Review of combined nano zero valent metal oxidation and ozone for degradation of wastewater

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Abstract. This research reviews nano zero valent metal oxidation coupled with ozone for degradation of wastewater effluent. The technology in wastewater treatment is gradually innovating. Car wash wastewater constitutes and promotes water and environmental pollution. In wastewater treatment, a variety of methods are available for treatment of wastewater. The chosen method should be cost effective and easy to operate. In the treatment of car wash wastewater, certain parameters are investigated such as pH, time, dosage of treating agent, presence of hydrogen peroxide, and competing cations. The characteristics of treated and untreated car wash wastewater are usually analysed, produced catalyst morphology and elements maybe observed and compared using the XRD, FTIR, SEM + EDx, and BET. A combined treatment of different phases is reported to remove total suspended solid (TSS), inorganic materials such as sodium chlorides (NACL), heavy metals such as lead, oil and grease, as well as phosphates and nitrates. This review will discuss on the treatment methods being practised in wastewater engineering field, chosen treatment methods after review with supports, and combination concerns on the chosen treatment methods along with consequences to the environment and human health.

1. Introduction
Car wash industries develop in nations since the evolution of vehicles [1]. The maintenance of vehicles is important as vehicles transport passengers and goods from one destination to another. General maintenance such as car wash helps in maintaining the service life of vehicles in terms of inhibition from corrosion in outer body structure of vehicles. High amount of fresh water is used while cleaning vehicles, especially for those car wash shops which are busy in business. A previous research shows that about 40-120 L of fresh water is used to clean up a single car [2]. Daily car wash services receive orders ranging from 50 to 150 vehicles, which leads to usage of approximately 18000 L of fresh water per day [2]. Meanwhile, wastewater produced are generally channelized to the roadside drain, bushes, front yard, or to the river stream.

Water and wastewater treatment concerns in protecting, preserving all kinds of potential water resources. Despite ensuring the environmental pollution to be controlled, it protects the aquatic lives, as well as ensuring clean water resources for human daily activities. Car wash wastewater refers to the fresh water being contaminated while refreshing the car body. Pollutants that can be found in car wash effluents are nitrates, ammonia, heavy metals such as leads, oil and grease, gasoline, organic matter and particles like dust, carbons and salts [2–4].
Previous researches in water and wastewater engineering show different research methods in degrading the pollutants in wastewater. Among those, nano zero valent metal is studied for removal of heavy metals [5] and nitrates [6].

Normally, car wash industries in Sibu Zone contribute to water pollution when the wastewater produced are channelized directly into drainage system to the river stream without any treatment. Pollutants detected in samples collected from local car wash shops are car wash detergents, nitrates, heavy metals, oil and greases, with the presence of high turbidity and chemical oxygen demand (COD). Previous research by Fateminia et al studied on degrading nitrates using nZVI [6]. There are other articles such as removing heavy metals in wastewater by Dave et al [7], removing arsenic by Rahmani et al [8, 9], and other organic matters [10].

2. Discussion
Wastewater Engineering begins when the concern on environmental health becomes prior in advance technology. The progress in technologies and human activities, somehow contribute to environmental pollution. Production of goods does not deny the fact where wastes are produced at the same time. Wastewater production from households and industries contain pollutants that jeopardise the environment, as well as the aquatic lives in the water. Hence, human puts hard work in wastewater treatment, not just to neutralise all the pollutants created, but to preserve the ecosystem in healthy state.

Despite chemical industries and households that produce wastewater, transportation do contribute to wastewater production. Car wash shops serve as light maintenance to vehicles. They clean and removes the impurities, dust and other pollutants where the vehicles carry along as they travel from one destination to another. The cleaning process includes the usage of gallons of fresh water with car wash detergent. Later, the wastewater flows into the drainage system and channelized to the river.

The concern on car wash wastewater treatment begins when the pollutants or compounds in car wash wastewater harms the environmental health. Critical pollutants such as heavy metals, oil and grease are known to affect the aquatic lives. Hence, researches on car wash wastewater treatment becomes common especially when human emphasis a lot more on environmental protection.

This chapter discusses history in wastewater treatment, ways and ideas in wastewater treatment, and the chosen treating methods in this research. Comparison and concerns are done so as to justify the optimum idea for the research conduction.

2.1. Engineering in Wastewater Treatment
Wastewater treatment involves the discovery of potential pollutants in wastewater following with solution to degrade such pollution in order to protect the environment health. History in water and wastewater engineering discover a lot of treatment method to handle different kind of water pollution and wastewater. There are filtration, chemical coagulation, ultrafiltration, ozonation, precipitation and flocculation[5], [11–14]. There are inventions on the oxidising agent and adsorbent to degrade the pollutants such as activated carbon, chemicals and nanoparticles. Other than that, there are application of machinery such as ultrasonic generator, bioreactor, ozone generator and electrocoagulation [15–17]. Each treatment methods have their own potential in overcoming different kinds of pollutants in wastewater. Wastewater is a main term to all kind of used or produced contaminated water sources, for instance, household sewage, domestic wastewater, commercial wastewater and industry wastewater. Car wash wastewater is one of the wastewaters produced from human activities.

2.2. Pollutant Characteristics in Car Wash Wastewater
Car wash wastewater refers to the used water in the cleaning process of the outer body of vehicles. The wastewater is normally channelized directly into the drainage system to the river. While not treated properly, there are pollutants in the wastewater which is unbeneﬁcial to the environment.

Despite protecting the environment and water resources, treatment of car wash wastewater is done to ensure the water can be recycled, reused for other daily activities, for instance, irrigation. Table 1
shows the comparison between pollutants characteristics in car wash effluent to the standard water quality for irrigation purposes as stated in Interim National Water Quality Standards (INWQS).

| Pollutants         | Bhatti et al [12] | Baddo et al [18] | Oleifer [19] | Hashim and Zayadi [2] | Hubadillah [3] |
|--------------------|-------------------|------------------|-------------|------------------------|---------------|
| Oil and Grease (mg/L) | 1.3-83.7          | 35               | 2.79-6.36   | 55-79                  | -             |
| COD (mg/L)         | 141-1019          | 403              | 681.3-893.33 | 89-398                 | 75.0-738.0    |
| Turbidity (NTU)    | 73-772            | -                | 68-180.3    | -                      | 34.7-86.0     |
| TDS (mg/L)         | 577.33-664.33     | 1200             | -           | -                      | 89.2-151.8    |
| pH                 | 7.89-8.75         | 7                | 7.85-8.80   | 7.38-8.33              | 6.51-8.74     |
| TSS (mg/L)         | -                 | 49               | -           | 56-268                 | 89.2-151.8    |
| Nitrates (mg/L)    | -                 | -                | -           | 0.4-2.57               | -             |

From Table 1, it can be seen that Hashim and Zayadi [2] found the existence of nitrates in car wash wastewater. The COD content in the effluents are high, which hits to a value of 1019 mg/L. This implies the concern in treating car wash effluents. Other than that, turbidity value in car wash wastewater ranges from 34.74 to 772 NTU. This leads to the need to treat the effluent before discharged to the environment. Oil and grease content is high, ranging from 1.3 to 83.7 mg/L. Hence, the wastewater shall be treated before being discharged or being reused for other purposes, for instance, water irrigation. Table 2 compares the pollutant contents in car wash effluents to the standard water quality for irrigation purposes.

| Parameter     | Combined Characteristics of Car Wash Wastewater Quality from Table 1 | Water Quality Index Malaysia Standard Class IIA for Irrigation Purposes [20] |
|---------------|-------------------------------------------------------------------|----------------------------------------------------------------------------|
| pH value      | 7.8-8.80                                                          | 6-9                                                                       |
| COD (mg/L)    | 75-1019                                                           | 25                                                                        |
| Turbidity (NTU) | 34.7-772                                                        | 50                                                                        |
| TDS (mg/L)    | 89.2-1200                                                         | 1000                                                                     |
| TSS (mg/L)    | 49-268                                                            | 50                                                                        |
| Oil and Grease | 1.3-83.7                                                         | 0.04                                                                      |

Referring to Table 2, it is seen that the pollutants in car wash wastewater does not reach the targets of referred standard water quality. With the pH value lies in the range of mentioned standard, the pH value is remained in existing condition without any changes to avoid any extra costs in neutralising back to required standard quality. The COD content is extremely high which makes it to be prior concern in treatment process. Then there goes the turbidity value which gives a value of 772 NTU, which is so much higher than that of the standard quality of 50 NTU. In short, car wash wastewater treatment is needed to protect the environment from the pollution.

2.3. Treatment History on Car Wash Wastewater

Car wash wastewater treatment is being practised in foreign countries. Table 3 shows the treatment methods by different researchers on car wash effluents. From Table 3, it is seen that with the application of aeration, oil was removed up to 96.3%. Then COD was removed up to 93.13% through alum treatment. Bhatti et al [12] used coagulant to degrade COD content in the wastewater while Baddor et al [18] practised adsorption method in treating these two pollutants. It reached up to 86.77% removal rate on oil and 81.64 % removal on COD content. Other than that, Oleifera [19] used alum as coagulant in removing COD in car wash effluent. The result gives a removal rate of 80%. This implies...
that COD content in car wash effluent can be removed through coagulation and adsorption, while the oil can be removed through aeration and adsorption.

### Table 3. Car wash wastewater treatment history.

| Pollutants | Bhatti et al [12] | Baddor et al [18] | Oleifera [19] |
|------------|-------------------|-------------------|---------------|
| Oil (mg/L) | Aeration          | Adsorption by Bentonite | -             |
|            | 96.3              | 86.77             | -             |
| COD        | Alum Treatment    | Adsorption by Bentonite | Alum as Coagulant |
|            | 93.13             | 81.64             | 80            |

#### 2.4. Nano Zero Valant Metals

Nanoparticles are now common adsorbent being used in wastewater treatment. Researches show the effectiveness of nanoparticles in removing nitrates, heavy metals such as platinum, lead and arsenic, as well as organic matters [6], [21–23]. In wastewater engineering field, three common types of studied nanoparticles are nano zero valent iron (nZVI), nano zero valent copper (nZVC), and nano zero valent iron-copper (nZVI-C). Each will treat the samples, later to be compared and analysed the optimum condition of application, so as the effectiveness of each as adsorbent in treating car wash wastewater.

**2.4.1. Nano Zero Valent Iron.** Nano zero valent iron refers to the nano formation of iron metal, free of charges. Typical size of nano zero valent iron varies in between 10 to 100 nm [5]. In wastewater treatment engineering history, nanoparticles are utilised in treating the waste particles, through degradation, coagulation and accumulation, there to remove the impurities, toxics, as well as harmful matters from treated water [12].

Previous researches by other researchers proves the effectiveness of nano zero valent iron, nZVI in treating heavy metals [5, 7, 24] and nitrates [6]. As mentioned by Yirsaw et al, the size of the nanoparticles affect the reactivity in degrading wastewater [25]. It is mentioned that smaller the particle size of the nanoparticles, higher the total surface area, thus higher the reactivity among the nZVI atoms with the treated samples to reach atom stabilisation. Figure 1 shows the analysis by Yirsaw et al. [25].

![Figure 1. Surface area to volume ratio reactivity versus particle size of nZVI](image)

In Figure 1, it can be seen that the smaller the particle size, the higher the surface area of the particles, hence the higher the reactivity of the particles. This is the key term that makes nanoparticles a superior option as treatment agent in wastewater treatment. Table 4 lists the treatment history using nano zero valent iron as oxidising agent in degrading pollutants in wastewater.
Table 4. Removal rate of pollutants using nZVI.

| Pollutants   | Removal Rate | Reference     |
|--------------|--------------|---------------|
| Nitrates     | 90 %         | [6, 26, 27]   |

Most of the studies proved the application of nano zero valent iron in degrading nitrates. However, no justification found on the treatment effect on COD. According to the research by Kahlil et al, pure nZVI induction into wastewater degrades up to 90% of nitrates within 5 minutes of reaction [27]. The addition of 0.25 g of copper (II) chlorides boosts the removal rate of nitrates to 100% within 15 minutes. The effectiveness in COD removal using nZVI will be studied through a preliminary test.

Preparation of nano zero valent iron can be done as follow: 4% of iron (II) chloride in mixed with distilled water in a conical flask labelled ‘Solution A’. 4% of sodium borohydride is poured into distilled water in conical flask labelled “Solution B”. Solution B is added drop by drop into Solution A through burette to produce nano zero valent iron. The product has to be stored in vacuum state so as to preserve the reactivity of produced nZVI.

2.4.2. Nano Zero Valent Copper. Nano zero valent copper (nZVC) refers to the nano-scale version of zero valent copper. nZVC works similarly to nano zero valent iron. Preparation is similar to that of nZVI. Mix Copper (II) acetate with ethylene glycol in ratio of 0.4 g per 200 mL as pre-solution. Later, add 400 mL of hydrazine hydrate drop by drop into the solution overnight to produce the copper nanoparticles. Wash the solution using ethanol 3 times and dried over room temperature then stored in vacuum state. Table 5 lists the treatment history on pollutants using nZVC.

Table 5. Removal rate of pollutants using nZVC.

| Pollutants     | Removal Rate | Reference |
|----------------|--------------|-----------|
| Dichloromethane| 40% (low dosage) | [28]      |
| Metronidazole  | 35%          | [29]      |

Huang et al [28] mentioned that sodium borohydride controlled the reaction rate on degradation of dichloromethane. At higher concentration, the degradation rate breaks the limit of 40% removal rate where the electron donor is no longer limiting factor. Hence, there is the idea where the reactivity of nanoparticles can be controlled by controlling the dosage of sodium borohydride during the production of nanoparticles. Other than that, Xu [29] mentioned that the degradation on metronidazole using nZVC reached to 35% after 120 minutes reaction. Additional factors are being manipulated so as to increase the removal rate of mentioned pollutant such as pH which increased the removal rate up to 92%. From here, there is the idea where treating agent may not be the only alternative to degrade pollutants where additional method can be introduced to assist the treatment results.

2.4.3. Nano Zero Valent Iron/Copper. Nano zero valent copper is the combination of nano zero valent iron and nano zero valent copper. The production process is similar to the production of nZVI, with addition of anhydrous copper chloride to the solution before it is being dried up into powder state [6], [30]. Table 6 shows the treatment history on wastewater using nZVI-C as treating agent.

Table 6. Removal rate of pollutants using nZVI-C.

| Pollutants | Removal Rate | Reference |
|------------|--------------|-----------|
| Nitrates   | 100%         | [26, 27]  |
| Ammonia    | 77%          | [31]      |
2.5. Ozonation

According to Morley, ozone is toxic to most types of living organisms [32]. The theorem applied whereby ozonation works is that ozone tends to break the cells and tissues in the medium where it contacts. Ozonation is known to remove taste and odours, heavy metals such as lead and aluminium, and microorganisms [16]. Ozone method has been practised in treating car wash wastewater with the combination of chemical coagulation method [33]. This indicates the opportunity in success of research by the combination of ozone method together with other treating method. Table 7 shows the wastewater treatment history using ozonation.

Table 7. Removal rate of pollutants through ozonation.

| Pollutants             | Removal Rate | Reference |
|------------------------|--------------|-----------|
| Chloride               | 64 %         | [34]      |
| Sulfamethoxazole       | 99 %         | [35]      |

At pH 3 with application of 5.5 mg/L of ozone, sulfamethoxazole was being degraded 99 % [35]. However, manipulation on pH is not considered as one of the options since re-neutralisation of pH value seems an extra step for wastewater which initially lies in range of standard quality. Hence, the combination of nanoparticles oxidation with ozonation is considered to see if the combined treatment methods show effectiveness as compared to the individuals. Since ozone stays in reactive state, ozone generator is commonly used so as to ease the treatment process.

2.6. Summary

Mentioned treatment methods are nano zero valent metals oxidation and ozonation. Nanoparticles chosen are nano zero valent iron (nZVI), nano zero valent copper (nZVC), and nano zero valent iron-copper (nZVI-C). Among these, nZVI-C gives higher removal of pollutants, although, other two treatment agents can stand against it with the assistance of ozonation. To ensure the efficiencies in removing chemical oxygen demand, pre-test is carried out to define the hypothesis. Table 8 shows the preliminary testing results in removing chemical oxygen demand (COD) using nano zero valent iron (nZVI).

Table 8. Preliminary testing results for COD using nano zero valent iron.

| Preliminary Tests                      | COD Value (mg/L) | Removal Percentage (%) |
|----------------------------------------|------------------|-------------------------|
| Untreated                              | 551              | -                       |
| Treated sample 1 (1 g nZVI without hydrogen peroxide) | 374              | 32.25                   |
| Treated sample 2 (1 g nZVI with 5 mL hydrogen peroxide) | 488.5            | 11.5                    |

From above results, it is seen that the removal rate of chemical oxygen demand (COD) in the car wash wastewater is significant (32.25%) with 1 g of nZVI. This shows the validity in application of nano zero valent iron as adsorbent in treating car wash wastewater.

On the other hand, Table 9 shows the preliminary results in reducing COD and turbidity range of car wash wastewater using ozonation method.
From above results, it is seen that the removal rate of COD and turbidity value on treated car wash wastewater sample is significant, especially on the turbidity value. The highest removal rate on both COD and turbidity value happens at frequency of 75 %. For sample B, there is an increment in COD value than untreated car wash wastewater sample. From observation during experimental process, the removal rate on studied factors can be affected by the insoluble particles in the car wash wastewater. Hence, it is suggested to add in filtration process to remove suspended solid.

In general, combined treatment method is suggested to be carried out to see if it gives significant effect when compared to the treatment method alone. The main idea is to not adjust the pH value of the wastewater, while controlling the reaction rate as low as possible, and to be environmental-friendly.

3. Conclusion
From the review, it can be concluded that nanoparticles are extremely reactive. Nanoparticle has the advantage of having extremely small particle sizes. Higher surface makes it more reactive to pollutants than normal size particles. Meanwhile, ozonation is known to degrade toxics, microorganisms, organic and inorganic materials. Since nano zero valent iron gives a good preliminary result in removing chemical oxygen demand, it is believed that with optimum dosage of nanoparticles, assisted with ozonation, will eventually lead to desirable removal rate of pollutants in car wash wastewater. The combination of nano zero valent metal oxidation with ozonation is believed to increase the degradation rate of pollutants in wastewater.

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