]        |
| Ozonation Assisted Biophotolysis | 44              | (Pisutpaisal, 2014) [32]        |

3.2 Treatment of Pesticide Wastewater

From the study of pesticide wastewater remediation, Xiong, Cheng and Sun were studying the effectiveness of ozonation alone on COD removal as well as a combined process of ultrasonic and ozonation. Results clearly shows that ultrasonic/O$_3$ combined process yields a significantly higher removal percentage compared to O$_3$ alone. According to the study, the dosage of O$_3$ plays the major role of the COD removal while ultrasonic functions more as an assistant to the overall treatment [23].
Table 5. COD Removal of Pesticide Wastewater from Ozonation [23]

| Treatment Method         | COD Removal (%) |
|--------------------------|-----------------|
| Ozonation (O3)           | 58.6            |
| Ultrasonic/O3 Combination| 67.2            |

3.3 Treatment of Textile Wastewater

In 2018, Malik published a journal article of his testing on the aerobic degradation of textile effluent, with pretreated effluents by ozonation (O3), and also pretreated effluents with combination of ozonation and nano zero valent iron (O3/nZVI).

Table 6. COD Removal of Pretreated Textile Wastewater with Aerobic Degradation [33]

| Pretreatment Method | COD Removal (%) |
|---------------------|-----------------|
| None                | 30.9            |
| O3                  | 42.8            |
| O3/nZVI             | 78.3            |

The results from the treatment shows that inclusion of a pretreatment method significantly increases the COD removal from textile wastewater especially with the combination of O3/nZVI. The reason is that the inclusion of the pretreatment enhances and accelerates the oxidation of recalcitrant compounds in the wastewater, turning them into easily biodegradable compounds [33].

4. Conclusion

Lots of researches has been done in recent decades on the usage of advanced oxidation processes (AOPs). From the few that has been reviewed, results showed that depending on the type of effluents treated, the treatment method can be a standalone treatment or more commonly adopted as a pre or post-treatment process to enhance the overall effectiveness of traditional biological treatment. The research also shows that both methods can be improved with the inclusion of ultrasound, where the ultrasonic waves helps disperse the particle more uniformly, providing better reaction rate and hence better treatment of the effluent. It can be concluded that lots of possible combinations are available for the two AOPs studied which are both effective in converting recalcitrant compounds to more biodegradable materials. Therefore, sufficient trials and combinations of treatment methods should be tested on different recalcitrant wastewaters in order to achieve the optimal treatment process, since it has been reviewed that different recalcitrant wastewaters requires different combination of AOPs and conventional treatment method to yield similar effectiveness of wastewater treatment.

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