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Biosynthesis and characterization of zerovalent iron nanoparticles and its application in azo dye degradation

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Zero-valent iron nanoparticles (nZVI) have been prepared a simple, green and eco-friendly route using leaves extract as reductants. The produced nZVI are characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), zeta potential measurement, X-ray fluorescence spectroscopy (XRF) and transmission electron microscopy (TEM) analysis to ascertain the formation of zero-valent iron nanoparticles. The FTIR results show that the polyphenolic compounds present in the leaf extract may be responsible for capping the nanoparticles synthesis. The X-ray fluorescence spectroscopy (XRF) spectrum confirms the presence of iron metal. The scanning electron microscopy (SEM) of the biosynthesized nZVI reveals that the nZVI had an average diameter of 26 nm.The green synthesized nanoparticles have been further utilized for the adsorption of methyl orange dye (MO) through a batch technique. The effective processing parameters for dye removal such as adsorbent (nZVI) dosage, initial dye concentration and the solution *p*H are investigated. The adsorption efficiency of MO reach to almost 100% within 30 min using 0.3 g/L nZVI at room temperature.

Keywords: Zero valent iron, Green synthesis, Leaf extract, Methyl orange dye, Degradation.

The use of synthetic chemical dyes in various industrial processes, including paper and pulp manufacturing, plastics, dyeing of clothes, leather treatment and printing has increased considerably over the last few years, resulting in the release of dye-containing industrial effluents into the soil and aquatic ecosystems. The release of these coloured materials into the water bodies causes eutrophication, reduces the reoxygenation capacity and makes severe damage to the aquatic organisms by hindering the infiltration of sunlight[1,2]. Moreover, highly coloured wastewaters can block the penetration of sunlight and oxygen, essential for the survival of various creatures. In addition, many of these dyes are mutagenic and carcinogenic and hence cause substantial injury to human life[3,4] and aquatic forms[4]. Therefore, it is necessary to remove these dyes from our water resources. Many approaches, including physical and/or chemical processes, have been used in the treatment of industrial wastewater containing dye but such methods are often very costly and not environment-friendly. Methods utilizing powdered activated carbon and activated bentonites as adsorbent materials have been commonly used. However, the large amount of sludge generated and the low efficiency of treatment with respect to some dyes have limited their use. Colour removal using ozone is also usually effective and fairly rapid, but not all the methods employed give satisfactory results especially for some dispersed dyes. Another widely used treatment method for coloured effluents is the physical-chemical flocculation with metal hydroxides assisted by polymer flocculants, while the application of pre-mixed polyelectrolyte complexes made by the interaction of aqueous solutions of polycation and polyanionishas accepted as a more practical method. Such complexes particles are able to bind disperse dyes effectively over large distances due to their size and structure via hydrophobic as well as electrostatic interaction forces. However, because dye molecules or their aggregates are incomparably smaller than such inorganic particles, and in some cases also uncharged, it is necessary to apply other flocculation principles[5-9]. Due to the chemical stability, the dye pollutants are usually resistant to degradationby physicochemical methods. Even though biodegradation methods are cost effective, they are inherently slow, not effective for dye degradation as dyes are toxic to microorganisms[10,11]. In recent years, nanocatalysis has emerged as an alternative to conventional water treatment methods. The finite size, large surface area to volume ratio and size dependent reactivity has made metal nanoparticles an efficient catalyst[12]. Now a days nanocatalysts are widely used for the effective removal of dye contaminants[13-16].

Zerovalent iron (Fe^0), an environmentally friendly reducing agent, can reduce the azo bond and cleaving dye molecules into products that are more amenable to mineralization in biological treatment processes[17]. Much attention has been paid on the treatment of azo dyes by ZVI in recent years[18]. The advantages of the ZVI decolorization process include the ease in use as a pre-treatment process, the spent iron powder can be easily recycled by magnetism as well as the low remaining iron concentration and finally, there is no necessity for further treatment of the effluents. During recent years development and use of zerovalent iron nanoparticles (nZVI) has rapidly been increased due to their unusual potential applications in the effective remediation of contaminated soils and water[19,20]. Many techniques of synthesizing iron nanoparticles (nZVI) have been investigated. Some are top-down approaches while others are bottom-up approaches. The top-down approach uses mechanical and chemical processes (ground/ ball milling, etching, and machining) to reduce the larger size ZVI (granular, macro- and microsizes). The bottom-up approach promotes the 'growth' of the particles on ZVI through several processes such as chemical synthesis or self-assembling[21]. These methods are generally expensive and require specific equipment. In one of the most widely used bottom-up processes, sodium borohydride is used to reduce iron (III) or iron (II) to zero-valent iron nanoparticles. This chemical process presents disadvantages related to safety issues associated with the use of a toxic reagent (sodium borohydride) and the formation of a flammable gas (hydrogen) during the process. Now a days special focus on ''green chemistry'' by researchers is strongly created because of increasing environment awareness. Utilization of non-toxic chemicals, environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in a green synthesis strategy. As a consequence, new processes are being investigated to prepare stable nanoparticles using stabilizers such as a soluble polymer or surfactant onto the nanoparticles[22]. Several studies have been carried out in order to obtain stabilized nZVI using different stabilizing agents such asresin, Fe_3O_4 particles and chitosan to prevent agglomeration of the nZVI[21]. In the last couple of years, a greener approach for the production of nZVI has been developed. In this approach, extracts of natural products (in most cases green tea leaves) with high antioxidant capacities were used. The plant extracts may act as both reducing agents and stabilizing agents in the synthesis of nanoparticles[23]. Typically, a plant extract-mediated bio-reduction involves mixing the aqueous extract with an aqueous solution of the relevant metal salt.The reaction occurs at room temperature and is generally complete within a few minutes. The main advantages of this method may are the lower toxicity of the used reducing agent compared with borohydride.

The objective of the present study is to use Guava leaf extract as a reducing as well as a stabilizing agent for the synthesis of zerovalent iron nanoparticles and to test their adsorption performance for methyl orange (MO)which is a model compound of common water soluble azo dyes, which are widely used in chemistry, textiles and paper industries.

Experimental Section

Reagents and solutions

Analytical grade ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) was purchased from Merck, India. Methyl orange dye and Ethanol were purchased from Sigma-Aldrich.

Guava leaf extract

The fresh leaves of Guava were collected from a local garden, Alexandria, Egypt (summer 2014). The leaves were washed thoroughly with distilled water then dried at 80°C under vacuum overnight. The dried leaves were ground to fine powder where five grams of the powder were suspended in 20 mL of ethanol. The suspension was heated at 70°C for 30 min and then filtered to get the extract used as a reducing agent. Deionized water was used throughout this study.

nZVI synthesis

For the green synthesis of iron nanoparticles, the prepared extract was added in a dropwise manner to a 50 mL solution of 0.5 M $FeSO_4.7H_2O$ under vigorous stirring at room temperature. After the addition of the extract (10 mL), the solution color changed from pale yellow to black, indicating the formation of iron nanoparticles. Finally, the formed nZVI were separated from the mixture and dried at 60°C under vacuum.

Characterization of materials

Powder X-ray diffraction (XRD) was performed by X-ray diffractometer operating with Cu Kα (k = 1.5406 Å) radiation. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 microscope, operating at 200 kV. The samples were prepared by dispersing the powdered product as slurry in ethanol with ultrasonic bath for about 5 min. Infrared spectroscopy (FTIR) was examined using Fourier Transform Infrared spectrophotometer (Shimadzu FTIR- 8400 S, Japan). The disc technique using KBr as a matrix was found to be suitable for FTIR examination.

For Scanning electron microscope (SEM), the ground samples were scanned to identify their structure and estimate their particle diameter at different magnifications using (Jeol JSM 6360 LA, Japan). The mean diameter of the grains was determined from the SEM pictures by measuring at least 5 crystals for each formulation using the software image tool. The Brunauer-Emmett-Teller (BET) surface area was determined using BET and the Barrett- Joyner-Halenda (BJH) adsorption methods. The Zeta potential of the synthesized materials was determined using ethanol as a dispersant (SZ-100 nanopartica) to evaluate the stability of the prepared nZVI.

Dye degradation by nZVI

The produced nZVI was assessed as an adsorbent for the removal of methyl orange dye from polluted water.The batch experiments were carried out in a number of 50 mL conical flasks. A series of dye solutions with concentrations ranging from 25 to 200 ppm were prepared by dissolving different amounts of methyl orange in distilled water. Each mixture was stirred till the equilibrium was reached. The sorption studies were also carried out at different temperatures (25, 50, 75°C) to determine the effect of temperature at the MO degradation efficiency. After adsorption, the concentration of the dye solution was determined using a UV–Vis spectrophotometer. The maximum absorbance wavelength for methyl orange is 465 nm. The removal efficiency was determined according to the following formula:

$$\%R = [(C_o - C_e) / C_o] *100 \quad \text{... (1)}$$

where C_o and C_e are the initial and equilibrium liquid-phase concentrations (mg/L) of adsorbate, respectively.

Suggested mechanism for methyl orange degradation using nZVI

MO degradation using the bio-synthesised nZVI from an aqueous solution occurred through a chemical reaction in which, nZVI nano particles dissociate the electrons and ferrous ions (Fe^{+2}) on iron surfaces then the separated electrons combined the azo dye (MO), resulting in reduction of the organic concentrations. nZVI particles with high surface activity can directly react with dye molecules, leading to the decolourization of the dye. The reaction between Fe^0 and H_2O or H^+ may produce atom H, which prompt the cleavage of azo bond (–N=N–), thus destroying the chromophore group and conjugated system of the azo dye. Moreover, the intermediate products of Fe^0 such as Fe^{2+}, Fe^{3+}, $Fe(OH)y^{2-y}$ and $Fe(OH)x^{3-x}$ were thermodynamically unstable and active[24]. During the reaction, iron corrosion and H^+ consumption lead to the increase of solution *p*H (final *p*H is 8-9) increased from. The formed passive iron oxides layers (Fe_3O_4, Fe_2O_3, $Fe(OH)_3$, and FeOOH)[25,26] could also adsorb dye molecules via the sulfonic group and reduce the colority of the dye wastewater through the formation of a bridged bidentate complex[27].

Results and Discussion

Material characterization

X-ray diffraction

Powder X-ray Diffraction (XRD) was used to investigate the crystal structure of iron nanoparticles

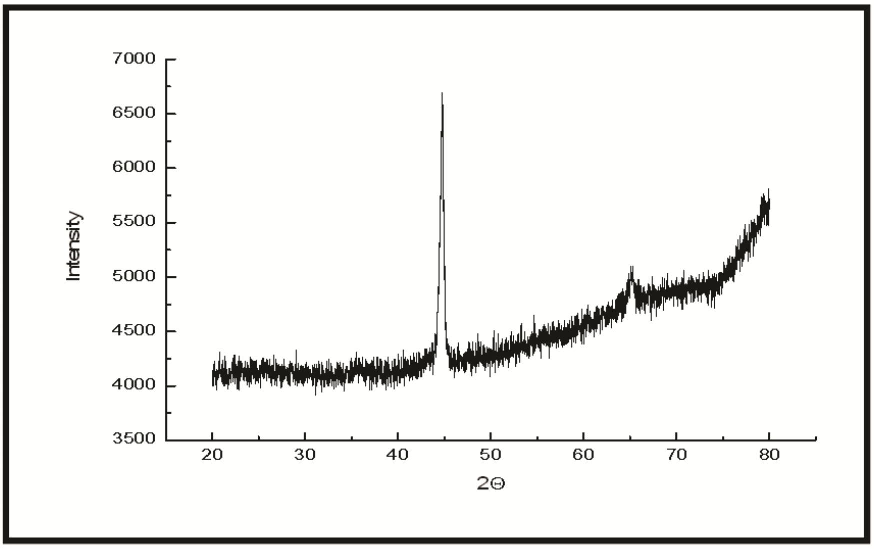

Fig. 1 — XRD pattern of the produced green nZVI particles.

(Schimadzu-7000, U.S.A.). Figure 1 investigates the XRD analysis of the produced nZVI. The broad peak confirms the existence of an amorphous phase of iron. The characteristic broad peak at 2θ of 45° indicates that the zerovalent iron is predominantly present in the sample[28].

SEM analysis

SEM analysis was conducted to observe the topology, shape and size of the synthesized zero valent iron nanoparticles. Figure 2 represents the SEM image revealing that the green nZVI are sphere-shaped nano particles and with average diameter of 26 nm.

Transmission electron microscope (TEM)

In order to further confirm the morphological structure of the synthetized nZVI, the typical TEM image of the biosynthesized nZVI is shown in Fig. 3. The green synthesized nZVI was spherical in shape and has 20 nm average size.

Fourier transform infrared spectrometer (FTIR) spectral analysis

FTIR technique provide information about vibrational state of adsorbed molecule and hence the nature of surface complexes. An FTIR spectrum of the produced iron nanoparticles was shown in Fig. 4. The earlier reports[28] showed polyphenols were responsible for the reduction of Fe^{+2}. From the spectrum, it can be shown that the phenol groups ((–OH), at stretch band 3440 cm^{-1}) were involved in the reduction of Fe^{2+} to Fe^0. Hence, it can be concluded that polyphenols present in the leaf extract were responsible for reduction and stabilization of nZVI[29].

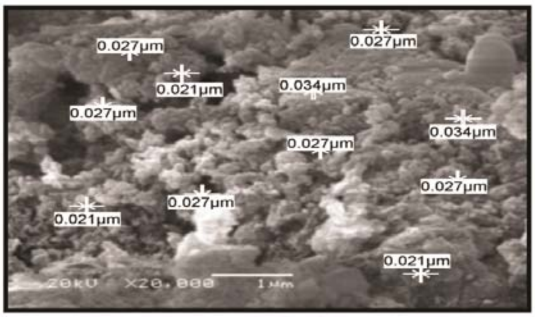

Fig. 2 — SEM image of iron nanoparticles synthesized using guava extract.

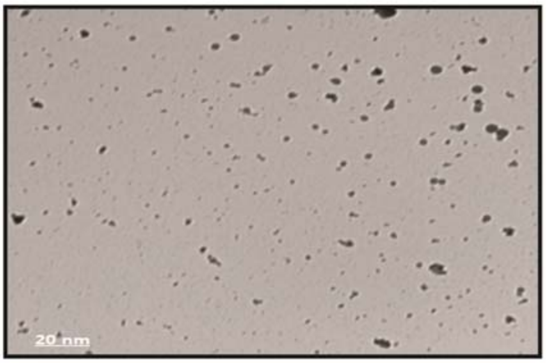

Fig. 3 — TEM image for the nZVI particles.

X-ray fluorescence spectroscopy (XRF)

The elemental composition of prepared powdered sample was measured using XRF analysis. The obtained results confirmed the significant presence of pure 98% iron with negligible contaminants such as Cu, Ag, Mn (Table 1).

BET surface area

The BET surface area value was determined as 39 m^2/g for nZVI from the straight line plot in the approximate relative pressure range of 0.05 to 0.3. This surface area value is expressively high compared with other previously reported values (14.5 m^2 /g[30], 33.5 m^2 /g[18] and 36.5 m^2 /g[31]. In comparison, commercially available Fe powder (<10 µm) has a specific surface area of only 0.9 m^2 /g. The increase in specific surface area reflects the important role of the phenolic compounds presence at guava leaves that act as surfactant agent. This surface agent maintains or keeps the produced nZVI dispersed and produced at nano-scale with high surface area value.

Zeta potential measurement

Particles with Zeta potentials more positive than +30 mV or more negative than -30 mV are stable. The Zeta

Table 1 — The elemental composition of prepared nZVI

No.	Component	Result	Unit	Statistical error	Detection error	Quantitation limit
1	Al	1.45	mass%	0.0437	0.0408	0.122
2	Si	0.304	mass%	0.0098	0.0026	0.0079
3	Ti	ND	mass%			
4	V	(0.0082)	mass%	0.0025	0.0070	0.0210
5	Cr	0.0251	mass%	0.0024	0.0061	0.0182
6	Mn	0.254	mass%	0.0058	0.0095	0.0286
7	Fe	98.0	mass%			
8	Co	ND	mass%	0.0107	0.0320	0.0961
9	Ni	ND	mass%	0.0020	0.0060	0.0180
10	Cu	ND	mass%	0.0010	0.0030	0.0090
11	Zn	ND	mass%	0.0012	0.0037	0.0112
12	Pd	ND	mass%			
13	Ag	0.0034	mass%	0.0005	0.0005	0.0016
14	Cd	ND	mass%			
15	W	ND	mass%			
16	Au	ND	mass%	0.0010	0.0029	0.0086
17	Hg	ND	mass%			
18	Pb	ND	mass%			

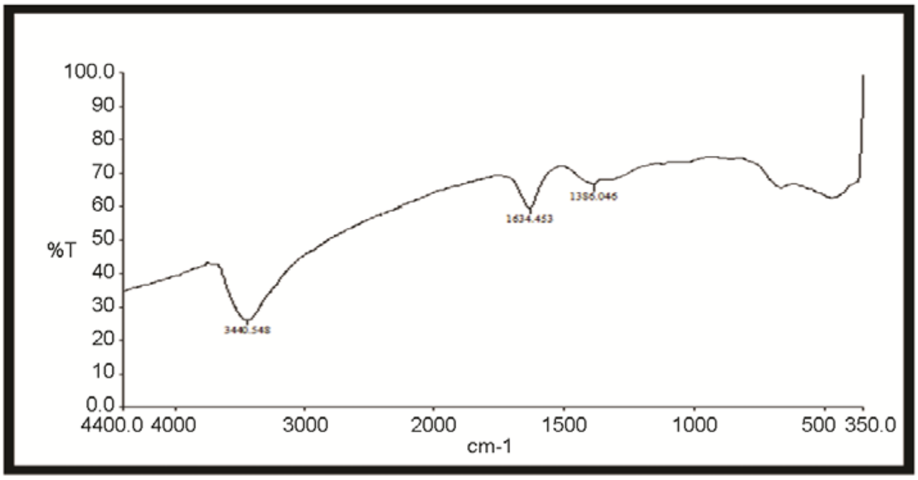

Fig. 4 — FT-IR spectra of biosynthesized iron nanoparticles.

potential of the synthesized nZVI was measured in ethanol as solvent. The Zeta potential (SZ-100 nanopartica) of Fe^0 nanoparticles synthesized was -80 mV.The high negative charge value approves the repulsion among the particles and thereby higher stability of the formulation.

Evaluation of nZVI for dye decolourization

Effects of reaction time

A series of experiments were carried out to investigate the effect of the reaction time on the MO dye degradation efficiency. As shown in Fig. (5a), at the given experimental condition, as the reaction time increased, the % dye removal increased. In general, the reaction proceeded rapidly within the first 15 min, and then decreased till reaching the equilibrium after 30 min. This can be attributed to that, at the beginning of the reaction, the mass transfer process of dye molecules towards the Fe^0 particles was easily done because of the strong adsorption and reduction ability of nZVI. Furthermore, the generated H_2 bubbles in the reaction media prevented the particles accumulation, removed the alteration products from particles and thus kept the surfaces free and maintaining the high reactivity of the particles[32]. As the reaction continued, the solution *p*H increased and the release of H_2 gas decrease. Also, the convection of the water and particles was markedly reduced, the surface reactivity sites of Fe^0 particles were gradually transformed into ferrous ions Fe^{+2} (corrosion product) that block the surface active sites of the material and hence reduces its reactivity toward MO degradation. All of the previously mentioned factors would greatly decrease the reaction rate.

Effects of initial MO concentration

A series of experiments were carried out to study the effect of initial MO concentration on the degradation efficiency. As shown in Fig. (5b), at the given experimental condition, decolorization efficiency decreased as the initial MO concentration increased. This may be due to that the higher the MO dye concentration, the higher the competition for the active sites on the nZVI particles.

Effect of reaction temperature

Usually, the rate of chemical reaction is very sensitive to temperature changes. Also, thetemperature effect is important in providing some insight into the reaction mechanism[33]. In the present work, a number of experiments were carried out at different temperatures (25–80°C) in order to study the temperature effect on MO degradation using the prepared nZVI particles. As shown in Fig. (5c), raising the temperature has a positive influence on the decolorization and complete degradation of MO can be achieved at 80°C.

Effect of the nZVI dosage

To evaluate the effect of the nZVI dosage on the degradation efficiency, MO concentration was fixed at 50 ppm. Figure (5d) depicts that at the same reaction time, higher degradation efficiency was obtained using higher nZVI dosage. This may be attributed to that there is more nZVI particles which are able to provide more iron surface-active sites for collision with azo dye molecules to ensure higher dye removal efficiency.

Effect of initial pH

Solution *p*H was considered as one of the most important factors influencing the dye removal rate

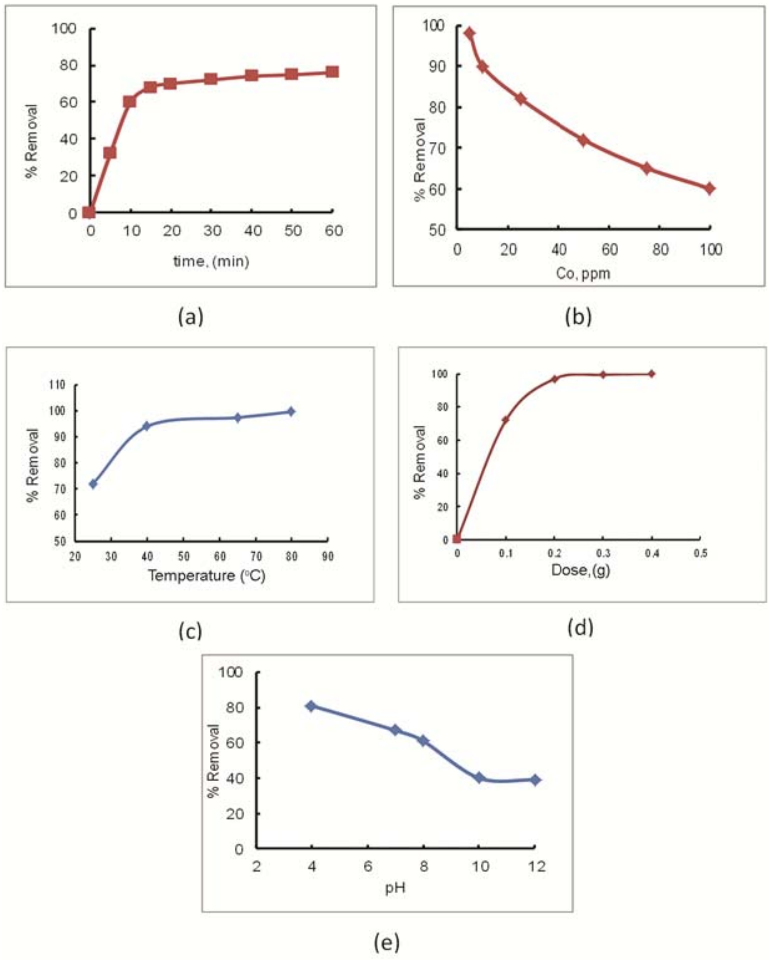

Figure (5)

Fig. 5 — Processing factors for dye degradation using nZVI. (a) Effect of reaction time on MO degradation using nZVI (initial dye conc. = 50 ppm; adsorbent dose = 0.1 g; solution volume, 25 mL, temperature = 25±2°C; agitation speed = 150 rpm, *p*H = 7); (b) Effect of initial dye conc. on MO degradation using nZVI (reaction time=30 min; adsorbent dose = 0.1 g; solution volume, 25 mL, temperature = 25±2°C; agitation speed = 150 rpm); (c) Effect of reaction temperature on MO degradation using nZVI (Initial dye conc. = 50 ppm; adsorbent dose = 0.1 g; solution volume, 25 mL; agitation speed = 150 rpm); (d) Effect of nZVI loading on MO degradation (Initial dye conc. = 50 ppm; reaction time = 30 min; solution volume, 25 mL, Initial conc. = 50 ppm, agitation speed = 150 rpm); (e) Effect of solution *p*H on MO degradation (Initial dye conc. = 50 ppm; reaction time = 30 min, solution volume, 25 mL, Initial conc. = 50 ppm; agitation speed = 150 rpm, nZVI dose= 0.1 g)

using zerovalent iron. As shown in Fig. (5e), results proved that the degradation of MO dye by the prepared nZVI particles was an acid-driven process. This may be attributed to that when the ferrous ions dissolved from the iron surface colliding with hydroxyl ions in alkaline solution, producing ferrous hydroxide precipitation on the iron surface occupying the reactive sites and hindering the reaction[34]. It can be concluded that acidic conditions are more favorable for this process.

Conclusion

In the present study, a green method for the synthesis of Fe^0-NPs using the extracts from Guava leaves was used. Such synthesis route was found to be of many advantages such as the low cost, the abundant resource and the environmental benignancy. The prepared Fe^0 particleswere characterized and found to possess nano spherical structure with an average particle size of 20 nm. The zero valent iron was prepared at high purity of 98% which was confirmed using XRF analysis. Zeta potential indicated the nanoparticles stability in aqueous media for a long time. The nanoparticles were stable in aqueous medium for a long time without any aggregation. The synthesized nanoparticles were proved to be remarkably competent catalysts for the degradation of organic dyes.

This new approach for the green synthesis of iron nanoparticles holds several valuable attractions and offers an efficient and economic route to environment protection.

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