

Rapid decolorization of textile wastewater by green synthesized iron nanoparticles

Z. Y. Ozkan, M. Cakirgoz, E. S. Kaymak and E. Erdim

ABSTRACT

The effectiveness of green tea (*Camellia sinensis*) and pomegranate (*Punica granatum*) extracts for the production of iron nanoparticles and their application for color removal from a textile industry wastewater was investigated. Polyphenols in extracts act as reducing agents for iron ions in aqueous solutions, forming iron nanoparticles. Pomegranate extract was found to have almost a 10-fold higher polyphenolic content than the same amount of green tea extract on a mass basis. However, the size of the synthesized nanoparticles did not show a correlation with the polyphenolic content. 100 ppm and 300 ppm of iron nanoparticles were evaluated in terms of color removal efficiency from a real textile wastewater sample. 300 ppm of pomegranate nanoscale zero-valent iron particles showed more than 95% color removal and almost 80% dissolved organic carbon removal. The degradation mechanisms are considered to be adsorption and precipitation to a major extent, and mineralization to a minor extent.

Key words | green synthesis, green tea (*Camellia sinensis*), iron nanoparticle, pomegranate (*Punica granatum*), textile wastewater

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INTRODUCTION

The textile industry is one of the numerous industries that produce colored wastewater, and discharge of the colored effluent without adequate treatment might pose a threat to the ecosystem in the receiving waterbodies. However, due to complex structures and synthetic origin of dyes, it is a difficult task to remove color, and conventional treatment schemes are considered to be inefficient in complying with the discharge limits. Nanotechnology refers to the nanoscale materials that exhibit superior properties, and it has been proposed that it will play an important role in solving the problems related to water and wastewater treatment. It seems possible to establish innovative treatment alternatives or enhance the efficiency/economy of existing plants using this technology. Among many engineered nanomaterials used for the treatment of polluted streams, nanoscale zero-valent iron particles (nZVI) are the most widely studied and most promising reactants because of their cost-effective, environmentally compatible and highly reactive nature (Noubactep 2008; Crane & Scott 2012; Mystrioti *et al.* 2014; Markova *et al.* 2015). Due to the smaller particle size, larger surface area and higher surface reactivity of nZVI, the removal of pollutants occurs at a rate several orders of magnitude higher than the rates observed with granular

ZVI particles (Crane & Scott 2012). nZVI can be synthesized by top-down or bottom-up approaches. The method presented in this work is a bottom-up method and is based on the growth of nanostructures by means of a chemical reaction between an iron precursor and a reducing agent. Commonly, a powerful compound (NaBH_4) has been used as the reducing agent; however, considering its toxicity and the safety issues associated with the production of hydrogen gas during the process, there is a great need for an alternative, preferably green, reducing agent. Therefore, a green synthesis method using water as the solvent and plant extracts that contain antioxidants based on polyphenols has been of great interest for generating iron nanoparticles. Plant polyphenols are known to be strong reducers and effective metal chelators, forming stable complexes with iron (Perron & Brumaghim 2009). The use of 26 different leaf extracts to produce nZVI was investigated and the resulting nZVI were found to be different in size, shape, agglomeration potential and reactivity (Machado *et al.* 2015). The use of polyphenols provides mutual benefits, both as reducing agent and capping agent for the nanoparticles (Njagi *et al.* 2010). However, each leaf extract might result in nanoparticles with different characteristics, so it

is suggested that the reactivity is case specific. The objective of this study is to compare the reactivity of nZVI synthesized with green tea leaves and pomegranate extract for the decolorization of a real textile wastewater sample. Green tea was selected as a reference material due to the considerable amount of published information on its effectiveness for nZVI production. Pomegranate is gaining great interest at the international level as fresh fruit and by the pharmaceutical and cosmetic industries (Seeram *et al.* 2005; Diamanti *et al.* 2017). The total pomegranate production in the world is about 2.5 million tonnes (Kahramanoglu & Usanmaz 2016). The use of pomegranate has been suggested for the synthesis of iron nanoparticles due to its high antioxidant potential, but iron nanoparticles synthesized with pomegranate extract have not been evaluated for color removal from aqueous solutions up to now.

MATERIALS AND METHODS

Materials

Dry leaves of green tea and pomegranate flowers were used as the source of polyphenols and supplied from a local market. Analytical reagent grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (>99.0% Merck, Germany) was used as the iron precursor and was used directly without further purification. Folin–Ciocalteu's phenol reagent (Sigma Aldrich, Switzerland), anhydrous sodium carbonate (Sigma Aldrich, Switzerland) and gallic acid (Sigma Aldrich, Switzerland) were used for the determination of total polyphenol content (TPC) in solution. Textile wastewater was supplied from a local factory in Turkey.

Preparation of extracts

Green tea leaves and pomegranate leaves were washed thoroughly with deionized (DI) water and oven-dried at 103 °C overnight prior to use. The plant extract (GT- or PG-) was prepared by brewing 20 g/L of the dry leaves at 80 °C for 20 min. DI water, an environmentally friendly solvent, was used as the extraction solvent. The 'cold brew' procedure was adopted for the extraction process. Briefly, dry leaves were kept in contact with the solvent at room temperature for 15 minutes and then the temperature was increased to 80 °C. Therefore, an additional contact time between the leaves and the solvent was provided to increase the extraction yield of polyphenols. The extract was vacuum filtered by a Whatman GF7 filter paper (0.7 µm).

Analysis of extracts

The TPC was determined as gallic acid equivalents (GAE) following the Folin–Ciocalteu method (ISO 14502–1). A UV/Vis spectrophotometer (Shimadzu 2450, Japan) was used to measure the absorbance of the standards/samples at wavelength (λ) equal to 765 nm. A calibration curve was constructed with five gallic acid standards (10 to 50 µg/mL; $R^2 = 0.9968$). pH and oxidation-reduction potential (ORP) were monitored with an online monitoring system (Tethys, France). The ORP was measured with a Ag/AgCl (3 M KCl) reference electrode.

Synthesis of iron nanoparticles

0.1 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution was prepared by dissolving the required amount in N_2 -purged DI water to avoid rapid oxidation. The extract and the iron precursor solution was mixed with a mechanical mixer at a 1/1 volumetric ratio at room temperature. The immediate appearance of black color indicated the formation of iron nanoparticles. Size and size distribution of the nanoparticles were determined with a Malvern ZS90 instrument.

Decolorization experiments

Batch experiments for color removal were conducted in duplicate in 500 mL flasks. nZVI prepared with green tea extract (GT-ZVI nanoparticles) and pomegranate extract (PG-ZVI nanoparticles) were applied in two different concentrations, 100 ppm and 300 ppm, in decolorization experiments. Briefly, a predetermined volume of nZVI from a stock solution (0.05 M) was introduced into 300 mL of textile wastewater and mixed at 150 rpm at room temperature without any pH adjustment. A UV/Vis spectrophotometer was used for obtaining the full spectrum of the samples. Dissolved organic carbon (DOC) of the samples was determined with a total organic carbon (TOC) analyzer (M5310, GE Sievers, USA) after filtering the samples through 0.45 µm pore size filter. True color was determined with a Hach-Lange spectrophotometer (DR 2800, Hach-Lange, Germany) as Pt-Co after filtering the samples through 0.45 µm cellulose membrane filter.

RESULTS AND DISCUSSION

Formation of nanoparticles was first assessed in terms of the total polyphenolic content of the plant extracts. TPC and absorption maxima of the GT- and PG- extracts are shown

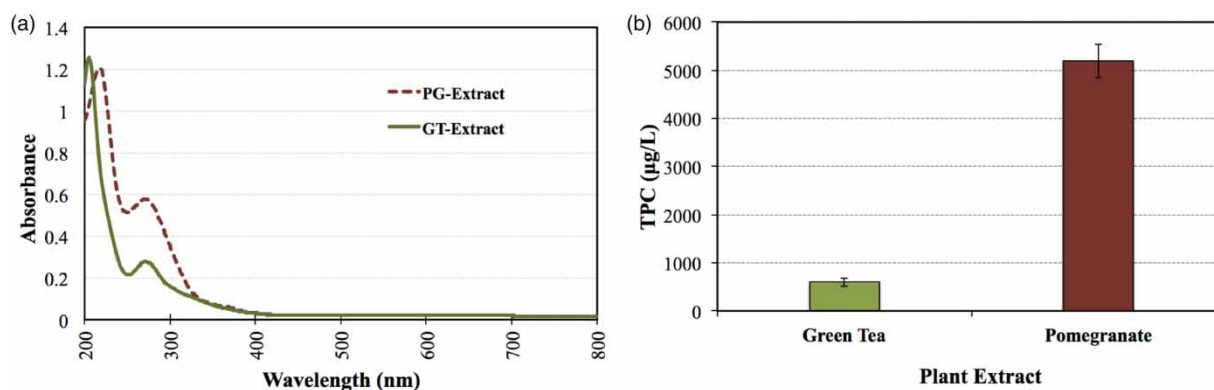
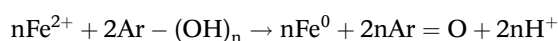


Figure 1 | (a) Total phenolic content and (b) UV/Vis spectra of GT- and PG- extracts.

in Figure 1(a) and 1(b), respectively. Pomegranate extract has a TPC value of nearly 5,000 µg/L, which is almost 10-fold higher than the phenolic content of the green tea leaves. Flavonoids, hydrolysable tannins, and condensed tannins are accepted as the major pomegranate polyphenols and Gill *et al.* (2000) suggested that the first two mainly extract into pomegranate juice (PJ) from whole fruits. The 200–400 nm bands, characteristic of flavonoid-type structures can be attributed as follows: 200 nm–250 nm for unsaturated (linear or cyclic) structures; 250 nm–295 nm for unsaturated aromatic structures; 300 nm–400 nm for chromophores bound to structures with extended conjugation (Spiridion *et al.* 2011). Thus, the presence of flavonoids in the extracts might explain their antioxidant properties along with their role as a reducing agent for the iron precursors.

Peaks at 205 nm and 275 nm in GT-extract correspond to tea polyphenols and caffeine, and the intensity of the peaks decreased after reacting with Fe²⁺ (data not shown). Similarly, PG-extract showed peaks at 275 nm and 208 nm, which showed a similar structure with the GT-extract, but at a lower intensity.

The synthesis of iron nanoparticles may be explained by the polyphenol content of the extracts, the major ones being flavonoids, hydrolysable tannins and condensed tannins for pomegranate, and tea polyphenols and caffeine for green tea. These structures play a key role in the synthesis process and can directly reduce iron ions to zero valent iron nanoparticles as shown below, where Ar stands for phenyl group (Smuleac *et al.* 2011).



Alternatively, they may undergo hydrolysis to produce different organic acids such as tannins, gallic acid and

catechin (Santos *et al.* 2012). During this process, the released electrons enable the reduction of iron salts to iron nanoparticles. Meanwhile, the oxidized polyphenols can act as capping/stabilizing agents for the dispersion of the nanoparticles. Size distribution of the green tea and pomegranate extract synthesized iron nanoparticles are shown in Figure 2. Although there is a significant difference between the polyphenol content of the extracts, a similar trend was not observed in the size of the synthesized nanoparticles. We could infer that the phenolic content is not the sole factor influencing the reduction ability of the metal precursor. Phenolic content might be affected by other bioactive compounds such as minerals and vitamins (Spiridion *et al.* 2011) that could hinder the effectiveness of reduction process.

PG-extract led to smaller-sized nanoparticles (10.1 nm) when compared to GT-ZVI nanoparticles (43.8 nm). Nanoparticles are routinely defined as particles with sizes between about 1 and 100 nm that show properties that are not found in bulk samples of the same material. Both of the nanoparticles fit the definition, but it is evident that as

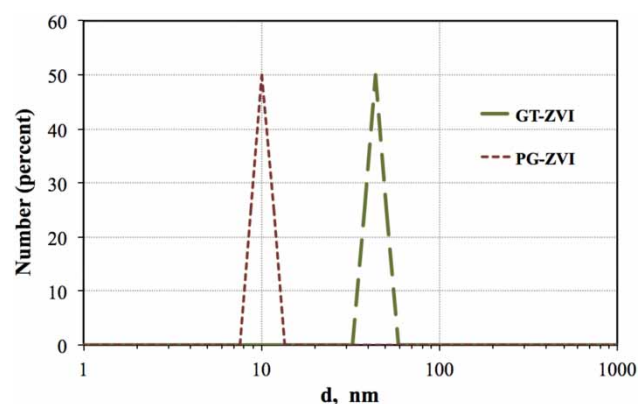


Figure 2 | Size distribution of GT-ZVI and PG-ZVI nanoparticles.

Table 1 | Characterization of the textile factory wastewater

Parameter	Raw wastewater
pH	7.27
TSS (mg/L)	98
Conductivity ($\mu\text{S}/\text{cm}$)	3,310
TOC (mg/L)	422
COD (mg/L)	1,210
Color (Pt-Co)	2,330

the nanoparticle size decreases the surface area increases thus leading to enhanced reactivity.

Decolorization with GT-ZVI and PG-ZVI nanoparticles

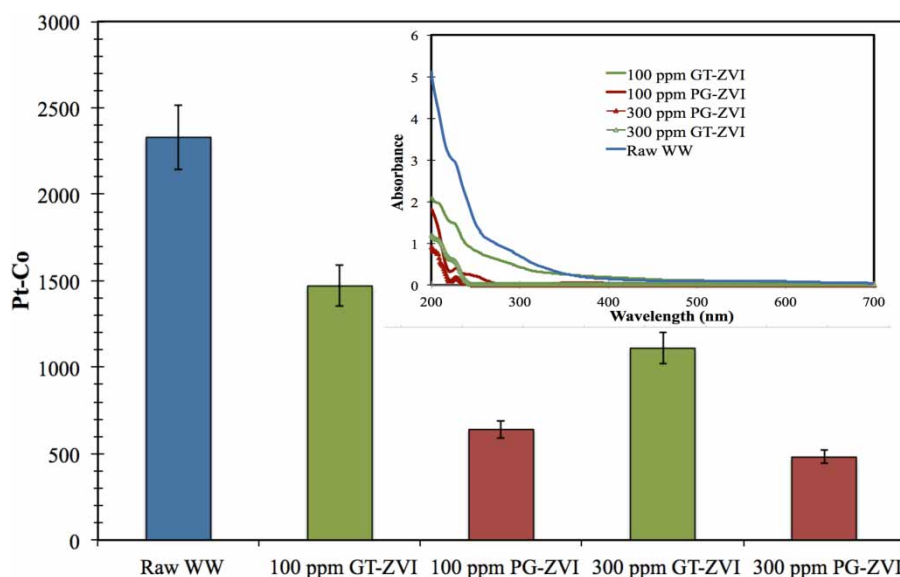
To compare the reactivity of the as-synthesized GT-ZVI and PG-ZVI nanoparticles, batch decolorization experiments were conducted with a real wastewater sample. Characterization of the textile industry wastewater is shown in Table 1. Total suspended solids (TSS), total organic carbon (TOC), chemical oxygen demand (COD), and color of the raw wastewater were determined following *Standard Methods* (APHA, AWWA & WEF 1998).

Two different nZVI concentrations, namely 100 ppm and 300 ppm were compared to assess the effect of concentration on color removal efficiency. Figure 3 shows the reduction in color quantified as Pt-Co after a 60 min reaction time. When the two different nanoparticles are compared, PG-ZVI nanoparticles are observed to perform better than

GT-ZVI nanoparticles regardless of the concentration applied. 100 ppm PG-ZVI nanoparticles provided 73% color removal while only 37% removal could be achieved with 100 ppm GT-ZVI nanoparticles. However, for the same type of nanoparticles the increase in concentration did not lead to a substantial enhancement in removal efficiency. For instance, with 300 ppm GT-ZVI nanoparticles the removal efficiency was 52%, being only 15% higher than 100 ppm GT-ZVI nanoparticles. Similarly, 300 ppm PG-ZVI nanoparticles provided 79% color removal, which was almost the same rate with 100 ppm PG-ZVI nanoparticles. The superior behavior of PG-ZVI nanoparticles could be evidence of the increased reactivity of smaller size of the nanoparticles.

Nevertheless, despite such high removal efficiencies the discharge limit for color (280 Pt-Co) to receiving waterbodies in Turkey could not be achieved. Therefore, a further treatment step was applied to the samples. The pH of the solutions were raised to 8.5 with 0.1 N NaOH, and subjected to 20 min slow mixing process at 40 rpm. Then samples were allowed to settle by gravity and color measurements were performed on the supernatant of the samples (Figure 4). Since the color (Pt-Co) increases as pH increases, the pH of the treated samples was decreased to the initial value prior to color measurement.

As seen in Figure 4, the PG-ZVI nanoparticles provided more than 95% removal, the resultant values being lower than 280 Pt-Co to comply with the discharge standards. However, with GT-ZVI nanoparticles the color of the supernatant was slightly higher than the limit value, regardless of the nanoparticle concentration. The inset of Figure 3 shows

**Figure 3** | Color removal with 100 ppm and 300 ppm GT-ZVI and PG-ZVI nanoparticles (60 min reaction time and UV/Vis spectra of the samples (inset), no pH adjustment).

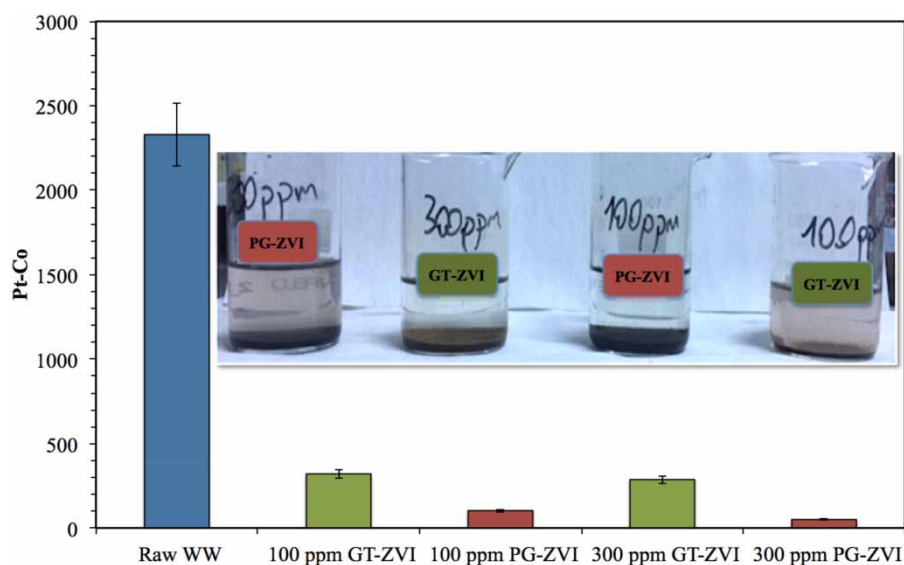


Figure 4 | Color removal with 100 ppm and 300 ppm GT-ZVI and PG-ZVI nanoparticles (pH adjusted to 8.5, samples allowed to settle for 2 hours).

the UV/Vis spectra of the raw textile wastewater as well as the end of the reaction time samples. A considerable decrease was observed in the absorbance, specifically in the UV range, with both types of nanoparticles (GT-ZVI and PG-ZVI), indicating that organic compounds might be eliminated by several mechanisms such as adsorption and precipitation to a major extent, and mineralization to a minor extent. Mineralization might have occurred due to the formation of reactive oxygen species (ROS). Under acidic conditions, oxidation of ZVI produces Fenton reagent ($\text{Fe}^{2+} + \text{H}_2\text{O}_2$) *in situ*, which is well known for generating hydroxyl radicals ($\cdot\text{OH}$) (Erdim *et al.* 2015). At near-neutral pH, in the absence of stabilizing ligands (e.g., EDTA) oxidation of ferrous ion (generated from ZVI) produces superoxide radicals ($\cdot\text{O}_2^-$) and subsequently hydrogen peroxide (H_2O_2) (Symons & Gutteridge 1998). Under ambient aqueous conditions, ZVI oxidation has been shown to produce ROS (Bergendahl & Thies 2004; Bremner *et al.* 2006; Boussahel *et al.* 2007).

The adsorption of a basic dye, Malachite Green, onto iron oxides and capping agents in GT-ZVI nanoparticles and following the degradation of the dye by nZVI has been reported (Weng *et al.* 2013). A similar mechanism might have occurred with GT-ZVI and PG-ZVI nanoparticles in this study. However, it was not possible to observe an apparent decrease in the visible range, presumably due to filtering of the samples prior to measurement (true color). The ORP and pH change during the experiment are shown in Figures 5 and 6, respectively.

Although all of the nanoparticle suspensions showed a reductive trend, PG-ZVI nanoparticles showed a higher

decrease (ΔORP : ~ 200 mV) throughout the reaction in agreement with the higher removal efficiency compared with GT-ZVI nanoparticles.

The pH values of the extracts were measured to be 5.6 for GT-extract and 3.9 for PG-extract. After mixing with the ferrous sulfate solution (pH: 4.1, ORP: 469 mV), the pH of the resulting solutions is further decreased to more acidic values (3.7 for GT-ZVI nanoparticles and 3.1 for PG-ZVI nanoparticles). This is primarily due to H^+ ion generation during the reduction of ferrous iron by the polyphenols. However, after mixing the nanoparticle suspensions with textile wastewater (pH: 7.27), the initial pH increased to 6.72–6.98, but then decreased throughout the reaction. The decrease in pH might be due to gradual degradation of residual organic compounds. According to the

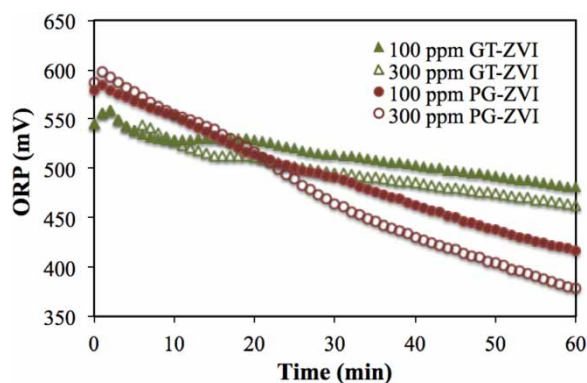


Figure 5 | ORP profile during 60 min reaction time (300 ppm PG-ZVI nanoparticles, 300 ppm GT-ZVI nanoparticles, 100 ppm PG-ZVI nanoparticles, 100 ppm GT-ZVI nanoparticles).

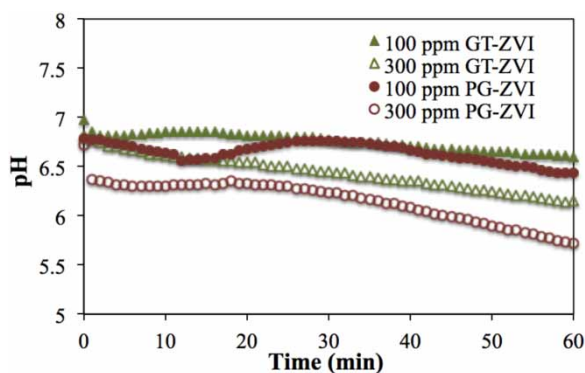


Figure 6 | pH evolution during the experiment (300 ppm PG-ZVI nanoparticles, 300 ppm GT-ZVI nanoparticles, 100 ppm PG-ZVI nanoparticles, 100 ppm GT-ZVI nanoparticles).

study of Sanchez *et al.* (2007) phenol- and quinone-like compounds can be degraded by dissolved O_2 within a time frame of 2–6 hours, under low temperature conditions (20–50 °C) in the presence of elemental Fe(0) and EDTA, which act as catalysts. According to the researchers the end products are low molecular-weight organic acids, such as formic, oxalic and succinic acids. These degradation reactions generate protons and could explain the low pH values observed during our experiments (Mystrioti *et al.* 2014).

Figure 7 illustrates the change in DOC content of the samples with time. Similar to the color removal efficiency results, PG-ZVI nanoparticles outperformed GT-ZVI nanoparticles in terms of DOC removal. Almost 80% decrease in DOC was achieved with 300 ppm PG-ZVI nanoparticles within the first 5 min while no further degradation was observed over the remainder of the reaction time. An explanation for the plateau could be the recalcitrant fraction of organic matter probably transformed into short-chain acids that cannot be further eliminated by nanoparticles (Torrades *et al.* 2004; Blanco *et al.* 2012). Considering the complex and recalcitrant nature of the wastewater, limits for DOC and

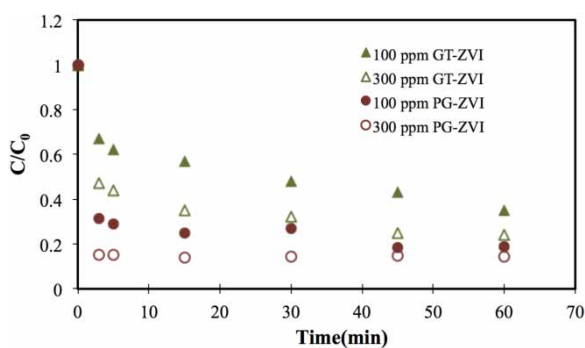


Figure 7 | Dissolved organic carbon (DOC) evolution throughout the reaction (300 ppm PG-ZVI nanoparticles, 300 ppm GT-ZVI nanoparticles, 100 ppm PG-ZVI nanoparticles, 100 ppm GT-ZVI nanoparticles).

COD parameters may not be achieved despite high removal efficiencies. Further studies can focus on increasing the reactivity of nanoparticles by using different plant extracts or by using different mixing ratios of the precursor and the extract.

CONCLUSIONS

In this study green tea and pomegranate extracts were used to synthesize iron nanoparticles and a comparative assessment was performed to decolorize textile wastewater. The polyphenolic content of the extracts was shown to be an important but not the sole factor in determining the size of the nanoparticles. However, size reduction was proved to have a pronounced effect on the reactivity of the nanoparticles. The main factor influencing the degradation efficiency was the choice of the plant extract rather than the concentration of nanoparticles. PG-ZVI nanoparticles performed better than GT-ZVI nanoparticles. Results indicated that adsorption and precipitation were the main removal mechanisms.

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