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Photocatalytic mediated remediation of synthetic dyes effluent using zero-valent iron: a comparative study

Muhammad Asim Rafique[a], Adil Jamal[b], Gulnaz Afzal[c], Shazia Abrar[d], Shumaila Kiran[d,*], Sofia Nosheen[e,*], Hafiz Mhuhammad Hammad Hussain[d], Tanveer Majeed[f]

[a]*School of Economics and Management, Yanshan University, Qinhuangdao, Hebei Province, China, email: asimchoudhary786@gmail.com*

[b]*Sciences and Research College of Nursing, Umm Al Qura University, Makkah-715, Kingdom of Saudi Arabia, email: adiljamalcemb@gmail.com*

[c]*Department of Zoology, Islamia University Bahawalpur, Bahawalpur, Pakistan, email: gulnaz.afzal@iub.edu.pk*

[d]*Department of Applied Chemistry, Government College University, Faisalabad-38000, Pakistan, emails: shumaila.asimch@gmail.com (S. Kiran), shaziaabrar@gcuf.edu.pk (S. Abrar), ch.hammad008@gmail.com (H.M.H. Hussain)*

[e]*Department of Environmental Science, Lahore College For Women University, Lahore, Pakistan, email: nosheen.sofia@yahoo.com*

[f]*Department of Biotechnology, Kinnaird College for Women, Lahore, Pakistan*

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ABSTRACT

In the present investigation, the zero-valent iron (ZVI) was synthesized using ferrous sulfate for the degradation of synthetic textile effluent. The process variables such as initial dye concentration, ZVI dose, contact time, pH, hydrogen peroxide (H_2O_2), and temperature, artificial and solar light intensities were optimized for maximum remediation of synthetic dyes effluent. The maximum degradation (68.64%) of synthetic dyes effluent was obtained at its concentration of 0.02% at pH = 8, ZVI dose 0.1 g mL^{-1}, 75 min reaction time, temperature = 40°C, while degradation efficiency of synthetic dyes effluent was raised to 76.74% using the artificial light intensity of 2,500 lux and 83.43% in solar light during noon timings. The catalytic efficiency of the studied method was assessed using chemical oxygen demand (86.7%) and total organic carbon (87.2%) measurements, which declared the degradation of synthetic dyes effluent. Our study results disclosed that ZVI has the capability and promising potential to decolorize and degradation of other toxic dyes present in wastewater.

Keywords: Artificial and solar light; H_2O_2; Photocatalytic decolorization; Synthetic dyes effluent; Total organic carbon and chemical oxygen demand; Zero-valent iron

1. Introduction

Dye is a colored substance that has an affinity to the substrate to which it is applied by the study of Chatha et al. [1]. Most dyes are used in an aqueous form and the fastness of the dye can be improved differently. The majority of dyes are strongly stable and difficult to natural eroding; entering these into the water body may cause environmental pollution because of their toxicity and carcinogenicity [2]. In such conditions, the removal of dyes from natural water resources turned into an important problem [3]. It is well known that water is an essential part of life but due to industrialization and urbanization, global wastewater has doubled every 10 y. Around 1,000 tons of dyes are relinquished into rivers and other water reservoirs [4]. Direct dyes were additionally used due to their versatile applications, color multiplicity, and outstanding color results. The large number of dyes released from textile, food, and paper

* Corresponding authors.

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industries cause ruthless water pollution [5]. According to estimation, more than 700,000 tons of dyestuff are manufactured annually and about 10%–20% of these dyes are released in effluents during the dyeing process. Around 50% of the reactive dyes are emancipated in effluent and the concentration of reactive dyes in wastewater is around about 10–200 mg L^{-1} [6].

Many approaches have been evolved to get rid of contamination in water like precipitation, electrolysis, adsorption, filtration, coagulation, oxidation, and membrane separation. From all of these methods, adsorption is a very well-known method for the removal of dyes from wastewater [2]. Biological degradation is key one an aerobic process that has the advantage of color removal, which facilitates chemical oxygen demand (COD) removal but it also has some drawbacks for a longer time [7,8]. The physical methods can be applied for decolorization on large scale but this method transfer waste dyes from only one form to another form rather than destroying them and it is only applicable on small scale [9,10]. Oxidation methods are effective for both soluble and insoluble colorants but they pose a problem with sludge disposal. These methods involve oxidation using Fenton's reagent and other oxidants which are used to decolorize the wastewater but it is a very expensive process [11].

Photocatalytic methods like Fenton reagent, photo-Fenton reagent [11], and $Fe_3O_4/ZnO/Si_3N_4$ nanocomposite are of major concern [12]. Nanocomposites have been effectively applied for the omission of noxious dyes from wastewater. Solar or artificial light is usually used for the activation of the catalyst. UV or visible light can be utilized for the excitation of photocatalyst and create electron-hole pairs [13], which in turn, can cause catalytic degradation of contaminants via free radical formation. The free radicals are produced as a result of oxidation-reduction reactions facilitated by the electron–hole pairs [14].

The zero-valent iron (ZVI) method has been applied as a successful method according to the environment and in the view of cost as well as easy to handle [15]. Due to specific properties of nanoscale ZVI (nZVI), such as large surface area, small size, high reactive and good reaction condition, it is used significantly for the treatment of wastewater containing various dyes, organic and inorganic compounds [16]. In the preceding year's more attention is required to be focused on the treatment of dyes by nZVI but in the past time, this limitation was solved by using active ZVI particles. The activity of ZVI can be enhanced by increasing the surface area of the iron particles [17]. Zero-valent iron particles are first-class electron donors and the dye molecules are good electron acceptors. In the aqueous medium, ZVI converts into Fe^{+2} or Fe^{+3} as well as hydroxyl or hydrogen ions are also produced during reduction reaction that play an important role to cleave the bonds of dye molecules [18]. ZVI has added much significance as an efficient catalyst for wastewater treatment vs. other physical, chemical and biological means [19]. ZVI has several benefits over other catalysts, that is, benign, worthwhile, easy to knob, greater surface area, and greater reactivity [20]. The comparison of our study with previous studies on decolorization/degradation of dyes depicting our work novelty is given in the following Table 1.

Keeping in view the catalytic features of ZVI, this study was planned to apply the ZVI for decolorization and degradation of synthetic industrial waste (a mixture of two direct dyes) using artificial and solar lights. Different variables were standardized. The optimized variables with higher efficiency towards decolorization and degradation of synthetic dyes effluent revealed that this economically easily operatable treatment process can be deployed in the remediation of industrial wastewater.

2. Materials and methods

All chemicals used in research work were of analytical grade and were purchased from Sigma-Aldrich (United States), and used as received without any further purification. Direct blue 15 and Direct violet 1 dyes were used in the current study to prepare synthetic dyes effluent.

Both dyes each 0.1 g were dissolved in 100 mL of de-ionized water separately and then were getting mixed. Prepared solutions were further centrifuged at 100 rpm at room temperature (25°C) for 10 min. Finally, 50 and 80 ppm solutions were prepared from stock solutions to a final dilution of 100 ppm solution. λ_{max} was measured using prepared dilutions using a double beam spectrophotometer (Model UV-1650Pc, Shimadzu Co., Japan) and it was found to be at a wavelength of 510 nm.

2.1. Preparation of synthetic dyes effluent

For the preparation of synthetic dyes effluent, blue and purple dyes were taken in an equal quantity (of each 0.15 g) and dissolved in 1,000 mL de-ionized water. The starch 0.013 g, sodium sulfate 0.0278 g, and sodium phosphate 0.028 g were added to it with constant shaking. The solution was placed on a magnetic stirrer for 90 min at 80 °C. The prepared solution's pH was adjusted to 12 (by adding acid or base) value using a pH meter (Hanna HI 9811-5) [16,26].

2.2. Preparation of zero-valent iron

Zero-valent iron (ZVI) was prepared in the laboratory. Sodium borohydride was used for the reduction of iron. Solution of sodium borohydride (0.31 M) was prepared by taking 0.756 g of $NaBH_4$ and dissolved in 200 mL of de-ionized water. Solution of $FeCl_3{\cdot}6H_2O$ (0.1 M) was prepared by dissolving 1.08 g of it in a beaker having 48 mL ethanol and 12 mL de-ionized water. After that, $NaBH_4$ solution (0.31 M) was added to $FeCl_3{\cdot}6H_2O$ solution (0.1 M) and shaked well. The reaction mixture was kept for at least 1 h till the appearance of a black precipitate of iron (Fe^0) called zero-valent iron (Eq. 1) with shaking at intervals.

$$4Fe^{+3} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3HBO_3^- + 12H^+ + 6H_2 \quad (1)$$

The generated iron particles were washed by ethanol and were dried using vacuum filtration assembly [27].

2.3. Characterization of zero-valent iron

The synthesized zero-valent iron particles were characterized by scanning electron microscopy (SEM). It clearly

Table 1
Comparison of our study with previous studies on decolorization/degradation of dyes

Sr. #	Source	Purpose	Reference
1	Advanced Fenton process using zero-valent metallic iron	Methyl orange (90%)	[21]
2	Nanostructured zero-valent iron	Orange G dye (90%)	[22]
3	Zero-valent copper nanoparticles	Reactive blue 4 dye (90%)	[23]
4	Zero-valent iron nanoparticles using UV light	Congo red dye (96%)	[24]
5	Zero-valent iron	Acid red 1 dye (91%)	[18]
6	Zero-valent iron doped polypyrrole nanocomposite using UV light	Malachite green dye (95%)	[25]
7	Zero-valent iron using artificial light and solar light	Synthetic dyes effluent (prepared using Direct blue 15 and Direct violet 1 dyes) (76.74% using artificial light intensity of 2,500 lux and 83.43% in solar light)	We applied two types of light sources (artificial light and solar light) for comparison purposes. The previous studies used only one type of light source in the study and one dye in the study. We prepared synthetic effluent of two dyes, so we studied if dyes are in mixture form, which is usually present in textile effluent, then how much be efficient our studied method would be? It was found to be an efficient way to degrade dyes mixture using artificial light (76.74%) and solar light (83.43%) in the current study)

indicates the surface morphology of synthesized materials. SEM images of synthesized zero-valent iron particles were recorded using the Hitachi S-4500 instrument (America) by means of a carbon-coated copper film for stacking the pulverized synthesized zero-valent iron particles on it.

2.4. Optimization of synthetic dyes effluent

70 mL of 0.01% synthetic dyes effluent was taken in a reaction vessel and 70 mL of each solution (H_2O_2, $FeSO_4$, and ZVI solution) was taken and mixed. pH and temperature remained unchanged and adjusted to 5 and 25 °C, respectively. The reaction mixture was performed for 75 min on a hot plate with a magnetic stirrer. Absorbance was measured for a prepared solution at a wavelength of 510 nm. Similarly, four sets of experiments were performed with varying effluent solution concentrations of 0.02%, 0.03%, 0.04%, and 0.05%. The experiment value was standardized at 60% (60% synthetic solution and 40% distilled de-ionized water) [4].

2.5. Optimization of pH, H_2O_2, and temperature

Optimized synthetic dyes solution was subjected to optimize pH values (3–9). Each experiment was performed at different pH. pH values were maintained using 0.1 M HCl or 0.1 M NaOH. In each set of experiments, 70 mL of each solution was taken. Optimized ZVI and synthetic dyes solution of 0.1 g and 60%, respectively were used for further experiments. Each solution was further mixed using a magnetic stirrer for 75 min at room temperature. Each solution was prepared separately and was checked for its maximum decolorization using a spectrophotometer at 510 nm [28].

Different experiments were performed at varying concentrations of H_2O_2 (0.01, 0.02, 0.03, 0.04 and 0.05 M). 0.01 M H_2O_2 was added in 100 mL de-ionized water. Later, 70 mL of H_2O_2 (0.01 M) solution was taken and 70 mL of each optimized solution was added further. The solution was kept on a magnetic stirrer for 75 min at room temperature. The absorbance value of each prepared was recorded at 510 nm. The optimized level of H_2O_2 in our experiments was calculated to be 0.04 M [11].

Temperature standardization was performed using different experiments with varying temperatures range (20-60 °C). 70 mL of each optimized solution was taken in a reaction vessel and mixed it. The optimized solution was stirred for 75 min at room temperature. The absorbance of solutions was measured at the λ_{max} of 510 nm. The optimized temperature in our experiments was figured as 40 °C [4].

2.6. Photocatalytic treatment using UV-Visible/ZVI and solar light/ZVI

Light intensity was ranged from 500–3,000 lux while keeping all other parameters constant. A solution of a known amount of tungsten oxide (0.121 g) was added and covered with a water filter to avoid the heat reaction. The sample was treated for a specific time interval (15, 30, 45, 60, and 75 min) during which a mixture of the standardized solution was let to run for 75 min in the presence of artificial light with 500 lux light intensity. Similarly, experiments were performed with varying light intensity (1,000; 1,500; 2,000;

2,500 and 3,000 lux). Decolorization percentage was calculated during the time interval [1].

Photocatalytic decolorization of synthetic dyes effluent was performed in the morning, mid-day and in the afternoon by following the same procedure described above, in the presence of solar light. Synthetic dyes effluent with standardized solutions was treated at specific time intervals (15, 30, 45, 60, and 75 min) for solar light analysis at 10 am. Similarly, the other two experiments were carried out in the presence of solar light at 2 and 5 pm [4].

2.7. Decolorization (%) efficiency

All decolorization experiments were performed in triplicate further to avoid any bias. Decolorization was calculated using the following formula:

$$\text{Percentage of decolorization} = \frac{(I-F)}{I} \times 100 \quad (2)$$

where I is the initial absorbance and F is the final absorbance of dye solution.

2.8. Mineralization study

Untreated and treated synthetic dyes effluent samples were subjected to chemical oxygen demand (COD) and total organic carbon (TOC) measurements using the standard procedures with few modifications [29,30].

2.9. Statistical analysis

Data were analyzed by computing standard errors of means. The experiments were performed in triplicate. The experimental values were calculated and expressed as mean ± S.D. [31].

3. Results

The wavelength of maximum absorption was scanned using the visible range of spectrum and it was found to be 510 nm (Fig. 1). SEM study was carried out to check the surface morphology of synthesized zero-valent iron particles. The prepared zero-valent iron particles were found to be semispherical in shape and well organized having a particle size of 100 μm (Fig. 2). Present work concluded maximum decolorization of the synthetic dyes solution following standardized conditions pH = 8, ZVI = 0.1 g, H_2O_2 = 0.04 g, 0.02% synthetic effluent and 40 °C temperature. Increase in synthetic dyes effluent concentration from 0.01% to 0.02%, resulted in increased percentage of decolorization, that is, from 15.57% to 54.34% (Fig. 3a). As the concentration of ZVI was augmented from 0.01 to 0.1 g, the percentage decolorization was increased from 32.29% to 58.86% (Fig. 3b). The concentration of ZVI higher than 0.1 g resulted in decreased decolorization percentage up to 41.85%. We observed that an increase in the pH value from 3 to 7, displayed the increased decolorization % from 15.57% to 60.34%. pH higher than 8, percentage decolorization was decreased to 51.70% (Fig. 3c). In the case of H_2O_2, a rise in the concentration of H_2O_2 from 0.01 to 0.04 M, resulted in increased percentage decolorization from 33.29% to 64.15% (Fig. 3d). The concentration of H_2O_2 higher than 0.04 M showed decreased percentage decolorization to 61.72% (Fig. 3d). In our results, the increase in temperature of synthetic effluent was from 20°C to 40 °C resulted in the augmented percentage decolorization from 45.53% to 68.64% (Fig. 4a). Increased temperature of synthetic effluent above 40 °C displayed a decrease in the percentage decolorization to 66.36% and 57.74% at 50 °C and 60 °C, respectively (Fig. 4a).

Our results also displayed that an increase in the light intensity (lux) from 500 to 2,500 lx, showed augmented percentage decolorization from 69.98% to 76.74% (Fig. 4b). As the artificial light intensity increased to 3,000 lx, a decrease in percentage decolorization was valued at 69.89% (Fig. 4b). Our results reported that 69.12%, 83.43%, and 74.12% decolorization during the daytime, noon, and afternoon, respectively (Fig. 4c). We observed that at noon time maximum degradation was existed due to the presence of maximum light intensity. During photocatalytic treatment in presence of artificial light intensity, the COD and TOC proportions were observed to be 73.4% and 74.2%, respectively for synthetic dyes effluent (Fig. 5a). While, photocatalytic

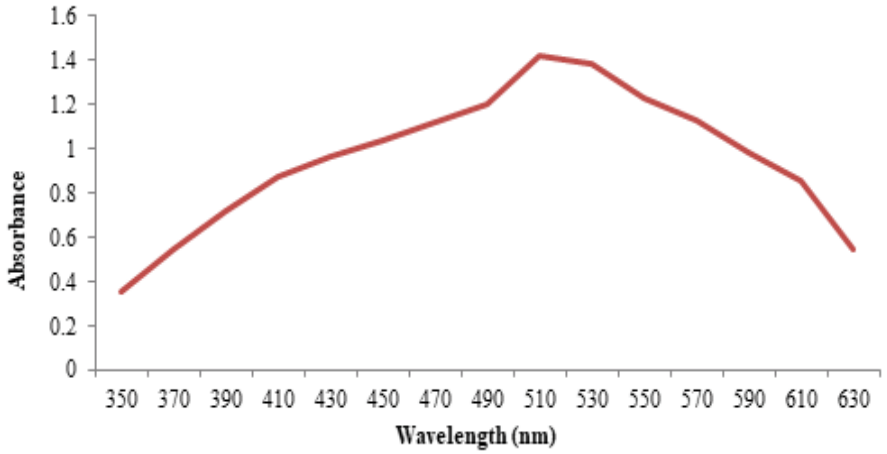

Fig. 1. Scanning of λ_{max} of synthetic dyes effluent.

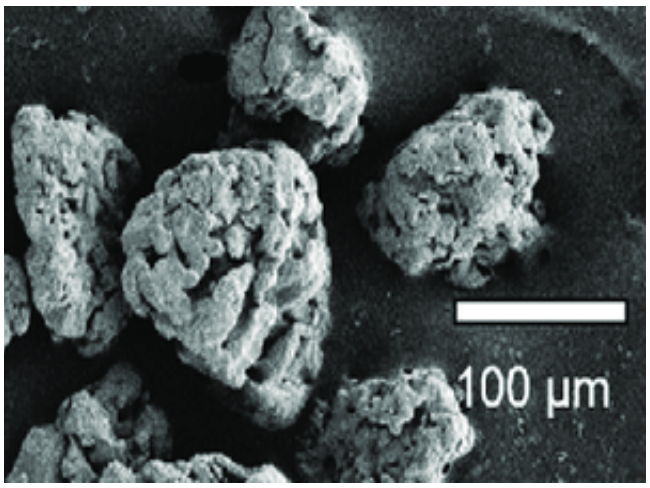

Fig. 2. SEM image of synthesized zero-valent iron.

treatment in the presence of solar light, the percentage reduction in COD and TOC were observed to be 86.7% and 87.2%, respectively for synthetic dyes effluent (Fig. 5b).

4. Discussion

The present work was planned to improve the dyes decolorization method containing wastewater. The concentration of synthetic dyes effluent higher than 0.02% resulted in decreased decolorization to 46.62%. The decrease in percentage decolorization at higher concentrations might be because a larger number of dye molecules may cause aggregation of dye particles hence may result in decline or reduced decolorization [10,32]. It might be because as the concentration of ZVI increases, the catalyst (ZVI) acts more efficiently performs degradation of dye particles. Initially, more dye molecules move towards Fe^0 due to more reduction and adsorption capability of ZVI and thus reaction completes and proceeds suitably. With time, reaction decreases due to reduced active surface area of Fe^0 which is following previous findings [33]. The decrease in percentage decolorization at higher pH resulted due to reduced activity of catalyst (ZVI). The result suggests that maximum decolorization exists in the basic situation, but the reaction may be slow down in the strong basic condition [34]. At the lower pH value, the surface of the iron particles are positively charged and dye molecules being negatively charged display potential for the adsorption of dye on the iron surface. Our findings are best elucidated by previous studies that documented similar findings [35]. It might be because as the concentration of H_2O_2 increases, the catalyst (ZVI) more efficiently works on the decolorization of dye particles. Decreased temperature yields reduced decolorization of dyes. An increase in the temperature of the reaction mixture resulted in enhanced percentage decolorization of synthetic dyes effluent, which may lead to the ZVI being more active for the degradation of dye particles. The decrease in percentage decolorization at higher

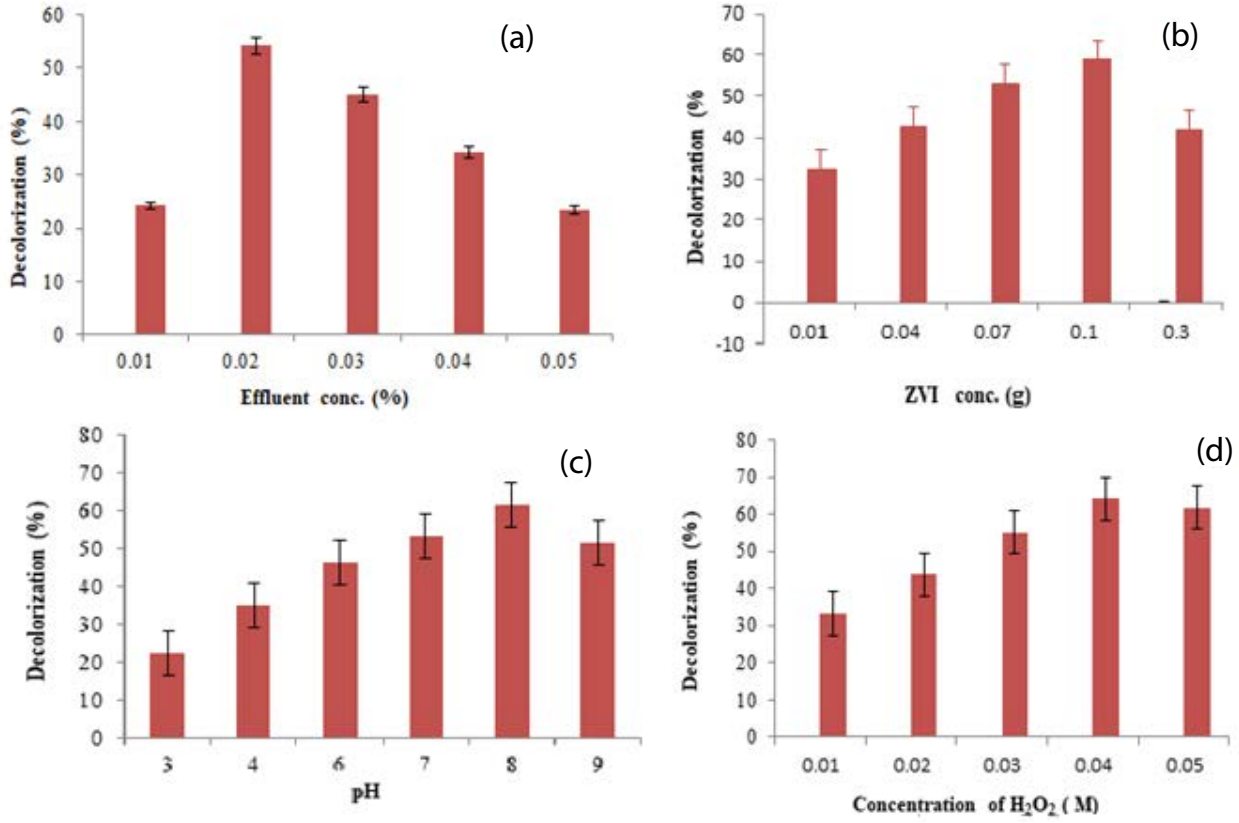

Fig. 3. Effect of (a) synthetic dyes effluent concentration, (b) ZVI concentration, (c) pH, and (d) concentration of H_2O_2 on decolorization (%) of synthetic dyes effluent employing zero-valent iron (ZVI) as a catalytic agent.

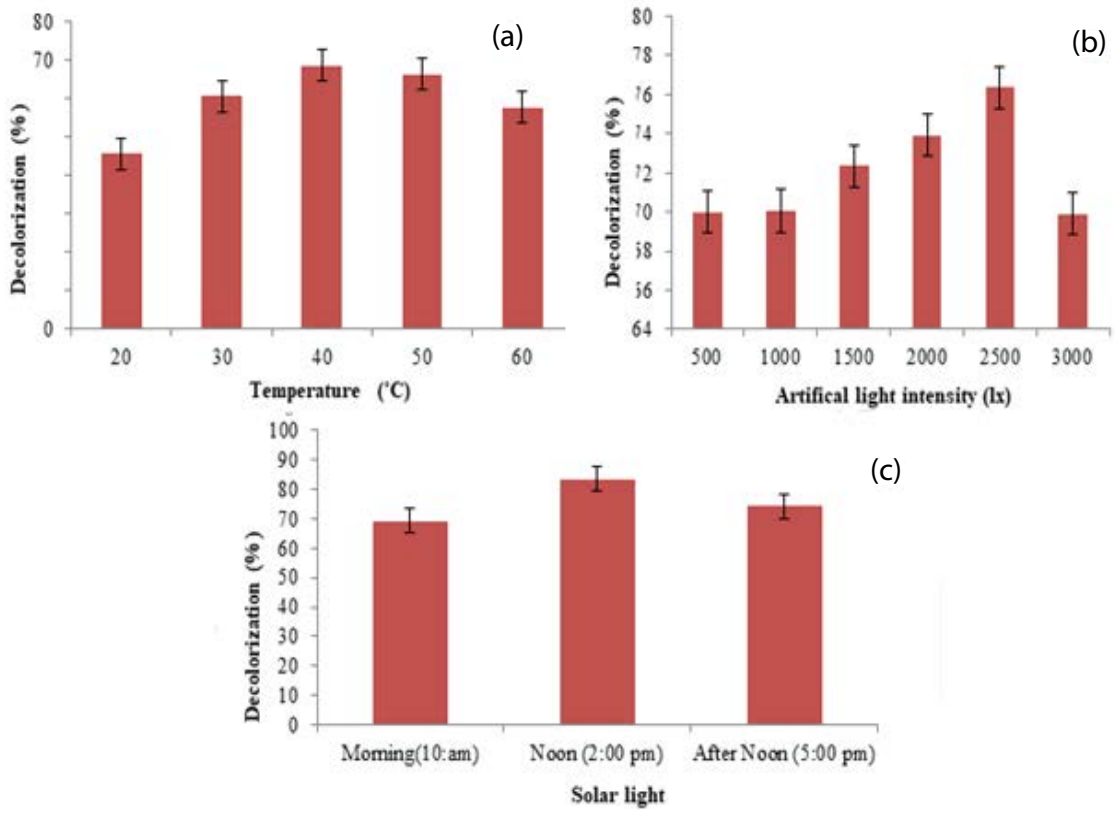

Fig. 4. Effect of (a) temperature, (b) artificial light, and (c) solar light on decolorization (%) of synthetic dyes effluent employing zero-valent iron (ZVI) as a catalytic agent.

temperatures is due to fact that a larger number of dye molecules may cause aggregation of particles which let them reluctant for decolorization of dyes [36].

Our results explained that higher activity of ZVI due to absorption of an increased fraction of the light quanta is similarly reported in previous studies. This may be attributed to the charge carrier density, the crystal structure, and band-gap energy [37]. Higher photocatalytic activity at noon timings under sunlight irradiation as compared to morning and afternoon time may be because of high temperature [14]. Similar results have been reported for higher photodegradation activity during the summer period. Photocatalytic activity is mostly affected by mass catalysts [34]. Our results showed a linear increase in photocatalytic degradation for both artificial and solar lights that can be attributed to the more active surface area of synthetic effluent to photocatalyst particles. As a result, an increase in the density of particles in the illuminated area is due to several dye particles adsorbed on the surface [38,39]. However, photocatalysis is not affected after reaching the maximum limit even after the addition of a sufficient amount of catalyst, so the decline in photocatalytic activity is observed [13]. It can be interpreted that photocatalytic activity lessens after certain solar and artificial light intensity due to ZVI activity, and the surface area of synthetic dyes effluent [40]. Light scattering may occur by catalyst particles with increased concentration which may lead to declined transmittance of solar radiations through sample heading to decreased light utilization [41]. This might be the reason for the decline in artificial and solar light utilization during the photocatalytic activity of wastewater treatment.

Photocatalytically treated synthetic dyes effluent using both artificial and solar lights, was subjected to COD and TOC measurements at different contact periods to assess the mineralization progress in presence of ZVI as a catalyst [20,40]. Both synthetic effluent samples depicted an increase in percent reduction as contact time was increased from 10 to 50 min. Percent reductions in TOC and COD for artificial light-assisted treated synthetic effluent were 74.3% and 73.4%, respectively at 50 min contact time. While percent reduction in TOC and COD for solar light-assisted treated synthetic effluent were 87.2% and 86.7%, respectively at 50 min contact time. Both artificial light-assisted and solar light-assisted photocatalytic reactions enhanced the degradation of synthetic dyes effluent in comparison to non-photocatalytic degradation of synthetic dyes effluent under study [42]. Both photocatalytic processes increased the removal percentage of both quality assurance parameters as the reaction time was increased depicted the mineralization progress [43].

5. Conclusion

This work provides a possible and remarkable method for the treatment of industrial dyes wastewater by using ZVI. The maximum decolorization (68.64%) of synthetic dyes effluent was obtained at its concentration of 0.02% at pH = 8, ZVI dose 0.1 g mL^{-1}, 75 min reaction time,

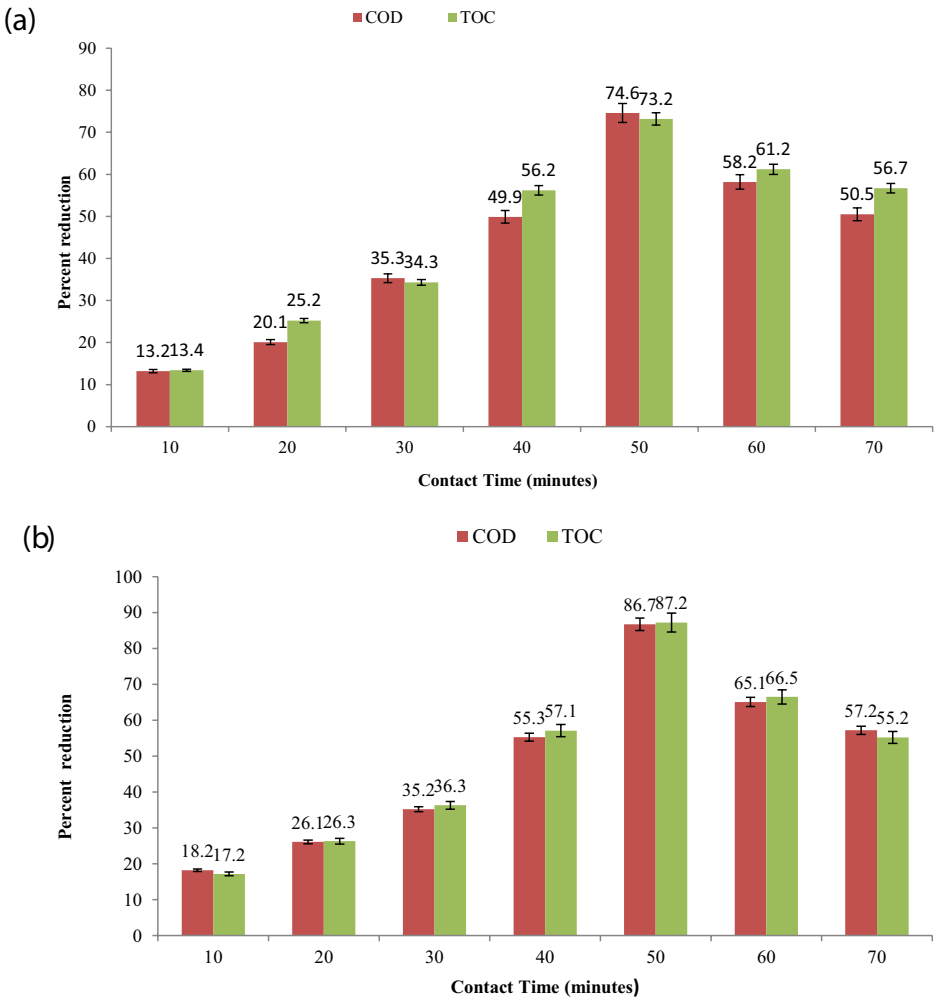

Fig. 5. Effect of photocatalytic treatment (of synthetic effluent) contact time on water quality parameters in presence of artificial light (a) and solar light (b).

temperature = 40 °C, while decolorization efficiency of synthetic dyes effluent was raised to 76.74% using the artificial light intensity of 2,500 lux and 83.43% in solar light during noon timings. The catalytic efficiency of the studied method was assessed using COD (86.7%) and TOC (87.2%) measurements, which declared the degradation of synthetic dyes effluent. Decolorization by ZVI is a rapid, effortless, and reasonable process. This approach can also be utilized promisingly for the decolorization of industrial wastewater in the presence of solar as well as artificial light.

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