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Green Synthesis of Zero Valent Iron (ZVI) using Tea Leaves Extract and its Application as Fenton like Catalyst for Textile Dyes Removal

Dian Nursyamsiah, Solihudin and Diana Rakhmawaty Eddy*

Department of Chemistry, Universitas Padjadjaran, 45363 Sumedang, Indonesia

*Corresponding author: E-mail: diana.rahmawati@unpad.ac.id

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This study aims to develop an alternative method in the green synthesis of zero valent iron (ZVI) from tea leaves extract and its application as a Fenton catalyst for textile dyes removal. Tea leaves extract having high polyphenolic contents were used as reducing agents in this study and the ZVI obtained from them was characterized by UV-VIS, SEM-EDS, FTIR, PSA and XRD techniques. The synthesized zero valent iron (ZVI) was utilized as a Fenton like catalyst for textile dyes removal. The results showed that this system was highly efficient regarding the dyes removal of about 95.96% using 80 mg/L ZVI. Moreover, using 100 mg/L ZVI, the COD number reduced to 94.68%.

Keywords: Dyes removal, Fenton, Tea leaves, Zero valent iron.

INTRODUCTION

Water is one of the most essential components in humans and its availability is vital in every aspect of life. According to the World Health Organization (WHO), human needs about 15-20 L of water per day, which includes 2.5-3.0 L for consumption and the remaining is for daily needs. However, the high industrial activities increase water pollution at an alarming rate. Dyes in wastewater from textile industry activities are one of these harmful pollutants and need to be treated properly. Several methods such as adsorption [1,2], coagulation and flocculation [3,4], electrocatalytic [5], filtration [6,7], distillation [8], photocatalyst [9] and biological treatment (aeration) [10,11] are generally applied for the wastewaters treatment. However, these methods are less effective in reducing organic and inorganic compounds with the addition of much coagulant, since a huge amount of sludge is produced which is almost difficult to be regenerated and also its low biodegradability [12-14].

Zero valent iron (ZVI) is a potential catalyst in water treatment and was initially applied as groundwater remediation [15,16]. However, the decreasing surface water quality caused due to water pollution leads to more efforts to apply this treatment method [16-19]. ZVI is defined as iron with zero valence (Fe^0), produced from the reduction of Fe(II) or (III) with sodium borohydride [20-22]. The nature of iron which is easily oxidized into Fe_3O_4 (magnetite) makes ZVI not stand alone, followed by Fe_2O_3 (hematite) and FeOOH. Moreover, it has a core-shell structure, which consists of iron with zero valence, while the shell contains iron oxide compound with < 3 nm thickness [20,23].

Another popular method for the treatment of wastewater, advanced oxidation processes (AOPs), which utilizes hydroxyl radical ($OH^•$) for degrading the highly toxic pollutants to the less toxic pollutants [12,14,24-26]. Ozonation, combination of catalyst, ozone and hydrogen peroxide based on photocatalytic system ($TiO_2/UV/O_3/H_2O_2$) and Fenton process are parts of AOPs system applied in the water remediations [16,27-29]. Subsequently, more studies emerged with averment that this method is effective in the oxidation of some organic compounds during the treatment of wastewater, marked by decreasing value of chemical oxygen demand (COD) and total organic carbon (TOC) [16,27,30]. Compared to the former method used in Fenton process, the application of zero valent iron provides more promising result in water remediation [16,27,31].

Presently, to avoid accumulating more pollutants, ZVI is made by green route using tea leaves extract having high polyphenolic contents as reducing agents [31-33]. The high polyphenol levels in leaves extract make the reduction of Fe(II) or Fe(III) to be easier [32]. Some tree leaves with high antioxidant capacity, such as strawberry, raspberry, eucalyptus, tea, pomegranate, mango peel and oak leaf have the potential reducing agents in the green synthesis of ZVI [31-34]. Furthermore, several investigations have proved the synthesis capability of ZVI from green route and $NaBH_4$. The zero valance iron obtained from green tea and eucalyptus exhibited a great potential in the removal of nitrates, degradation of bromothymol blue, cationic and anionic dyes [27,31,34,35]. Generally, Indonesia is the second largest producer and the third biggest tea exporter in Asia [36]. With this commodity abundance and its high flavonoids and polyphenols content, tea leaves have potential to be explored as reducing agent in the zero valent iron (ZVI) synthesis.

EXPERIMENTAL

The chemicals used in this study were sodium hydroxide, sulfuric acid, hydrogen peroxide, iron sulfate hexahydrate, potassium dichromate, mercury sulfate, potassium hydrogen phthalate and procured from high-grade commercial sources. Tea leaves were collected from local farm in Sumedang city, Indonesia while the wastewater sample was collected from the local textile dyes industry in Bekasi, Indonesia.

Synthesis of zero valent iron (ZVI): The tea leaves were dried at 50 ºC for 72 h, ground using chopper and sieved until < 10 mesh. Then, 37 g of dried tea leaves were mixed in 1000 mL deionized water for 80 min at 90 ºC and the mixture was filtered to obtain the leaves extracts. Zero valent iron (ZVI) was synthesized by mixing leaf extracts to 0.1 M $FeSO_4$ in a ratio of 1:1 at room temperature. The formation of black precipitate indicated that ZVI was formed and dried by evaporating the water using hot plate.

Characterization: Zero valent iron (ZVI) was characterized using UV-VIS (Genesys 10S), the particle size distribution was analyzed using HORIBA SZ-100. Then, scanning electron microscopy was used with energy-dispersive X-ray spectroscopy (SEM-EDS Hitachi SU3500) to investigate the metal percentage in particle surface. In addition, FTIR spectra of ZVI and tea leaves extract were determined by Fourier transform infrared spectroscopy Shimadzu IRPRESTIGE-21. The X-ray diffraction was analyzed by D8 Bruker Advance and Visible spectrophotometer HACH DR 3900.

Dyes degradation procedure: Before the textile dyes treatment with Fenton process, pH of the wastewater sample was adjusted by 0.1 N H_2SO_4 and 0.1 N NaOH until the solution pH reached 3. Then, 2.5 mL of 12% H_2O_2 and various doses of ZVI (20, 40, 60, 80, 100, 120 mg/L) were added into 25 mL of wastewater samples. The solution was diluted ten times, stirred for 20 min at room temperature and filtered. The filtrate absorbance was determined using visible spectrophotometer HACH DR 3900 at 536 nm. The dyes removal efficiency was calculated by the following equation [27]:

$$E\ (\%) = \frac{A_o - A}{A_o} \times 100$$

Finally, the COD was determined in the sample before and after treatment to find out the effect of the Fenton process in water remediation.

RESULTS AND DISCUSSION

UV-VIS spectra: The formation of zero valent iron (ZVI) was analyzed by UV-VIS spectrophotometer in the range of 200-600 nm. The UV-Vis spectra (Fig. 1) showed that a shift in a wavelength occurred at ZVI, which differentiated from the tea leaves extract and 0.1 M $FeSO_4$ solution.

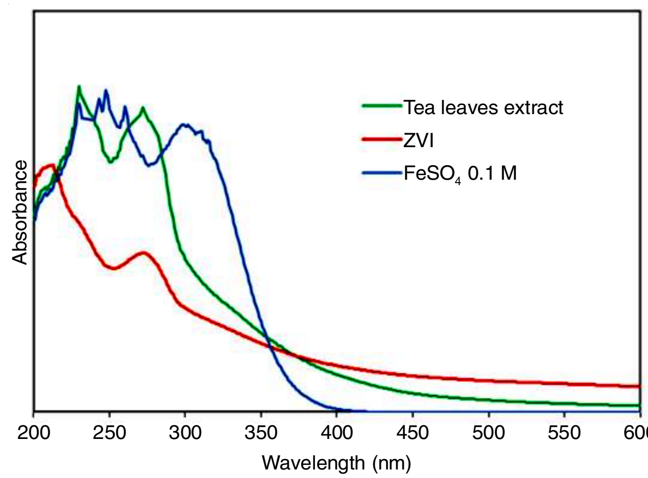

Fig. 1. UV-vis spectra of tea leaves extract and ZVI

XRD studies: The ZVI was characterized by XRD technique and the pattern is shown in Fig. 2. A weak signal in the spectrum confirmed that ZVI is amorphous in nature [27,34,35]. Corresponding to JCPDS file No. 00-006-0696, ZVI peak appeared at 2θ = ~ 44.8º, in this study, the ZVI was observed at 43.3º. In addition, FeOOH, Fe_3O_4 and SO_2 were also reflected in the spectrum. Moreover, the appearance of FeOOH, Fe_3O_4 and SO_2 originated from sulfuric acid and iron sulfate used in this research.

Morphology: The SEM was carried out to determine the morphology and physical appearance of ZVI, additionally,

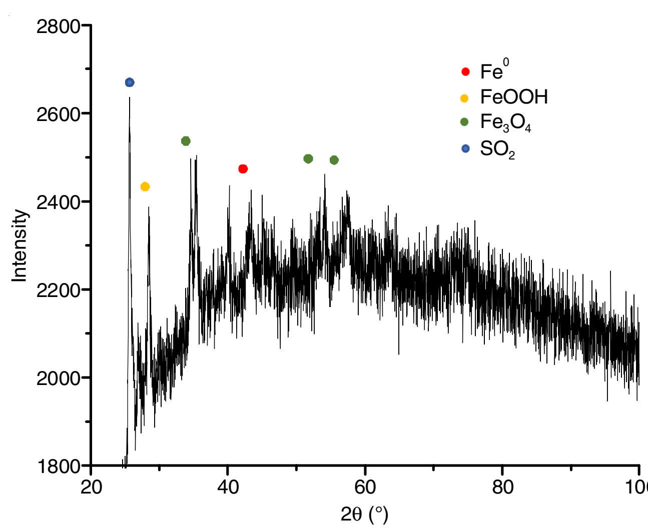

Fig. 2. XRD spectrum of zero valent iron (ZVI)

EDS confirmed the presence of some elements in the particles. The diversity of size and shape indicated the presence of agglomeration (Fig. 3) [27,34,37]. This occurred because of the formation of organic layer from tea leaves extract and iron oxide on ZVI surface [34,38,39]. In addition, the EDS spectrum (Fig. 4) showed oxygen and carbon as the dominant elements on ZVI surface with values of 36.97% and 19.97% (Table-1). Moreover boron, nitrogen and potassium were also attributed to tea leaves extract [27,37]. While sodium and sulfur were obtained from NaOH and H_2SO_4 used when adjusting the pH and originated from $FeSO_4$ as a precursor.

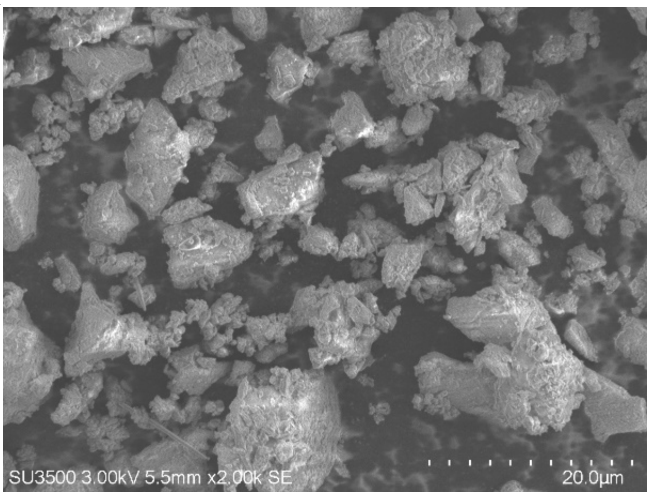

Fig. 3. SEM image of zero valent iron (ZVI)

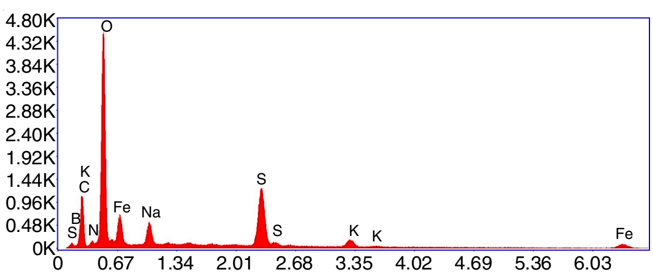

Fig. 4. EDS spectrum of zero valent iron (ZVI)

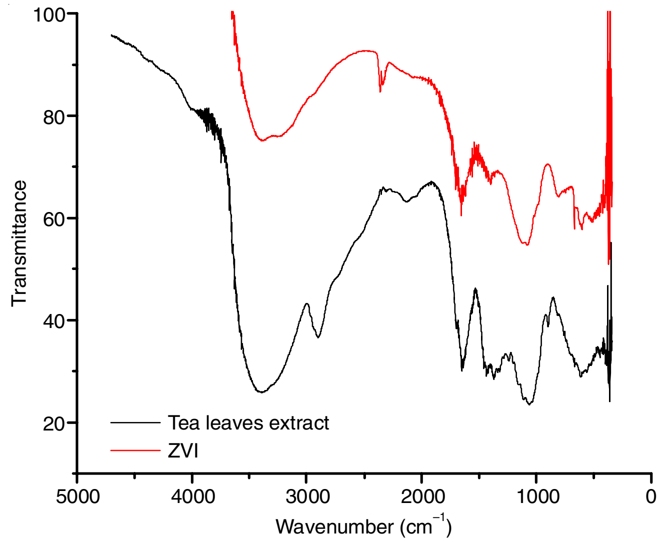

Fig. 5. FTIR spectrum of tea leaves extract and zero valent iron (ZVI)

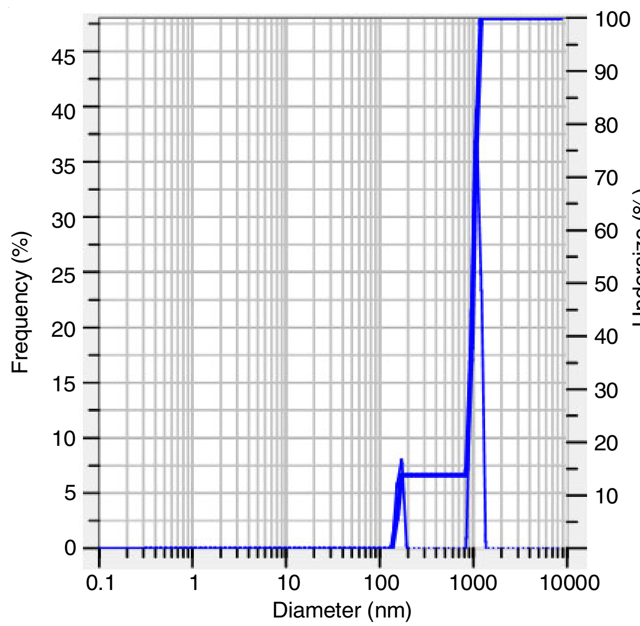

Fig. 6. Distribution size of zero valent iron (ZVI) particle

FTIR studies: FTIR was employed in ensuring the capping on the ZVI surface area. The tea leaves extract and ZVI showed broad and strong bands at 3384 and 3376 cm^{-1} and assigned O–H stretching vibrations from phenol (Fig. 5) [34,38,39]. The peaks observed at 1634 and 1648 cm^{-1} indicated the presence of C=C aromatic rings from polyphenol functional group or C=O ketone [25,33,40]. In addition, 1062 and 1079 cm^{-1} showed the appearance of C–O–C and O–H bands [39]. Some other appeared functional groups helped to sustain the stability and reactivity of ZVI [38-40].

Distribution size: The distribution of ZVI was determined by particle size analyzer. Two peaks appeared in the spectrum, which indicated that ZVI has two different sizes (Fig. 6). The average value of the first peak was observed at 1012.7 nm, while the second peak was observed at 153.4 nm. Based on SEM results, it occurred probably due to the aggregations among the particles. Even though this material was uncategorized and has potentials to be nano by more optimization. Several investigations have been verified that green synthesis of ZVI from leaves extract produced nanosize [31,34,37,41,42].

Applications: Fig. 7 shows the maximum wavelength of the wastewater sample at 536 nm. Fenton process was applied at 20 min using several different doses of ZVI. A change in the colour of dyes sample after the Fenton process reaction in Fig. 8 indicated that a higher amount of ZVI degrades more dyes

TABLE-1
THE ELEMENTAL PERCENTAGE DATA OF ZERO VALENT IRON (ZVI) ANALYZED BY EDS

Element	O	C	S	Fe	B	Na	K	N
Weight (%)	36.97	19.97	13.39	10.12	9.86	3.42	3.32	2.97

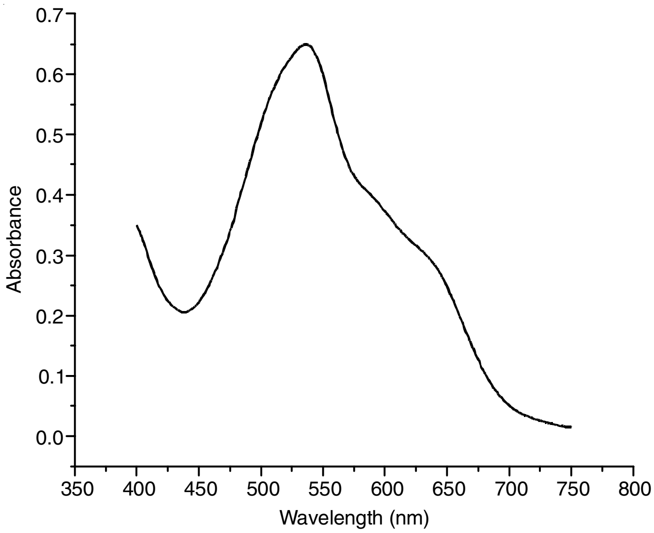

Fig. 7. Absorbance of textile dye wastewater sample

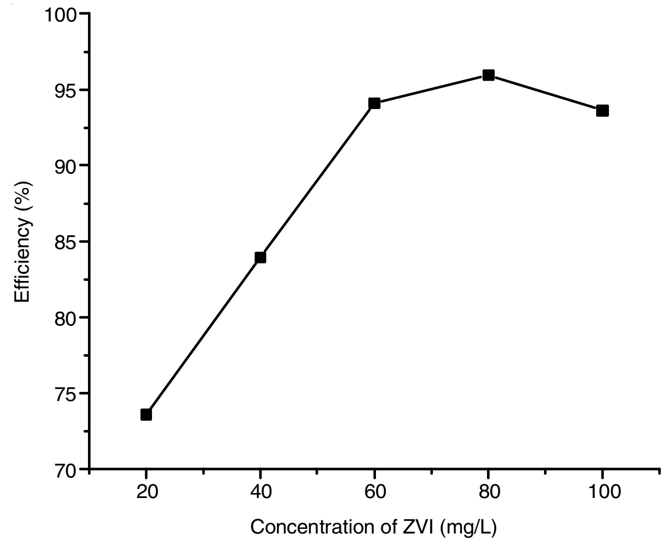

Fig. 9. Removal efficiency (%) of textile dye after 20 min reaction

in wastewater samples. Fig. 9 shows that 80 mg/L of ZVI provided the most efficient concentration in degrading dyes in the wastewater samples with efficiency up to 95.96% (Table-2). In wastewater treatment, it is important to determine the number of chemical oxygen demand (COD) before and after treatment. In this study, COD in the sample decreased after the Fenton process (Fig. 10), while the largest degradation was achieved by the addition of 100 mg/L ZVI with the percent removal of about 94.68% (Fig. 11).

TABLE-2
EFFICIENCY OF DYE REMOVAL
BEFORE AND AFTER TREATMENT

Cons ZVI (mg/L)	Absorbance	Efficiency (%)
Sample before treatment	3.121	–
20	0.825	73.57
40	0.501	83.95
60	0.184	94.10
80	0.126	95.96
100	0.199	93.62

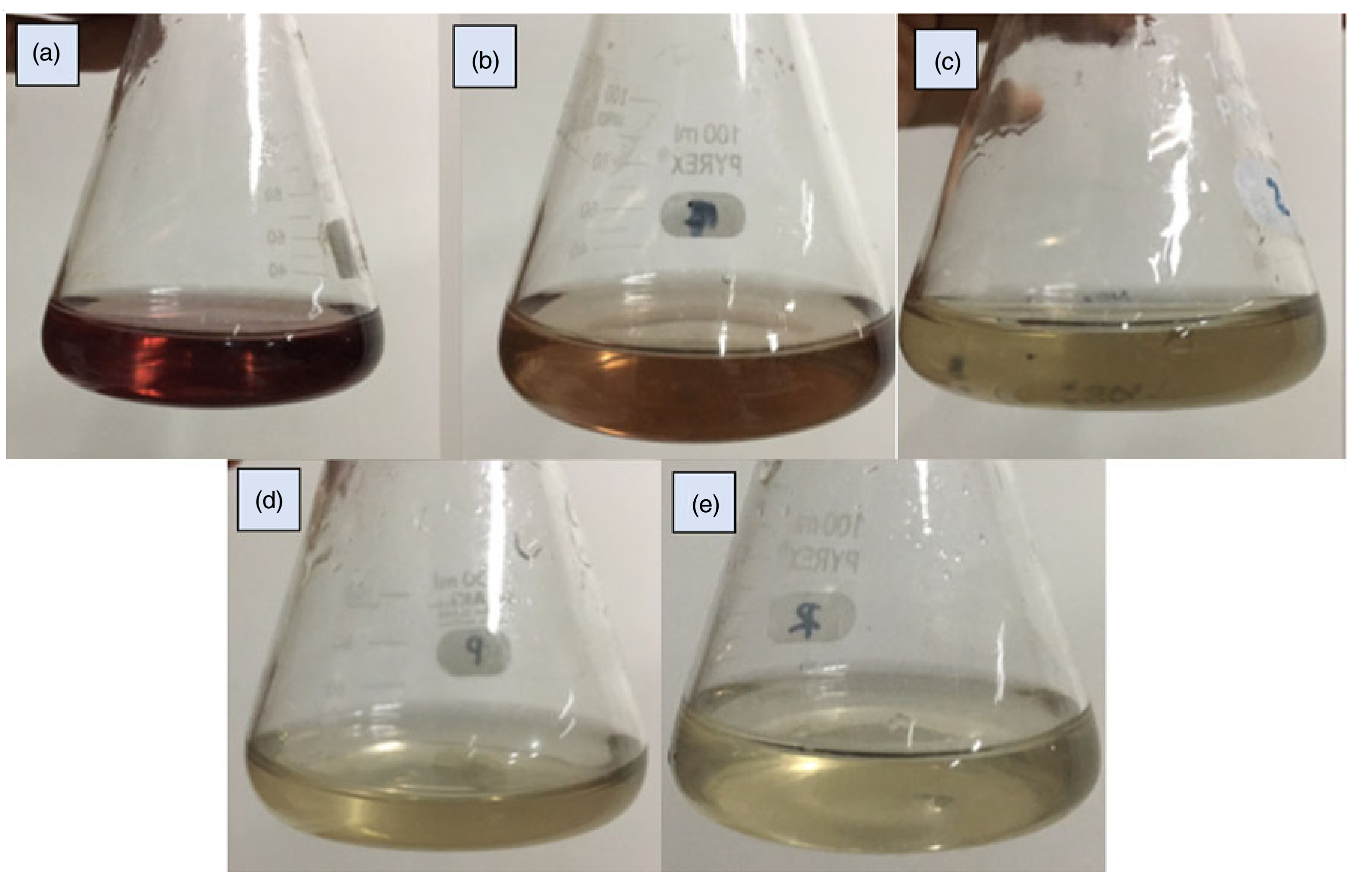

Fig. 8. Dye wastewater sample after Fenton process reaction with zero valent iron (ZVI) 20 (a); 40 (b); 60 (c); 80 (d); and 100 mg/L (e)

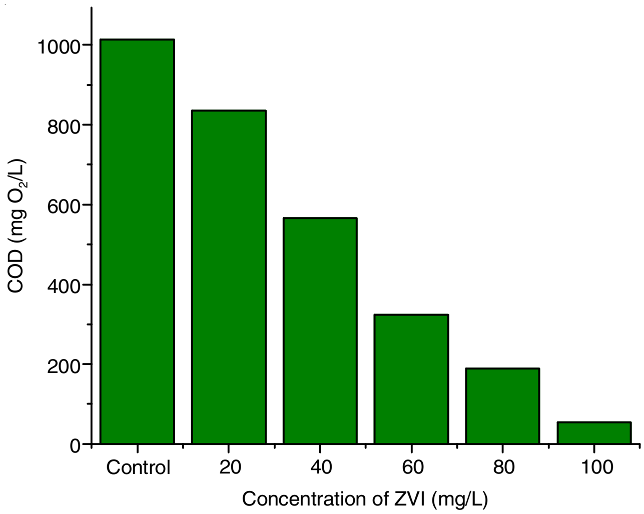

Fig. 10. COD number of samples before and after treatment

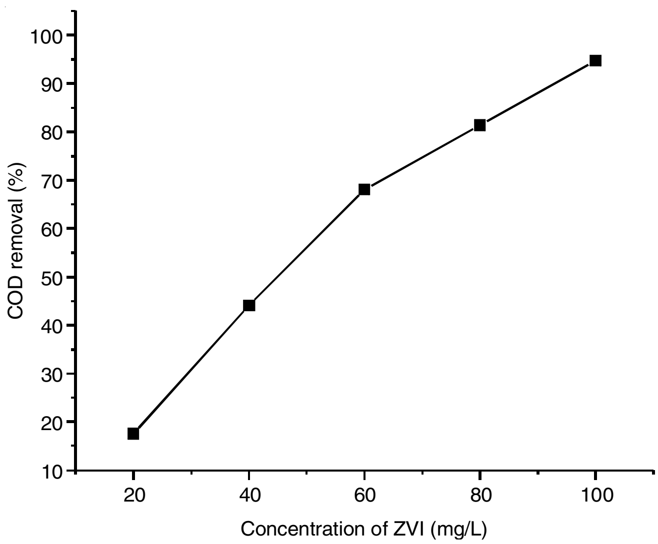

Fig. 11. COD removal percentage of dye sample after Fenton reaction

Conclusion

The green synthesis of zero valent iron (ZVI) from tea leaves extract has been successfully conducted. The removal efficiency of the dye from the textile wastewater gave a satisfying result. The efficiency of Fenton reaction increased with increasing ZVI in the system. In optimized conditions with 80 mg/L ZVI, the maximum value of dye removal was achieved to 95.96%. Moreover, the COD number after the treatment sample reduced to 94.68% using 100 mg/L ZVI.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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