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Review of Nano Zero Valent Iron Oxidation and Alginate Beads for Degradation of Chemical Oxygen Demand and Turbidity in Wastewater

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Abstract: This research reviews degradation of wastewater through the treating method of nano zero valent iron oxidation and alginate beads. Unlike other regions in Malaysia, car wash wastewater in Sibu Zone, Sarawak is not concerned on its contribution to environmental pollution. An amount of about 150L fresh water is used to wash a car. Detergents, oil and grease, dust and sand washed away by water is let flow into bushes, or roadside drain without any treatment. High chemical oxygen demand and turbidity in car wash wastewater will pollute the water source when discharged to the river without any treatment. Treatment of car wash wastewater requires preparation of nano zero valent iron and calcium alginate beads respectively. The research will observe the effectiveness on the chosen method by studying the significance of each treatment method independently, then combine two of them to study the overall effectiveness. Hence, this review collects the statement where nano zero valent iron oxidation and alginate beads are effective in degradation of pollutants in wastewater.

Keywords: Car Wash Wastewater, Nano Zero Valent Iron, Alginate Beads, Chemical Oxygen Demand Removal, Turbidity Removal

INTRODUCTION

Wastewater treatment engineering is widely studied to reach the aim of providing clean water resource and protecting the environment from polluted wastewater. Car wash wastewater treatment is studied in several region in Malaysia, for instance Johor Bahru, but yet to be practiced in Sibu, Sarawak [2]. Pollutants in car wash wastewater such as oil and grease, chemical detergents, sand, dust, and lead is harmful to the environment [11];[25];[30]. Figure 1 shows the car wash service in Sungai Merah, Sibu.

Figure 1: Free flow of car wash wastewater to the road (Source: Photograph by researcher)

As shown in Figure 1, car wash services in Sibu area discharge produced wastewater directly to the roadside drain to the river, or into bushes. This condition happens not only in one car wash service centre but all the car wash shops in Sibu zone. Free discharge of car wash effluent to the environment leads to the flow of pollutants to the streamline which degrades the aquatic living environment. With such concerns treatment is indeed needed for car wash effluent so as to protect the environment from those harmful pollutants.

Al-Gheethi *et al*. [2], uses combined method to treat car wash wastewater, which natural coagulation is coupled with filtration system [2]. Al-Gheethi *et al*. [2] mention the presence of high turbidity is due to high content of dirt and sand particles,
which shows the high value of total suspended solids in wastewater [2]. Besides, Bhatti *et al*. [6] practices chemical oxidation to degrade the pollutants in car wash effluent [6]. The authors design a combined treatment system, that is, aeration to remove oil and grease, and alum as coagulant to remove the pollutants. From these two research, it is understood that different methods are effective in treating different pollutants. Hence, combined treatment system is designed in this research to achieve maximum pollutant removal rate.

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CHARACTERISTICS OF CAR WASH WASTEWATER

Wastewater is required for treatment when the pollutants characteristics in the effluent exceeds the standard water quality. In this research, the standard water quality is set based on the standard water quality for irrigation purposes [31]. Table 1 below shows the characteristics of car wash wastewater.

Table 1: Treatment History of Wastewater Engineering Using Nano Zero Valent Iron

Pollutant	Characteristics based on Class IIA by Standard National Water Quality Index for Irrigation Purposes		Combined Characteristics of car wash effluent	
	Value	Reference	Value	Reference
Oil and grease	-	[31]	1.3-84.0	[2];[4];[6];[12]
pH	6-9	[31]	7-8.8	[2];[4];[6];[12]
COD (mg/L)	25	[31]	141-1019	[2];[4];[6];[12]
Turbidity	50	[31]	73-772	[2];[6]
TSS	1000	[31]	49-268	[4];[6]

In reference to Table 1, chemical oxygen demand of raw car wash wastewater exceeds the standard water quality, which means raw car wash wastewater is not suitable for agricultural purposes, not to mention for safe drinking [31]. Next, turbidity level of raw car wash effluent exceeds limit stated which is 772 NTU. High turbidity implies high content of mud and dirt in wastewater which is washed down from car body during cleaning process [23]. Although high turbidity always come with high total suspended solid content, the characteristics of car wash effluent gives tolerantly acceptable total suspended solid content in reference to national standard water quality index Malaysia [31]. Last but not least, the pH value of the raw car wash wastewater is within the acceptable range of water quality. Hence, chemical oxygen demand and turbidity value of the car wash wastewater is targeted as critical pollutant to be treated in this research.

NANO ZERO VALENT IRON OXIDATION

Nano zero valent iron is the nano-scale version of zero valent particles [7]. The rises of application of nanoparticles is due to the discovery of higher reactivity of nanoparticles as compare to common size particles [17];[19]. Higher surface area makes the nanoparticles easily to be inserted into any porous medium [29]. There, reaction between particles of adsorbent and pollutant are easily reached and degradation of pollutants can be done easily [24]. Research by Dongsheng *et al*. [9], prove the significance of nano zero valent iron in removing heavy metal [9]. Besides, Fateminia and Falamaki [10] find that nano zero valent iron is effective in reducing nitrate content in wastewater [10]. They state that nano zero valent iron is stable in carrying out oxidation due to the neutral charge of iron nanoparticles [10]. Though the articles mention the effectiveness of mentioned adsorbent in treating effluent, the concern on removing the adsorbent after usage is not mentioned for environmental cause. Hence, the implication of a medium to carry the nano zero valent iron powder is concerned in this study.

Table 2: Treatment History of Wastewater Engineering Using Nano Zero Valent Iron

Treated Pollutant	Removal Rate (%)	Reference
COD (mg/L)	72	[8]
Nitrates	55.5	[10];[17]
Phosphates	78.49	[3];[6];[16];[32]
Ibuprofen	95	[21]

From Table 2, it is seen that nano zero valent iron is effective in removing chemical oxygen demand, nitrates, phosphates and ibuprofen [3];[6];[10];[32]. However, removal efficiencies do not hit the target of 100 %. This implies the hypothesis that individual treatment method does not cover full efficiencies in removing different pollutants. Other than that, nano zero valent iron is produced in powder form. There is concern in removing efficiencies of used adsorbent from treated effluent in open environment. Nano zero valent iron rusts when immersed in liquid for more than a week. This will lead to environmental pollution during practices. Hence, the idea of applying combined treating method rises so as to seek for maximum pollutant removal while being environmentally friendly.

Production of Nanoparticles

Production of iron nanoparticles requires following items: iron chloride, sodium borohydride, and ethanol [26]. The production of iron nanoparticles is as stated in equation below:

$$4Fe^{3+} + 3BH_4{}^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3{}^- + 12H^+ + 6H_2$$

Distilled iron chloride is mixed into distilled sodium borohydride and later shall be washed with ethanol for 3 times. The solution is later filtered and dried to obtain the powder [26]. Preparation shall be carried out in vacuum state due to the high reactivity of iron nanoparticles when produced, will rust immediately when exposed to oxygen [26];[28]. Figure 2 shows the produced iron nanoparticles stored in closed medium.

Figure 2: Produced nano zero valent iron stored in closed medium

As seen in Figure 2, nano zero valent iron produced by researcher is stored in vacuum state so as to prevent the powder from rusting. Nano zero valent iron is extremely reactive, hence shall be stored properly to preserve its condition for further experiment.

ALGINATE BEADS

Alginate beads is good in encapsulating matrix. In accordance to Isik *et al*. [13], bare calcium alginate beads, when added with adsorbent such as zinc oxide, will increase the removal of dye. This calls the fact that bare calcium alginate beads have no function on its own. Research by Isik *et al*. [13], uses zinc oxide as adsorbent. Here, researcher will substitute the idea from Isik *et al*. [13] by mixing the produced iron nanoparticles powder as the reagent.

Treatment History using Alginate Beads as Entrapment Medium

Alginate beads is not functional on its own. Instead, it acts as capsule for treating agent. In engineering fields, alginate beads is popular in used due to its entrapment matrix that coats treating agent perfectly for handling purposes, not to mention to enhance the treatment process [5];[13]. Table 3 shows the application of alginate beads in engineering fields.

From Table 3, it is seen that alginate beads do not stand alone as a treatment agent. In fact, it coats the treatment agent in order to reach the objective of removing pollutants. Researchers mention that with the presence of alginate beads as encapsulating medium, the treatment process is boosted up and the removal rate of pollutant studied is increased as well [5];[13];[33].

Table 3: Application of Alginate Beads in Treating Pollutants

Treated Pollutant	Coated Adsorbent/Treatment Agent	Reference
Copper (II) ions	Iron Carbide	[1]
Phosphate and Nitrates	Chitosan	[15]
Dye	Zinc Oxide and Titanium Dioxide	[13]
Phosphorus	Zirconium Oxychloride Octahydrate	[20]
Chromium	Tetraethylenepentamine	[22]

Preparation of Bare Alginate Beads

Preparation of bare calcium alginate beads is done by dropping alginic solution into distilled calcium chloride. To prepare bare sodium alginate beads, drop the distilled calcium chloride into the alginic solution.

Preparation of Nano Zero Valent Iron Coated in Calcium Alginate Beads

In order to prepare iron nanoparticles coated in alginate beads, first step will be the preparation of sodium alginic solution and nano zero valent iron respectively. Preparation of nano zero valent iron is done by mixing distilled iron chloride into distilled sodium borohydride drop by drop [18]. Later the solution set to rest for 20 minutes, then filtered in vacuum state to extract the iron nanoparticles in powder formed [14]. Dilute the sodium alginate in distilled water. Mix the iron nanoparticles powder into alginic solution before mixing the solution into calcium chloride. Mixed solution shall be set to rest for 20 minutes before furthering the experiments [13];[27].

DISCUSSION

From reviews done, it is seen that nano zero valent iron is effective in removing chemical oxygen demand, turbidity and total suspended solids. However, it comes along with the problem in removing the adsorbent after treatment. On the other hand, alginate beads act as entrapment medium can easily solve the problem. Mixing adsorbent powder in alginate beads helps in removing them from treated effluent. Alginate beads, when stands alone, does not give much effect in removing pollutants [13]. When mixed in the adsorbent, which is zinc oxide in researcher's articles, it shows

100% colour removal [13]. Hence, researcher tends to study the difference when nano zero valet iron is capsulated and not capsulated in alginate beads to investigate if the combination of two will be effective in removing car wash effluent in Sibu zone, Sarawak. Preparation of nano zero valent iron is a challenging task since the extraction of iron powder from the solution has to be done in vacuum states. When exposed in atmosphere at warm temperature, nano zero valent iron is easily oxidised and thus will reduce its reactivity in the treatment process. On the other hand, calcium alginate beads may act as capturing medium to the iron nanoparticles. This may stabilise the iron nanoparticles before experiment. Hence, the idea of coating nano zero valent iron in calcium alginate beads is considerable.

CONCLUSION

The application of nano zero valent iron through oxidation is believed to give effective results in degrading the pollutants in car wash effluent. The chemical oxygen demand and turbidity is believed to be treated to standard water quality requirement which is suitable for agricultural purposes.

Nano zero valent iron is considered metal which is not suitable to be used in high dosage for treatment. Hence, optimum dosage of nano zero valent iron will gives optimum degradation rate to the pollutants, but over dosage will reduce the removal efficiencies, while perhaps contribute to pollution. Hence, alginate beads might do well in handling the nano zero valent iron.

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