Removal of methylene blue, a basic dye, from aqueous solutions using nano-zerovalent iron

Simin Arabi and Mahmoud Reza Sohrabi

ABSTRACT

In this research, the preparation of nanoparticles of Fe^0 (nano-zerovalent iron, NZVI) as adsorbent is discussed and the capability of adsorbing methylene blue (MB) is studied. The morphology of the adsorbent was evaluated with transmission electron microscopy. Batch studies were performed to delineate the influence of various experimental parameters such as pH, adsorbent dosage, initial dye concentration, temperature and contact time. Optimum conditions for MB removal were found to be pH 9.5, adsorbent dosage of 0.5 g L^{-1} and equilibrium time of 1 min. The experimental equilibrium data were adjusted by the adsorption isotherms from Langmuir and Freundlich models, and their equilibrium parameters were determined. The adsorption of MB dye by NZVI obeyed both the Freundlich and Langmuir isotherm. The adsorption capacity of NZVI for MB in terms of monolayer adsorption was 208.33 mg g^{-1}.

Key words | adsorption, adsorption isotherm, dye removal, methylene blue, nano-zerovalent iron

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INTRODUCTION

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries (Gulnaz *et al.* 2004). Colored material discharged from these industries poses certain hazards and environmental problems. These colored compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystems. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade (Barragán *et al.* 2007). Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities. These materials are the complicated organic compounds and they resist light, washing and microbial invasions. Thus, they cannot be decomposed easily (Wang *et al.* 2008). Direct discharge of dye-containing effluents into the municipal environment may cause the formation of toxic carcinogenic breakdown products. Methylene blue (MB) is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3SCl$. It is the most frequently used substance for dyeing silk, wood and cotton and has a number of biological uses. It has severe impact on human health; for example ingestion through the mouth may cause nausea, vomiting, diarrhea, etc. Thus, removal of MB from wastewater is of great concern from an environmental point of view. The conventional methods for treating dye-containing wastewaters are electrochemical treatment, coagulation and flocculation, chemical oxidation, liquid–liquid extraction and adsorption (Oguz & Keskinler 2007). Use of clean methods of low-priced and biodegradable adsorbents could be a good tool to minimize the environmental impact caused by dye manufacturing and textile effluents. Currently, adsorption processes have been studied because of their low cost, easy access and effective dye removal whereby dissolved dye compounds attach themselves to the surface of adsorbents, and adsorption techniques are by far the most versatile and widely used. The most common adsorbent materials are alumina silica, metal hydroxides and activated carbon. The zerovalent iron (ZVI), an environmentally friendly strong reducing agent, has been widely studied for environmental remediation in recent years. Now, it has been used in treating and remedying wastewaters contaminated with chlorinated compounds, nitro aromatic compounds, nitrates, and heavy metals, and even for the deoxidization of more complex anthropogenic chemicals including pesticides and dyes (Uzum *et al.* 2008). Among these compounds, dyes are easier to be deoxidized than to be oxidized (Ghauch *et al.* 2009). Thus, deoxidization with ZVI is one of the most

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important paths of degradation. An innovative method using nano-zerovalent iron (NZVI) particles to increase the specific surface area of the ZVI has also been developed for decolorization of dyes. The advantage of ZVI particles for dye color removal include ease in use as a pre-treatment process and easy recycling of the spent iron powder by removal with magnets, as well as low residual iron concentration and no necessity for further treatment of the effluents. These ZVI particles were proposed as a reactive material in permeable reactive barriers due to their great ability in reducing and stabilizing different types of pollutants (Cho & Park 2006). ZVI particles have many advantages, such as nontoxicity, iron being abundant in nature, low cost, high reactivity, tiny particle size and higher density of reactive surface sites. This material with particle size at the nanoscale exhibits superior activity because of its larger surface area and higher activity (Cundy *et al.* 2008). However, similar to other nanomaterials, this ultra-fine powder has a strong tendency to agglomerate into larger particles, resulting in an adverse effect on both effective surface area and catalyst performance. Palygorskite as a supporting material for NZVI was investigated (Frost *et al.* 2010). ZVI was used for MB removal and, comparing with ZVI and unmodified polygorskite, palygorskite-supported ZVI showed much higher efficiency for MB removal with a very small amount of NZVI supported. It is likely that co-precipitation with *in situ* generated corrosion products is the main reason for the uptake of MB from solution (Schwertmaann *et al.* 2005). The discoloration of MB in Fe^0/H_2O systems was investigated and the results showed that co-precipitation in Fe^0/H_2O systems may be primarily regarded as a non-specific mechanism in the decolorization MB. The mechanism of MB removal by Fe^0-based materials which may be suitable for environmental remediation (cast iron, low alloy steel) has not yet been systematically investigated. The mechanism of adsorption of MB and its congeners onto stainless steel particles was investigated (Imamura *et al.* 2002). MB has also been used for corrosion inhibition of mild steel in acid solution (Oguzie 2005). The literature on 'Fe^0 Technology' is characterized by the fact that, since the effectiveness of Fe^0 reactive walls to degrade solvents has been demonstrated, applying Fe^0 to treat other compounds can be performed without previous systematic investigations. Giles and co-workers have clearly shown that the concept of contaminant adsorption and co-precipitation as fundamental removal mechanism (Giles *et al.* 2011). Miyajima and Noubactep investigated the effect of mixing Fe^0 and sand on the efficiency of MB discoloration. The efficiency of the Fe^0/sand system for contaminant reduction corroborates the adsorption co-precipitation concept (Noubactep 2010, 2011a, b). In this paper, the possibility of using nanoparticles of ZVI to remove MB from aqueous solution was investigated using batch adsorption studies. The effect of various factors such as contact time, pH, initial dye concentration, temperature and NZVI dosage on the removal efficiency of NZVI was also studied. Adsorption isotherms and kinetic studies were also investigated in order to understand the adsorption mechanism and efficiencies of NZVI.

EXPERIMENTAL

Materials

The following chemicals were used in this study. Sodium borohydride ($NaBH_4$) and ferric chloride ($FeCl_3.6H_2O$) were purchased from Merck. MB (C.I. 52015) was obtained from Alvan Sabet Co. and was used without further purification. All other reagents were analytical reagent grade. Deionized water was used throughout this study. Adjustment of pH of the dye solution prior to adsorption was carried out with NaOH or HCl from Merck.

Preparation of NZVI particles

NZVI particles were prepared by liquid phase reduction method. All solvents were degassed and saturated for 30 min with N_2 before use. NZVI was synthesized by adding 1 M $NaBH_4$ solution into 0.5 M $FeCl_3$ solution during vigorous stirring under N_2 atmosphere. The mixture's color turned from red brown to light yellow and then eventually to black. At the same time the mixture gradually produced more black particles in the three-neck flask. Ferric iron (Fe^{3+}) was reduced to elemental iron according to the following reaction:

$$4Fe^{+3} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0(s) + 3H_2BO_3^-(aq) + 12H^+ + 6H_2 \quad (1)$$

Then black NZVI particles were vacuum-filtered and washed with deionized water and 1:1 (V/V) ethanol/acetone. Doing so prevented the NZVI from oxidizing, and then the resulting gray-black solid was dried under nitrogen atmosphere before use (Zhang 2003). In addition, the surface morphology of NZVI was observed with transmission electron microscopy (TEM, JEM-2100F HR, 200 kV).

Adsorption experiments

Adsorption of MB on NZVI was carried out using a batch experiment method. The effect of contact time, solution pH, temperature and NZVI dosage was investigated. For the determination of adsorption isotherms, 50 mL of dye solution of known initial concentration (10–100 mg L^{-1}) was shaken with a certain amount of the adsorbent (0.5 g) on a rotary shaker at 150 rpm. The contact time was varied from 0 to 140 s. Sample solutions were withdrawn at predetermined time intervals for the color removal analysis. In the pH study, the pH of MB solution was adjusted in the range of 2.5–12 by adding 0.5 M HCl or 0.5 M NaOH. About 0.5 g NZVI was then added to the solution and shaken for a predetermined time. In the experiment to investigate the effect of NZVI dosage on MB adsorption, various amounts of adsorbent in the range of 0.1–0.9 g were added to 30 mg L^{-1} MB without pH adjustment and shaken until equilibrium. The influence of temperature on the dye adsorption was investigated at 298, 308, 318 and 328 K under the optimized conditions of 60 s of contact time and 0.5 g of NZVI. After shaking the flasks for predetermined time intervals, all samples were withdrawn from the conical flasks and the MB solutions were separated from the adsorbent by filtration then followed by centrifugation. The residual dye concentration in the supernatant solutions was analyzed using a spectrophotometer (Varian CARY-300 UV-visible spectrophotometer, BioTech) at a wavelength of 665 nm. The adsorption capacity of dye on adsorbent was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where C_0 and C_e are the dye concentrations in mg L^{-1} initially and at a given time t, respectively, V is the volume of dye solutions in L, and w is the weight of sorbent in g.

Characterization

Figure 1(a) shows the TEM image of freshly synthesized iron nanoparticles. Surface morphology shows that there exist two layers in the NZVI particle. The layer of the inside core represents the Fe^0, and the outer layer surrounding the Fe^0 was iron oxide(s). Figure 1(b) shows that the MB molecules covered the NZVI surface confirm the successful attachment of MB to the NZVI.

RESULTS AND DISCUSSION

Characterization of the synthesized NZVI particles

The Brunauer–Emmett–Teller surface area analysis indicated that the average specific surface of the synthesized NZVI was 35 m^2 g^{-1}. Figure 1(a) shows the image of the synthesized NZVI particles as observed by TEM. The TEM image shows that most of the NZVI particles were less than 100 nm in diameter. The synthesized nanoparticles had a uniform shape and the powdery particles had a spherical morphology. The chain-like structures may have resulted from both the effects of static magnetism and surface tension. Several large-sized particles may have come from agglomeration of nanoparticles due to their magnetic properties.

Effect of contact time

The influence of contact time on adsorption of MB was studied under the following experimental conditions: initial concentration 30 mg L^{-1}, and NZVI dosage 0.5 g per 50 cc. As shown in Figure 2, uptake of dye increased instantly and reached a high value within 60 sec. This meant that a large number of adsorption sites on the NZVI surface were available at this process. Thereafter, the amount of adsorbed MB

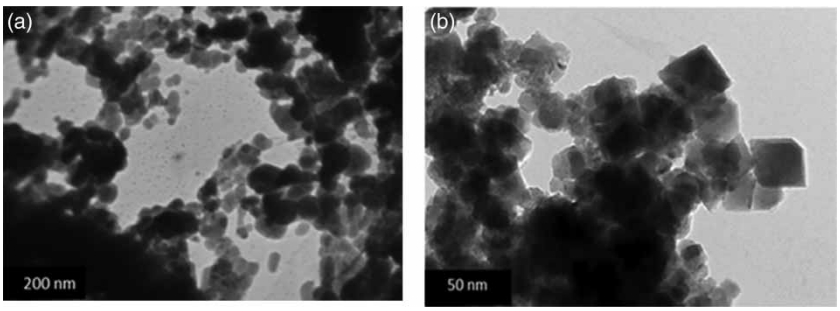

Figure 1 | TEM images of (a) NZVI and (b) NZVI after adsorption of MB.

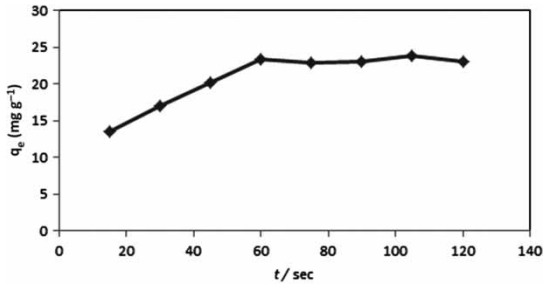

Figure 2 | Effect of contact time on the adsorption of MB onto NZVI.

did not significantly change with time due to the equilibrium of the repulsive forces between the MB molecules on the solid and in the bulk phases. This trend indicated the NZVI was saturated with the adsorbate at this stage. Based on the results, the adsorption time was fixed at 1 min for the rest of the batch experiments to make sure that adsorption equilibrium was reached.

Effect of initial concentration

The effect of initial dye concentration on the removal of MB by NZVI is shown in Figure 3. It is evident from the figure that an increase in the initial concentration leads to a decrease in the adsorption efficiency. This is due to increase in initial dye concentration, and adsorption sites on the surface area of the NZVI are saturated. Therefore, it can be said that the adsorption is increased instantly at initial steps due to rapid attachment of dye to the surface of the NZVI, and then keeps increasing gradually until the equilibrium is reached and then remains constant.

Effect of pH

Dependence of dye adsorption on pH is shown in Figure 4. Dye adsorption efficiency is affected by pH variation. The adsorption of MB increased with an increase in pH. The

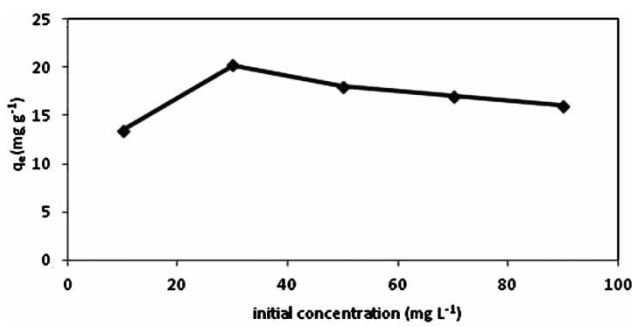

Figure 3 | Effect of the initial dye concentration on the adsorption of MB onto NZVI.

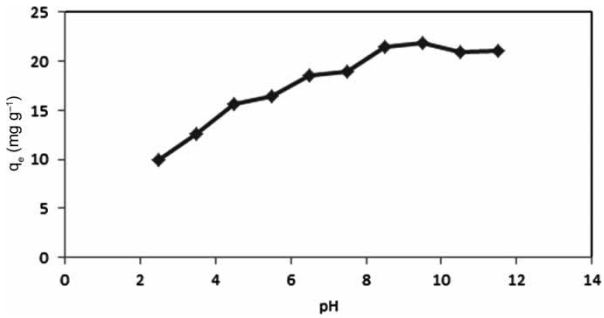

Figure 4 | Effect of solution pH on the adsorption of MB onto NZVI.

optimum pH for the adsorption of MB was found to be 9.5. This can be explained by considering the electrostatic attraction that exists between the negatively charged surface of the NZVI and MB, a cationic dye. Lower adsorption at acid pH was probably due to the presence of excess H^+ ions competing with the dye cations for adsorption site. The surface of the NZVI is positively charged and, as MB dye is a cationic dye, a positively charged surface site on the NZVI does not favor the adsorption of dye cations due to the electrostatic repulsion. At alkaline pH, the number of positively charged sites decreases and the number of negatively charged sites increases, which favors the removal of the cationic dye. Similar trends were observed for the adsorption of Malachite green onto agro-industry waste (Garg *et al.* 2004) and MB onto various carbons (Kannan & Sundaram 2001).

Effect of NZVI dosage

The effect of NZVI dosage on the removal of MB by NZVI at initial concentration ($C_0 = 30$ mg L^{-1}) is shown in Figure 5. Results express that MB removal increase up to a certain limit and then it remains almost constant. It can be interpreted that the dosage of NZVI increased the adsorptive

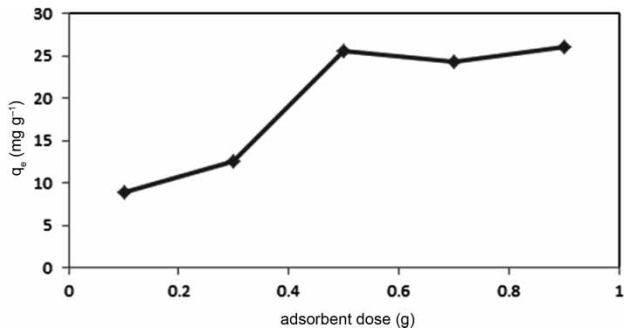

Figure 5 | Effect of adsorbent dosage on the adsorption of MB onto NZVI.

surface area and the number of active sites correspondingly increased since the removal process had occurred at the Fe^0–H_2O interface. The equilibrium removal time of NZVI in removing the MB was prolonged when the dosage of NZVI increased for a given initial concentration. This may be attributed to the decrease in removal surface area and active sites available to dye molecules resulting from intermolecular competition and formation of iron oxide on the surface of NZVI particles. Furthermore, the removed amount of dye gradually decreased as reaction time increased. A similar result has been reported for degradation of azo dye acid Black 24 when using NZVI (Shu *et al.* 2007).

Effect of temperature

The effect of temperature on adsorption of MB on NZVI was investigated by varying adsorption temperatures at 298, 308, 318 and 328 K using 0.5 g of adsorbent NZVI at pH 9.5. Figure 6 shows that an increase in the temperature from 298 to 328 K leads to an increase in the adsorption capacity at an equilibrium time, indicating the endothermic nature of the adsorption reaction. This increases the amount of material to be adsorbed on the surface. Increase in temperature also decreases the activation energy barrier thereby increasing the rate of adsorption (Shukla *et al.* 2002). The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbate and NZVI, creation of some new adsorption sites or the increased rate of intraparticle diffusion of MB molecules into adsorbent at higher temperatures (Karthikeyan *et al.* 2005).

Adsorption isotherm

Langmuir isotherm

Langmuir theory is based on the assumption that adsorption is a type of chemical combination or process and the adsorbed layer is unimolecular. The theory can be represented by the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{3}$$

where C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount of dye adsorbed at equilibrium (mg g^{-1}) and Q_0 (mg g^{-1}) and b (L mg^{-1}) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The values of Q_0 and b were determined for all adsorbents from intercept and slopes of the linear plots of C_e/q_e versus C_e (Figure 7). The good fit of the experimental data and the correlation coefficient (R^2) of 0.99 indicated the applicability of the Langmuir isotherm model.

The constants b and Q_0 can be calculated from the slope and intercept of the plot, and the values are tabulated in Table 1. The maximum monolayer adsorption capacity of NZVI was found to be 208.33 mg g^{-1}. The shape of the

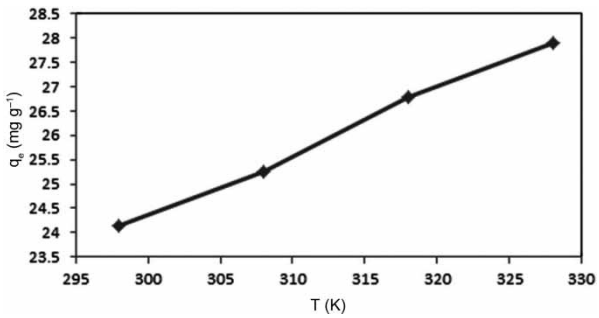

Figure 6 | Effect of temperature on the adsorption of MB onto NZVI.

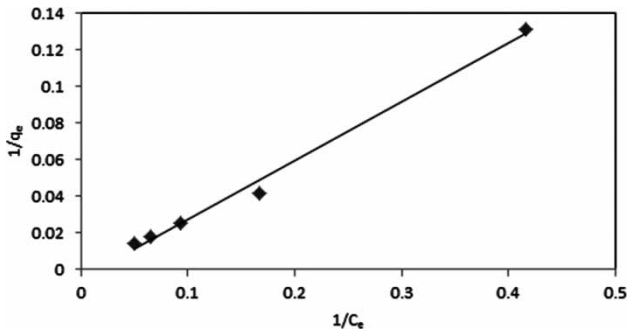

Figure 7 | Langmuir adsorption isotherm for MB adsorption on NZVI.

Table 1 | Parameters of Langmuir and Freundlich isotherms for MB adsorption on NZVI

	Langmuir isotherm				Freundlich isotherm		
	Q_0 (mg g^{-1})	b(L mg^{-1})	R_L	R^2	K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	1/n	R^2
MB	208.33	0.6149	0.05	0.9927	3.3304	1.0352	0.9902

Langmuir isotherm was investigated by the dimensionless constant separation factor or equilibrium parameter (R_L) to determine high affinity adsorption. R_L was calculated as follows:

$$R_{\mathrm{L}} = \frac{1}{1 + bC_0} \tag{4}$$

where C_0 is the initial dye concentration (mg L^{-1}). R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). In the present study, the value of R_L was observed to be in the range 0–1 indicating the adsorption process is favorable (Figure 7).

Freundlich isotherm

The Freundlich adsorption model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surfaces. The amount of solute adsorbed, q_e, is related to the equilibrium concentration of solute in solution, C_e, following:

$$q_e = K_F C_e{}^{1/n} \tag{5}$$

This expression can be linearized to give the following equation:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{6}$$

where K_F (L g^{-1}) is a constant for the system related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto NZVI for a unit equilibrium concentration (a measure of adsorption capacity, mg g^{-1}). The slope $1/n$, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for $1/n$ below 1 indicates a normal Freundlich isotherm while $1/n$ above 1 is indicative of cooperative adsorption. The model parameters and R^2 value (0.99) indicated that this model showed high correlation with the experimental data (Figure 8). The value of slope $1/n$ (1.0352) indicates a cooperative isotherm. The adsorption of MB dye by NZVI obeyed both the Freundlich and Langmuir isotherm.

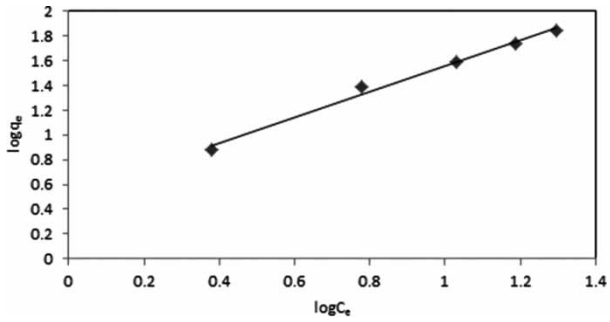

Figure 8 | Freundlich adsorption isotherm for MB adsorption on NZVI.

Kinetic studies

A quantitative understanding of the adsorption is possible with the help of kinetic models. The pseudo-first-order kinetic model can be written as:

$$\log\,(q_e - q_t) = \log\, q_e - \frac{k_1}{2.303}t \tag{7}$$

where q_e and q_t are the amounts of MB (mg g^{-1}) at equilibrium and at time t, respectively, and k_1 is the pseudo-first-order equilibrium rate constant (sec^{-1}). A plot of log (q_e–q_t) vs t (Figure 9) gives a straight line confirming the possibility of the applicability of the pseudo-first-order rate equation ($R^2 = 98.71$). From the plot, k_1 and q_e are determined from the slope and intercept respectively as shown in Table 2.

The pseudo-second-order adsorption rate equation may be expressed as follows (Bouhamed *et al.* 2012):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where k_2 (g mg^{-1} s^{-1}) is the rate constant of second-order adsorption. If second-order kinetics is applicable, the plot of t/q_t versus t should show a linear relationship (Figure 10).

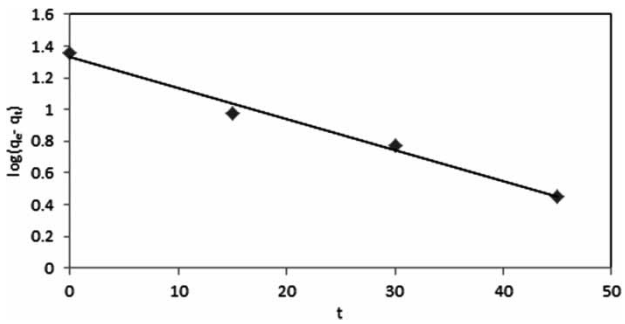

Figure 9 | The pseudo-first-order kinetic of MB adsorption on NZVI at 30 °C.

Table 2 | The values of parameters and correlation coefficients of kinetic models for MB adsorption on NZVI

	Pseudo-first-order k_1(1/sec)	q_e(mg g^{-1})	R^2	Pseudo-second-order k_2(g/mg sec)	q_e(mg g^{-1})	R^2
MB	0.01960	21.468	0.9871	0.0022	27.472	0.9948

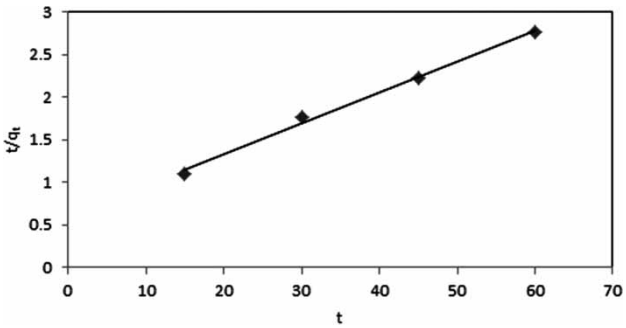

Figure 10 | The pseudo-second-order kinetic of MB adsorption on NZVI at 30 °C.

The values of q_e and k_2 can be determined from the slope and intercept of the plot. The correlation coefficient for the pseudo-first-order ranged between 0.98 and 0.99 whereas the value for the second-order ranged between 0.99 and 1. The higher correlation coefficient indicates that the experimental data best fitted into the pseudo-second-order and suggests that the process of adsorption follows pseudo-second-order kinetics.

CONCLUSIONS

The findings suggest the NZVI is a strong reducing agent for the treatment of dyeing industry wastewater. The experimental data were well described with Langmuir and Freundlich isotherm models. The pseudo-second-order kinetic model fits very well with the dynamical adsorption behavior of MB dye. It was shown that the rate of adsorption of MB on NZVI increases with the increase in temperature, thus suggesting the reaction to be spontaneous and endothermic in nature. The present study indicated that NZVI could be employed as a reactive medium for the removal of MB from industrial and other effluents.

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