Green Synthesis and Utility of Nano Fe for Cr(VI) Treatment

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Abstract

Zero valent iron (ZVI) nanoparticles have been considered as effective materials for environmental remediation because of their strong reducing ability, high reaction activity, and excellent absorption properties. In this study, we synthesized iron nanoparticles using an environmentally friendly method in order to treat Cr(VI) ions in an aqueous medium. Polyphenols from green tea leaf extracts were used as both the reducing agent and the stabilizer for ZVI nanoparticles. Modern techniques, including scanning electron microscopy (SEM), dynamic light scattering (DLS), X-ray diffraction (XRD), and infrared spectroscopy (FTIR), confirmed that ZVI nanoparticles were successfully prepared and surrounded by polyphenol molecules. Cr(VI) ion treatment of the nanoparticles was most favorable at pH 2.0, and 0.04 g ZVI nanoparticles for a 50 mg L^{-1} Cr(VI) solution. Under some treatment conditions, removal efficiency was 100%, suggesting that the synthesized ZVI nanoparticles can be used as materials for Cr(VI) ion removal.

Keywords

Cr(VI) treatment, green synthesis, green tea leaves extract, zero valent iron nanoparticles

Introduction

Recently, the developement of zero valent iron (ZVI or Fe^0) nanoparticles for treatment of the environment has been highly investigated worldwide. ZVI nanoparticles are used instead of larger iron particles (> 50 μm) because they possess a large specific surface area, have high activity, and possess the ability to transfer to the ground or ground water (CityChlor, 2013). The synthesis of NZVI can be divided into two main groups: mechanical grinding or chemical reduction methods (Stefaniuk *et al.*, 2016). According to the chemical reduction method, many authors have synthesized iron nanoparticles by reactions of Fe(II) or Fe(III) salts with the $NaBH_4$ reductant (Meyer *et al.*, 2004; Wu and Ritchie, 2006; Gunawardana and Swedlund, 2012). The nanoparticles obtained are often prone to accumulation due to electromagnetic interactions. The strong

reductivity of the particles makes them susceptible to oxidation and it can be difficult to separate them from the environment. To overcome these traits, researchers combined the iron nanoparticles with other metals by covering their surface, bringing them to polymer networks, or emulsifying them (Lu *et al.*, 2016). In addition to NaBH4, plant anti-oxidant extracts can be used in iron nanoparticle preparation. It has been shown that this is a novel, environmentally friendly research direction resulting in increased reductivity or enhancement of the physical structure of the iron nanocrystals (Hoag *et al.*, 2009; Oakes, 2013; Mystrioti *et al.*, 2015; El-Kassas and Ghobrial, 2017; Devatha *et al.*, 2016). All of these studies have confirmed the effectiveness of ZVI nanoparticles in the treatment of a wide spectrum of environmental contaminants such as Cr (VI), pigments, PCBs, and TCE.

In Vietnam, ZVI nanoparticle preparations were also carried out by mechanical grinding or using the reducing agent NaBH4. The mechanical grinding method requires expensive equipment and techniques. In addition, the nanoparticles obtained are not uniform in size (Trung and Le, 2013). Meanwhile, the chemical method performed by reducing iron (II) or iron (III) using sodium borohydride NaBH4 is much less expensive (Dung, 2012; Huan and Quynh, 2013; Toan, 2014). These studies have used ZVI nanoparticles to treat NO_3^- (Huan and Quynh, 2013), Cr(VI) (Dung, 2012; Trung and Le, 2013), Pb(II) (Dung, 2012), methylene blue (Toan, 2014), or DDT (Huan, 2011). The ability of the nanoparticles to remove the pollutants depends on the pollutant concentration, the pH of the solution, and the amount of nanoparticles used.

In spite of the effective pollutant removal, using sodium borohydride in a preparation of ZVI nanoparticles has several disadvantages. NaBH4 is a relatively expensive chemical that has to be used in surplus quantities, which can generate highly flammable gas (hydrogen). High levels of toxic NaBH4 residue may affect safety during work and require further separation (Soliemanzadeh *et al.*, 2016). Therefore, this study aimed to synthesize ZVI

nanoparticles in a green process, in which no hazardous chemicals are used or generated, in order to treat Cr(VI) ions in an aqueous medium. The synthesis used the reductive source of polyphenols, a type of antioxidant, found in green tea leaves. This is a cheap, popular, environmentally safe source of polyphenol that is completely non-toxic and does not need to be removed. In particular, polyphenols are capable of forming complexes with iron so they are capable of stabilizing the ZVI nanoparticles, preventing them from aggregating (Truskewycz *et al.*, 2016). At the same time, with their antioxidant properties, polyphenols are capable of protecting the iron nanoparticles from oxidation in the environment, thus helping the particles maintain activity (Lin *et al.*, 2017).

Materials and Methods

Materials

Analytical grade ferrous sulfate heptahydrate (Mohr salt FeSO4.7H2O), potassium dichromate (K2Cr2O7), and 1,10-phenanthroline were used without further purification. Green tea leaves were purchased from Trau Quy, Gia Lam, Hanoi, Vietnam. Double distilled water was used throughout all experiments.

Preparation of ZVI nanoparticles

Green tea leaf extract was obtained by boiling 20 g of green tea leaves with 1 L of water at 80°C for 1 h. Then, 50 mL of 0.1 M FeSO4 solution was quickly added to 150 mL of the tea extract at room temperature. The color of the reaction mixture turned from brown to dark blue and black precipitates appeared. Solid samples for further characteristics were obtained by centrifugal settling and dried in a desiccator.

Characterization of ZVI nanoparticles

ZVI nanoparticle characterization was performed according to similar reports on ZVI nanoparticles (Kumar *et al.*, 2013; Weng *et al.*, 2016). Phase structure of the materials was determined by X-ray diffraction (D8 ADVANCE

Figure 1. (a) The green tea extract turned to black when reacting with iron (II) solution; (b) ZVI nanoparticles

Table 1. Experimental conditions

Series	pH	Time (h)	Cr (VI) concentration (mg L^{-1})	ZVI mass (g)
Effect of pH	2.0 – 10.0	2	99.04	0.02
Effect of time	2.0	1 - 6	99.04	0.02
Effect of initial Cr(VI) concentration	2.0	6	~50 - ~300	0.02
Effect of ZVI mass	2.0	2	99.04	0.01 - 0.04

Bruker). Molecular structure of the materials was characterized by Fourier transform infrared spectroscopy (FTIR, SHIMADZU spectrophotometer) using KBr pellets in the wave number region of 400 - 4000 cm^{-1}. Size and shape of the particles were investigated by Field Emission Scanning Electron Microscopy (SEM) on a Hitachi S-4800 system. Size distribution was measured by the dynamic light scattering (DLS) method in a Nano Zetasizer, Malvern UK.

Determining the efficiency of Cr (VI) treatments

The effects of different factors on Cr(VI) treatment efficiency were investigated by applying a certain amounts of ZVI nanoparticles to 50 mL of different Cr (VI) solutions for a set period of time. The detailed conditions of the experiments are listed in Table 1.

The Cr(VI) concentration at equilibrium was analyzed by chemical titration with Mohr salt with 1,10 - phenanthroline. The experiments were conducted three times to determine the mean value.

The treatment efficiency was calculated using the formula:

Efficiency (%) = $(C_0 - C_e)/C_0 * 100\%$

in which C_0 is the initial Cr(VI) concentration,

and C_e is the Cr(VI) concentration at equilibrium or at the end of each experiment.

Data processing was completed using Microsoft Excel software (2010).

Results and Discussion

Characteristics of the obtained sample

Size and size distribution

The Fe-SEM images (Figure 2) show that the particles are flattened, smooth, and fairly uniform in size. The particle size ranges from 50 to 60 nm. At this size, they have the advantage of increased contact potential, so faster, easier, and more efficient surface processing is achieved. In solution, ZVI nanoparticles had an average size of 72 nm with a narrow size distribution (small polydispersity index of 0.1). The hydrodynamic particle size measured by the DLS method was larger than that in Fe-SEM images because the ZVI nanoparticles were bounded by hydrophilic polyphenol molecules that expand the particle size due to their interaction with an aqueous medium.

XRD analysis

In the X-ray diffraction diagram of the ZVI nanoparticle sample, it can be seen that the peaks

for Fe (0) typically occur with the greatest intensity at 44.8° (corresponding to the red line). In addition, the presence of additional peaks of Fe_3O_4 and Fe_2O_3 suggested that the Fe nanoparticles were partly oxidized at room temperature (t = 26°C). However, their appearance was negligible. This result is quite similar to that of Dung (2012). Thus, the "green" synthesis can produce ZVI nanoparticles with an equivalent crystalline structure compared to the $NaBH_4$ utility synthesis.

FTIR spectra

In the FTIR spectrum of the particles, the stretching vibrations of the O-H groups appear at 3437.50 cm^{-1} (Figure 5). Other peaks are also characteristic for bonds in organic compounds of green tea extract: 1634.2 cm^{-1} for the C=C, 1366.38 cm^{-1} and 1207.63 cm^{-1} for the CN and C-O-C bonds, respectively. The formation of

the Fe-O bond of ZVI with the polyphenols at the peak of 606.78 cm^{-1} showed that the Fe nanoparticles formed were bound by the polyphenols from the tea leaves, helping to increase the stablity of the particles.

Cr(VI) treatment of ZVI nanoparticles

It was reported by Fang *et al.* (2011) that nano Fe reacts with Cr(VI) in 3 steps:

Step 1: The Cr(VI) ion is exposed to the environment consisting of ZVI nanoparticles and reduction occurs at the solid-liquid surface. Cr(VI) was reduced to Cr(III) and Fe was oxidized to Fe^{2+}:

$$3Fe^0 + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Fe^{2+} + 2Cr^{3+} + 7H_2O$$
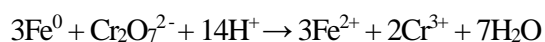
Step 2: Fe^0 reacted with H^+ ions in the solution to form Fe^{2+}, and then the Fe^{2+} ions transfered their electrons to Cr(VI) to form Cr^{3+} and Fe^{3+}:
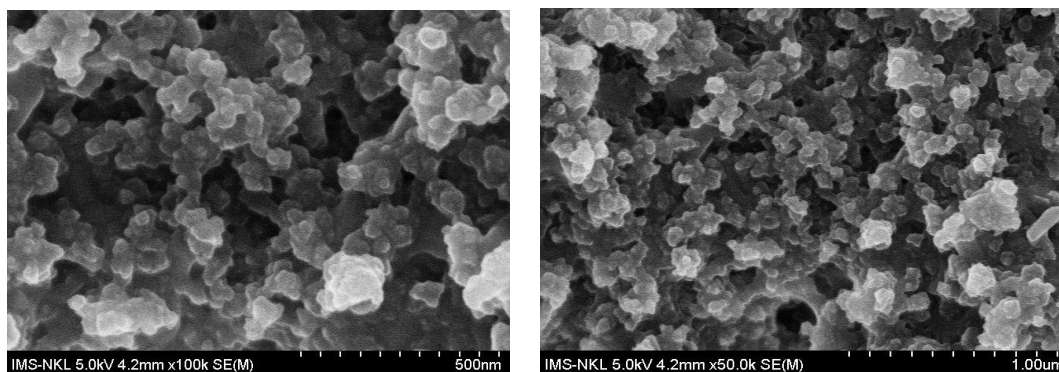

Figure 2. Fe-SEM images of ZVI nanoparticles obtained in the experiment
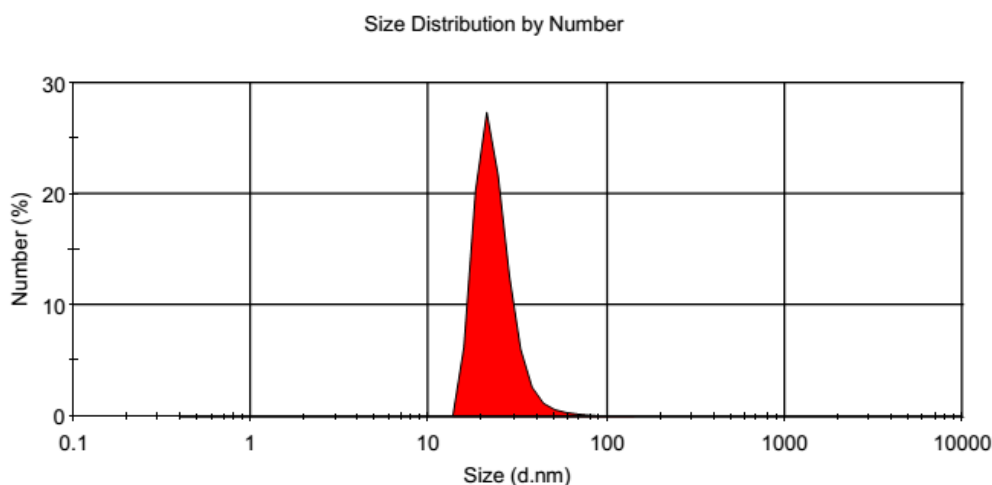

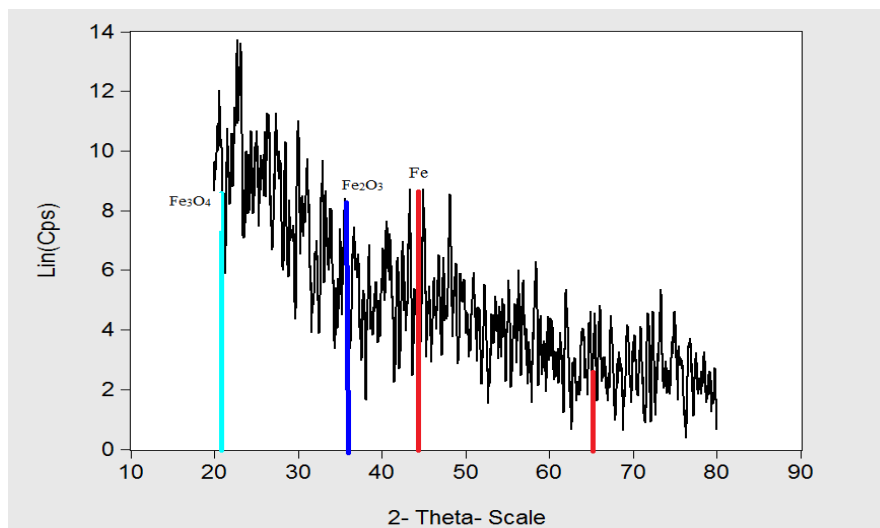**Figure 3.** Size distribution of ZVI nanoparticles obtained in the experiment
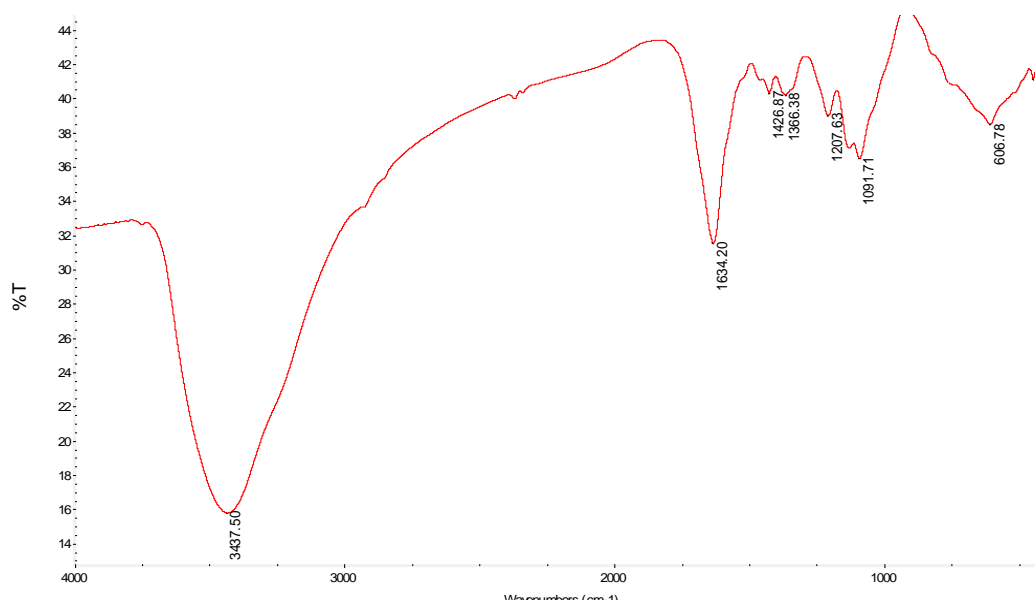
Figure 4. XRD diagram of the ZVI sample

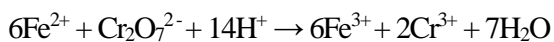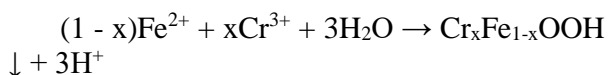**Figure 5.** FTIR spectrum of ZVI nanoparticles obtained in the experiment

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Step 3: Both Cr^{3+} and Fe^{3+} formed an (oxy) hydroxide of Cr or Fe in precipitation form and adhered to the surface of the particles:

$$(1 - x)Fe^{3+} + xCr^{3+} + 3H_2O \rightarrow (Cr_xFe_{1-x})(OH)_3 \downarrow + 3H^+$$

$$(1 - x)Fe^{2+} + xCr^{3+} + 3H_2O \rightarrow Cr_xFe_{1-x}OOH \downarrow + 3H^+$$
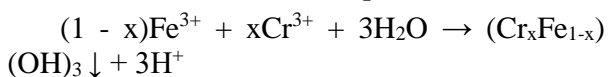
Another study also reported that the reduction of Cr(VI) by Fe depends on the pH of the solution, reaction time, Cr(VI) concentration, and the amount of ZVI nanoparticles (Kunwar *et al.*, 2011). In this study, the effects of similar factors on Cr(VI) removal via ZVI nanoparticles were examined and the results are described below.

pH solution

Figure 6 shows that at the pH level of 2.0, the Fe nanoparticles achieved the highest treatment efficiency of 63.95% and this rate gradually decreased to 14.94% at pH 10.0. The treatment efficiency increased as the pH decreased and vice versa. In an acidic environment the reaction mechanism by the ZVI nanoparticles is:
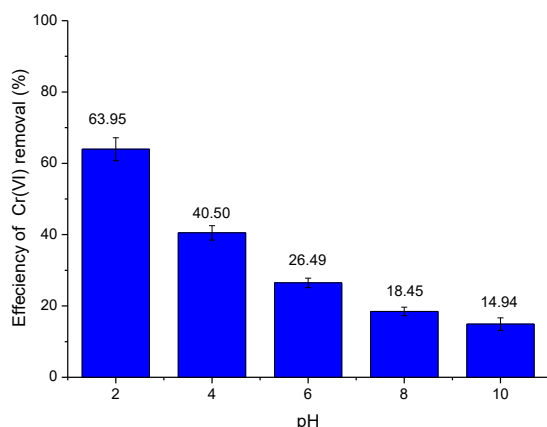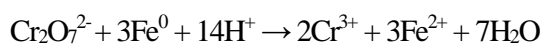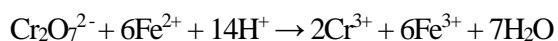
Figure 6. Efficiency of Cr(IV) removal dependence on pH

Figure 7. Efficiency of Cr(IV) removal dependence on reaction time

$$Cr_2O_7^{2-} + 3Fe^0 + 14H^+ \rightarrow 2Cr^{3+} + 3Fe^{2+} + 7H_2O$$

As more H^+ was added, the formed Fe^{2+} ions continued to react with Cr (VI) according to the reaction:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Therefore, when H^+ concentration increases, it facilitates the molecules to react continuously and rapidly, stimulating the surface activity of the ZVI particles by removing the oxy hydroxide surface (Rivero-Huguet and Marshall, 2009), and resulting in a higher Cr(VI) treatment efficiency. In an OH^- containing atmosphere, it is difficult for Cr(VI) to be reduced to Cr(III) because of the formation of $Fe(OH)_3$ precipitate which reduces the treatment efficiency. A similar trend was observed by Liu *et al.* (2005).

Reaction time

To determine the affect of reaction time, the experiment was run for 1 h to 6 h at pH 2.0 and 0.02 g ZVI nanoparticles (Figure 7). The results revealed that under the same conditions of material weight, pH of the solution, and concentration, the reaction time affected the efficiency of Cr (VI) treatment. The treatment efficiency increased as the reaction time increased. For the reaction time of 6 h, the efficiency reached nearly 100% (94.04%), so it is not essential to prolong the time reaction beyond 6 h.
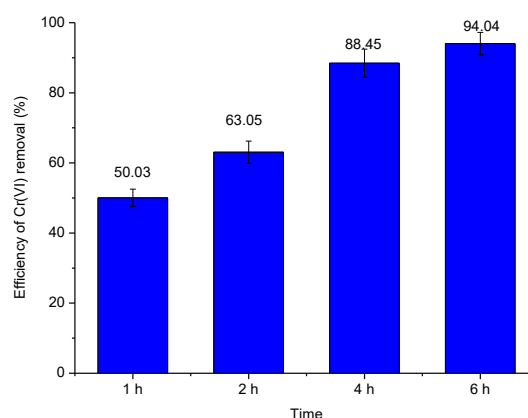
Initial Cr(VI) concentration

The effects of initial Cr(VI) concentration on the treatment efficiency are shown in Figure 8. The results showed that the lower the Cr(VI) concentration was, the higher the efficiency was. At concentrations lower than 50 mg L^{-1}, approximately 100% of the Cr(VI) was removed. When the concentration was doubled to 99.04 mg L^{-1}, the efficiency decreased to 94.04%. At the concentrations of 155.64 mg L^{-1} and 300.68 mg L^{-1}, the efficiency significantly decreased. It is possible to explain this phenomenon by the fact that the Fe^0 content is only able to remove Cr(VI) within a certain range. If the concentration of Cr(VI) is higher, complete removal requires a higher Fe^0 content. Other authors also reported that the removal efficiency of Cr(VI) and the initial pollutant concentration were inversely proportional. According to Liu *et al.* (2005), the removal efficiency of Cr(VI) in nano Fe^0 fluid was negatively correlated with the initial Cr(VI) concentration. At the initial concentration of 25 mg L^{-1}, the researchers found that removal efficiency was 42% and reached 100% when the initial concentration was decreased to 10 mg L^{-1}. Thus, our results and those of others suggest that the concentration of pollutants treated by Fe^0 nanoparticles should be tested before treatment. Moreover, our green synthesized ZVI nanoparticles were more effective within a larger range of pollutant concentrations.
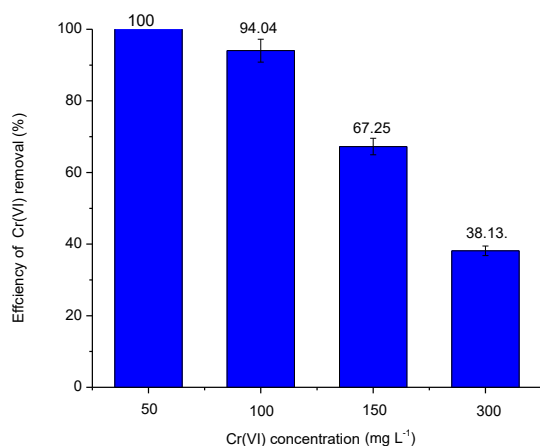
Figure 8. Efficiency of Cr (IV) removal dependence on initial Cr(VI) concentration
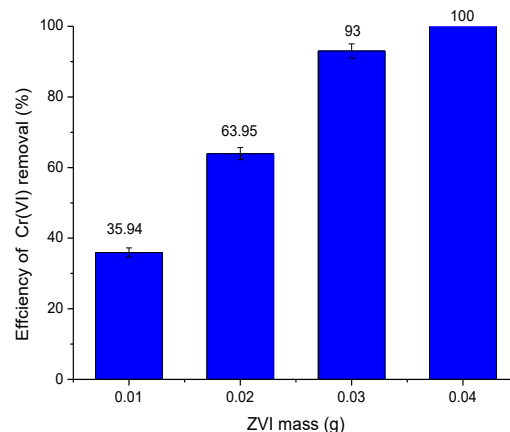

Figure 9. Efficiency of Cr (IV) removal dependence on ZVI mass

The amount of ZVI nanoparticles

The amount of ZVI nanoparticles was adjusted from 0.01 g to 0.04 g to examine how this rate impacted Cr(VI) removal. As aforementioned, if the reaction time was 6 h and Cr(VI) concentration was 49.53 mg L^{-1} or lower, the predicted efficiency would be approximately 100% at the Fe^0 content of 0.02 g. Therefore, the reaction time was set to be 2 h and the Cr(VI) concentration was set to be 99.04 mg L^{-1} to be able to more clearly see the effect of Fe^0 content on the efficiency of the treatment. The results showed that an increase in Fe^0 content resulted in a higher processing efficiency of Cr(VI) removal (Figure 9). The amount of 0.04 g ZVI nanoparticles completely eliminated Cr(VI) in 50 mL of 99.04 mg L^{-1} solution in 2 h. The effectiveness of ZVI nanoparticles in treating Cr(VI) is confirmed.

Conclusions

In conclusion, ZVI nanoparticles were successfully synthesized by using polyphenols in an extract from green tea leaves with a simple procedure. Analyses showed that the synthesized ZVI particles were about 50 - 60 nm in size, had a lattice structure of iron, and were bounded by the polyphenols which helped prevent oxidation. The results revealed that within the range of our experimental variables, the Cr(VI) treatment was most favorable at the conditions of pH 2.0, reaction time 6 h, Cr(VI)

concentration of 49.52 mg L^{-1}, and Fe^0 content of 0.04 g. Under certain conditions, the efficiency of Cr(VI) treatment by ZVI nanoparticles can reach 100%. The results demonstrate that ZVI nanoparticles can serve as a suitable material in the field of environmental treatment.

Acknowledgements

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