Synthesis of Nanoscale Zero-Valent Iron from Weed Extracts and Their Application for Azo Dye Decolorization

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Abstract

Green nanoscale zero-valent iron particles represent a new tool of treatment of environmental pollution that could provide cost-effective, high surface energy, eco-friendly and high reactive activity to some of the most challenging environmental cleanup problems. In this study, nanoscale zero-valent iron particles (nZVI) were synthesized from weed extracts. Twelve kinds of weed were studied to compare which one is the most suitable for synthesis of nZVI. From the results, *Euphorbia hirta* possesses the highest phenolic content (3.28 mg GAE/g) and reducing power (586.34 mg/g). nZVI was successfully synthesized by using *Euphorbia hirta* extract. The synthesized nZVI was used for the decolorization of azo dyes. With an initial dye concentration of 100 mg/L and nZVI dose of 1g/l, the removal efficiency reached over 99% within 60 min.

Keywords: *Weed extract, Nanoscale zero-valent iron, Azo dyes, Decolorization*

1. Introduction

Nowadays, some of human's activities are constructing the negative effects on the environment. The polluting and poisoning of water, soil, and air with harmful chemicals have been paid priority attention (Fazlzadeh et al, 2017). Color is a distinct contaminant that can produce a high concern to the environment, especially on water systems. The industries that used dyes and pigments in their manufactures usually discharged dye-containing effluent into water systems, which results in bad effects on the living condition of aquatic lives, plants, and humans (Phihusut & Chantharat, 2017). Approximately, 7 x10^5 tons of synthetic dyes are annually produced worldwide, greatly consumed by the textile industry and about 10-50% of dyes are released to the environment (Rajamohan & Rajasimman, 2013). The discharge of dyes into the water system not only affects their appearance nature but also destroys all the living things in water by polluting and reducing the sunlight into the water (Shahul Hameed et al, 2017). More than 50% of commercial dyes are azo dyes. At least 3,000 kinds of azo dyes are widely used in many industries and represent the largest class of dyes (Hunger, 2002; Ziarani et al, 2018).

Nanoscale metallic particles have been investigated as a new technology for environmental remediation such as water or soil contamination. The proportion at the surface of atom increases as the particle size decreases, which results in their tendencies to adsorb, interact and react with other atoms. For example, Crane and Scott (2012) concluded that macroscale silver is a kind of chemical inert, but at the nanoscale particle size, silver is an active chemical that is used in multiple applications including antimicrobial sterilization, a catalyst for numerous chemical reactions and solar system energy absorption. Gheju (2011) observed that when compared microscale iron nanoparticles with nanoscale zero-valent iron, the nanoscale particles can be more reactive from 10 to 1000 times. Nanoscale zero-valent iron has been become the focus of investigation due to their efficient property in removing of many kinds of contaminants (heavy metal removal, degradation of dyes, biocide agent and wastewater treatment) from aqueous solutions (Madhavi et al, 2013). The synthesis of iron nanoparticles has been studied by using chemical and physical techniques (Fazlzadeh et al, 2017), for example, the popular toxic chemical for synthesis nZVI was sodium borohydride. In recently year, green techniques for synthesis by using natural reagents such as biodegradation polymers, vitamins, plant extracts and microorganisms as reductants and capping agents could be considered as the new generation nanotechnology (Kharissova et al, 2013). Plant extracts are wealthy in reducing power and polyphenols, which are high in antioxidant properties that are suitable for binding catecholate or gallate ligand to Fe^{3+} forming semiquinone which reduces Fe^{3+} to Fe^{2+} and Fe^0 (Borja et al, 2015). Green synthesis seems to be the best choice for the biosynthesis of nanoparticles due to their unique physicochemical properties, high surface energy, high catalytic activity, high reactive activity, cost-effectiveness, eco-friendliness and high stability (Ebrahiminezhad et al, 2018; Raju et al, 2017).

This research focuses on choosing one of the weeds that contains the highest reducing power and phenolic content to synthesize nanoscale zero-valent iron by green nanotechnology method (weed extract). The product of nanoscale zero-valent iron from green synthesis was utilized for the decolorization of azo dyes.

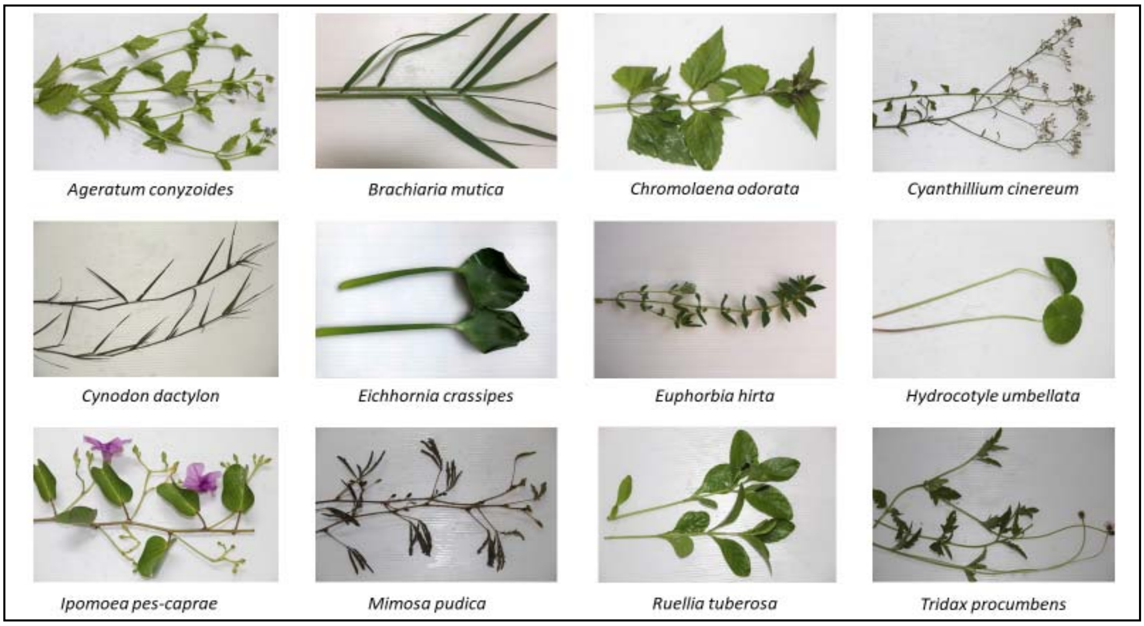
2. Objectives

1. To select the potential weed that contains the highest phenolic content and reducing power
2. To synthesize nanoscale zero-valent iron from weed extract
3. To decolorize azo dyes by using nanoscale zero-valent iron

3. Materials and Methods

3.1 Comparison of twelve weed extracts for nZVI synthesis

3.1.1 Samples preparation



Ageratum conyzoides *Brachiaria mutica* *Chromolaena odorata* *Cyanthillium cinereum*
Cynodon dactylon *Eichhornia crassipes* *Euphorbia hirta* *Hydrocotyle umbellata*
Ipomoea pes-caprae *Mimosa pudica* *Ruellia tuberosa* *Tridax procumbens*

Figure 1 Picture of types of weed sample

Each fresh weed (around 1 kg) was collected in Pattani province and rinsed with deionized water to remove the dust and other particles. The weeds were cut into the small size and dried in the oven at 60ºC for 48 hours until there was no change in weight. The sample of dried weeds was ground and sieved by using sieve No. 35. The powder samples were kept in the plastic bag at room temperature until ready for extraction (Wong et al, 2006). The pictures of each weed sample with the scientific name was shown in Figure 1.

3.1.2 Extraction experiment

For extraction experiment, 25 mL of distilled and boiling water (80 ºC) was added to 2.5 g of coarse powders of each sample. The mixture was shaken on the shaker at 200 rpm for 20 min and then the extract was filtered through the gauze sheet. Then, the sample solutions were centrifuged at 12,000 rpm for 10 min to make the solutions to be clear (Rajendrakumar et al, 2014).

3.1.3 Reducing power analysis

Reducing power of the weed extract was estimated by adding 0.25 mL of weed extract solution to 1.25 mL of sodium phosphate buffer (0.1 M, pH 6.6) and 1.25 mL of potassium ferricyanide (1.0%). The mixed solution was vortex and was incubated at 50 ºC for 20 min, to reduce ferricyanide to ferrocyanide. Then, 1.25 mL of 10% trichloroacetic was added to the mixed solution and centrifuged again at 10,000 rpm for 5 min. Finally, the upper layer 2.5 mL of the solution was mixed with 2.5 mL of distilled water and 0.5 mL of 0.1% ferric chloride solution and the absorbance was read at 700 nm. A blank was prepared by using all the same reagent with the preparing sample, but without adding extract. Ascorbic acid at a concentration from 10 to 100 µg/mL was used as standard. The experiment will be performed thrice and results are averaged (Rajendrakumar et al, 2014).

3.1.4 Total phenolic content analysis

Total phenolic content was estimated by using Folin-Ciocalteau reagent. Briefly, 0.5 mL of weed extract was mixed with 2.5 mL of Folin- Ciocalteau reagent and 2 mL of 7.5% sodium carbonate. The mixture was allowed to occur in the darkness at room temperature for 30 min. The absorbance of the mixed solution was read at recorded at 765 nm using spectrophotometer. Gallic acid (0.1 to 0.5 mg/mL) was used as reference standard for calibration curve and the absorbance was read at 765 nm in spectrophotometer (Rajendrakumar et al, 2014).

3.2 Synthesis of iron nanoparticle

To synthesize iron nanoparticles, one of weed extract that contains the highest reducing power was mixed with 0.1 M of ferric iron (dissolve 27 g of $FeCl_3$ $6H_2O$ in 1 L of deionized water) solution at volume ratio 1:2 at room temperature by applying vigorous agitation at 300 rpm for 30 min. The particles were separated by using a magnet and were washed three time with 30 mL of ethanol. Finally, the powder of iron nanoparticles was produced after drying with silica jell in a desiccator for 12 hours (Mystrioti et al, 2016).

3.3 Azo dyes decolorization

Five azo dyes with the molecular formula as shown in Table 1 were used for the decolorization capacity of nZVI. The dye solutions (25 mL) with the initial concentration (100 mg/L) were added to 0.025g of nZVI. The solutions were shaken at 200 rpm for 1 hour at room temperature. The particles in the mixed solutions were separated by using a magnet. The upper layer around 3 mL were centrifuged at 10,000 rpm for 3 min and the clear solutions were measured with spectrophotometer at different wavelength (Wang et al, 2015).

Table 1 Azo dyes

Names of Azo Dyes	Molecular Formula
Reactive black 5	$C_{26}H_{21}N_5Na_4O_{19}S_6$
Reactive blue 221	$C_{33}H_{24}ClCuN_9Na_3O_{15}S4$
Reactive green 19	$C_{40}H_{23}Cl_2N_{15}Na_6O_{19}S_6$
Reactive red M5B	$C_{19}H_{10}Cl_2N_6Na_2O_7S_2$
Reactive violet 5	$C_{20}H_{16}N_3Na_3O_{15}S_4$

4. Results and Discussion

4.1 Reducing power

The reducing power of each weed sample was analyzed and calculated by using ascorbic acid as the standard for calibration curve. The concentration of reducing power were shown in Figure 2. All of the results in this study were analyzed by SPSS and the data are expressed as mean ± SD ($n = 3$). The highest reducing power of weed extract was found in *Euphorbia hirta* (5.86 ± 0.01) mg/g, followed by *Ipomoea pes-caprae* (4.65 ± 0.00) mg/g, *Hydrocolyte umbellata* (4.30 ± 0.01) mg/g, *Eichhornia crassipes* (4.21 ± 0.00) mg/g, *Mimosa pudica* (3.99 ± 0.00) mg/g, *Chromolaena odorata* (3.71 ± 0.01) mg/g, *Ageratum conyzoides* (3.63 ± 0.01) mg/g, *Cynodon dactylon* (3.62 ± 0.00) mg/g, *Brachiaria mutica* (3.32 ± 0.00) mg/g, *Cyanthillium* *cinereum* (2.81 ± 0.00) mg/g, *Tridax procumbens* (1.24 ± 0.00) mg/g, and *Ruellia tuberosa* (0.777± 0.01) mg/g was the lowest in reducing power.

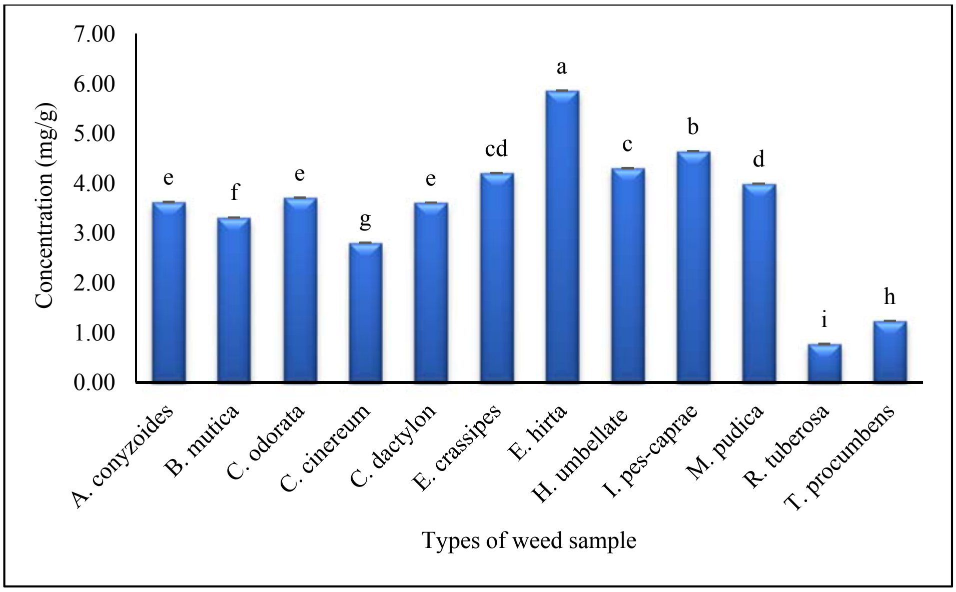


Figure 2 Reducing power of weed extract

4.2 Total phenolic content

The concentration of total phenolic content was shown in Figure 3. Gallic acid was used as a reference standard curve, and the results were expressed as milligram gallic acid equivalent (mg GAE)/g dry weight of weed extract. The data are expressed as mean ± SD (*n* = 3). The highest total phenolic content of weed extract was found in *Euphorbia hirta* (32.79 ± 0.01) mg GAE/g, followed by *Ipomoea pes-caprae* (32.08 ± 0.01) mg GAE/g, *Ageratum conyzoides* (28.19 ± 0.01) mg GAE/g, *Chromolaena odorata* (27.13 ± 0.00) mg GAE/g, *Eichhornia crassipes* (26.75 ± 0.01) mg GAE/g, *Brachiaria mutica* (26.69 ± 0.00) mg GAE/g, *Hydrocolyte umbellata* (23.84 ± 0.01) mg GAE/g, *Mimosa pudica* (23.22 ± 0.00) mg GAE/g, *Cynodon dactylon* (20.44 ± 0.00) mg GAE/g, *Cyanthillium cinereum* (12.33 ± 0.00) mg GAE/g, *Ruellia tuberosa* (9.10 ± 0.00) mg GAE/g, and *Tridax procumbens* (8.15 ± 0.00) mg GAE/g. The results of total phenolic content show that *Euphorbia hirta* and *Ipomoea pes-caprae* are not significantly different, so for further research, the researcher should consider which one is easier to find or collect in the local, either *Euphorbia hirta* or *Ipomoea pes-caprae* could be used to test for synthesis nZVI.

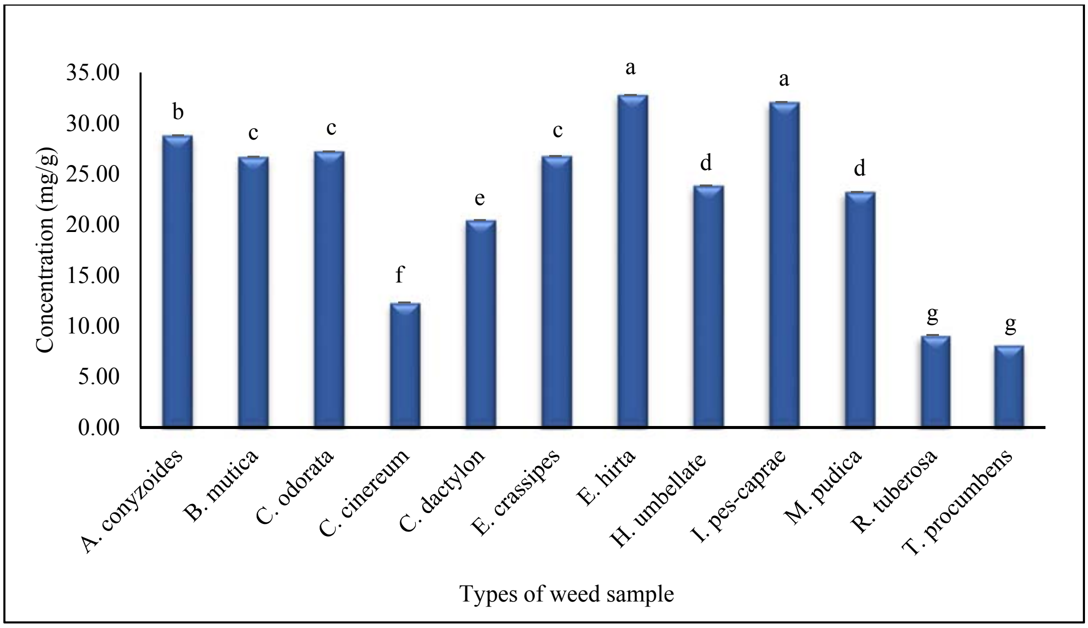


Figure 3 Total phenolic content of weed extract

4.3 Synthesis of iron nanoparticle

Depending on the comparison of total phenolic content and reducing power of weed extract samples, *Euphorbia hirta* was the highest in both of total phenolic content (32.79 ± 0.01) mg GAE/g and reducing power (5.86 ± 0.01) mg/g. nZVI was successfully synthesized by using *Euphorbia hirta* as be shown in Figure 4. The convenient reaction between the weed extract solution and ferric iron occurs immediately at room temperature. The sediment of nZVI can be shown by the change of color from pale yellow to dark greenish/black. The synthesis of nZVI by this costless weed is suitable to apply in further research, but to know more specific of nZVI property, the researcher should study the characterization of nZVI.

Figure 4 Synthesized iron nanoparticle

4.4 Azo dyes decolorization

The removal efficiency of five azo dyes increased to nearly 100 % within the contact time 60 min. nZVI particles dissociate into ferrous iron, as results in releasing two electrons in aqueous medium ($Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + OH^-$). The azo dye or another organic compound that contained in the aqueous medium can rapidly combine with the released electron, thereby the reduction of organic compounds (Dutta et al, 2016). As can be seen from Figure 5, the removal efficiency of reactive black 5 was 98.05 ± 0.05 %, reactive blue 221 was 97.89 ± 0.20 %, reactive violet 5 was 97.88 ± 0.08 %, reactive red M5B was 99.17 ± 0.20 % and reactive green 19 was 98.13 ± 0.14 %. From these results, the synthesized nZVI from *Euphorbia hirta* was suggested as the effective adsorbent for azo dye decolorization. The change of color before and after decolorization was shown in Figure 6. There were five pairs of test tubes for comparison of azo dye before and after decolorization. From left to right side, the first pair was reactive black 5 followed by reactive blue 221, reactive green 19, reactive red M5B and the last pair was reactive violet 5. A clear solution after decolorization shows the high-efficiency removal of azo dyes by nZVI. The synthesized nZVI in this study is suitable for the removal of azo dyes from aqueous solutions. For further research, the researcher should study about the variable experiment such as the effect of pH, contact time or effect of dye concentration.

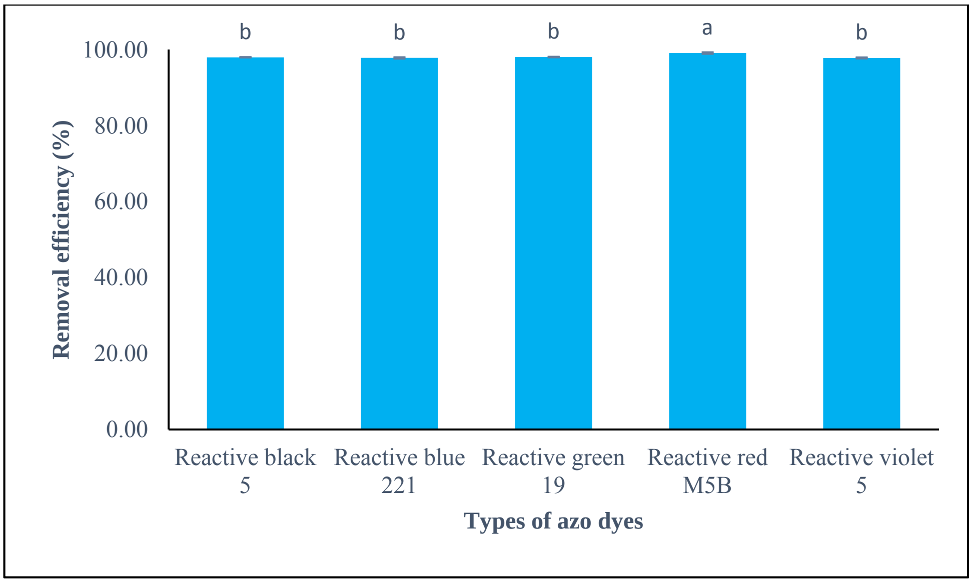


Figure 5 The efficiency of removal of azo dyes

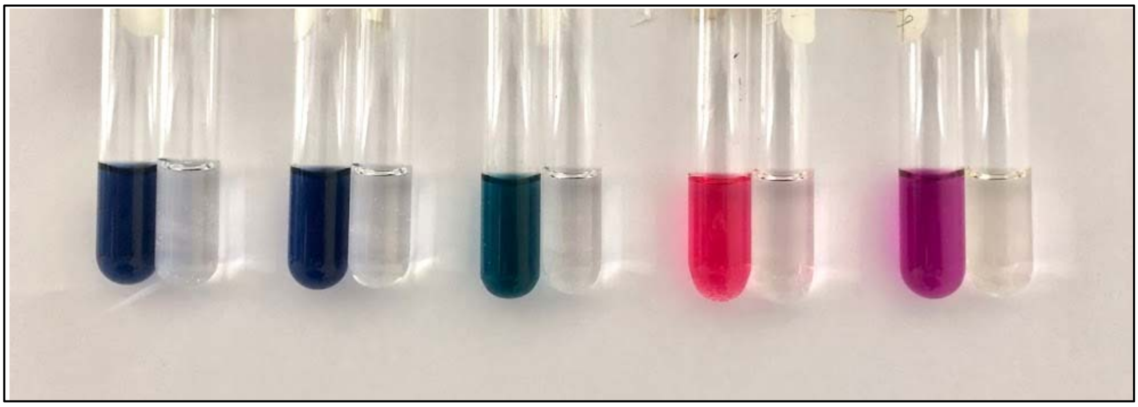


Figure 6 The change of color of azo dyes before and after decolorization

5. Conclusion

Iron nanoparticles were successfully synthesized by using the costless weed extract, *Euphorbia hirta*, that possesses the highest phenolic content and reducing power. The properties of iron nanoparticles by weed extract were highly effective in azo dyes decolorization. Green synthesis nZVI could be an efficient and inexpensive tool for the separation and transformation of the contamination. This research shows that nZVI could be prepared by using the costless weed instead of the chemical synthesis or green synthesis by using costly plant extract, which could be the benefit for further studies. However, this research still has limitations. For example, nZVI can be easily oxidized by oxygen in the air, which results in losing its inactivation ability.

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