Adsorption kinetics and thermodynamics of vat dye onto nano zero-valent iron

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Received 25 September 2012 ; accepted 12 November 2012

Nano zero-valent iron (NZVI) particles have been synthesized by the aqueous phase borohydride reduction method, and the synthesized NZVI particles are used for the removal of Vat green 1 dye in aqueous solution. The effect of parameters like initial dye concentration, pH, adsorbent dose, temperature and contact time on the adsorption process are investigated. The studied adsorbent exhibits high efficiency for vat green 1 adsorption and the equilibrium state is achieved in 1 min. For equilibrium studies, three isotherm models, namely Langmuir, Freundlich and Temkin are used. It is found that Freundlich is fitted very well with the experimental data. In the kinetics studies, pseudo-first order, pseudo-second order and intra-particle diffusion model are tested. The pseudo-first order equation provides the best correlation with the obtained data. Different thermodynamic parameters, like Gibb’s free energy enthalpy and entropy of the adsorption process have also been evaluated. Observed thermodynamic parameters indicate that the process is spontaneous and endothermic.

Keywords: Adsorption kinetics, Isotherms model, Nano zero-valent iron, Thermodynamic parameter, Vat green 1 dye

Dyes are organic compounds consisting of two main groups, namely chromophores (responsible for color of dye) and auxochromes (responsible for intensity of color)\(^1\). Dyes having the synthetic origin show complex aromatic molecular structures which make them more stable and more difficult to biodegrade\(^6\). It is estimated that 10-15% of the dye is lost in the effluent during the dyeing process\(^3,4\). Vat dyes are extensively used for dyeing cotton fabrics. Amongst vat dyes, Vat green 1 is commonly used for dyeing of denim\(^5\). Cotton is the most widely used fabric among all textiles, hence vat dyes are frequently discharged in large quantities into the environment. Vat dyes due to their poor exhaustion properties (5-20% of the applied initial dye) remain unfixed and ends up in effluents\(^6\). Due to its properties, vat dye is mainly used in the textile industry\(^7-11\). There are many physical, chemical and biological methods used for the removal of dye from aqueous solution, including chemical coagulation, flocculation, chemical oxidation, photochemical degradation, membrane filtration, reverse osmosis, and aerobic/anaerobic degradation. All of these techniques suffer from one or more limitation, and none of them is able to completely remove dyes from wastewater\(^8,11\).

Thus, there is a need to find alternative methods that are effective in removing dyes from large volumes of effluents. Zero-valent iron nanoparticle technology is becoming an increasingly popular choice for treatment of hazardous and toxic wastes, and for remediation of contaminated sites. Research is currently actively being conducted to better understand the advantages of using nanoscale versus micro scale particles, as well as the fate and transport of nanoparticles once released into the environment. The diminutive size of the iron nanoparticles helps to faster effective subsurface dispersion where as their large specific surface area corresponds to enhanced reactivity for rapid contaminant transformation. In recent years, nanoscale zero-valent iron (NZVI) technology has received growing attention for its high efficiency in eliminating a variety of pollutants, including heavy metals\(^12-16\), chlorinated organics\(^17-19\), nitroaromatic compounds\(^20,21\), polybrominated diphenyl ethers\(^22,23\), nitrates\(^24,25\), pesticides\(^26,27\), dyes\(^28,29\), etc. Vat dyes being water insoluble have to be first converted into water soluble form (Leuco dte) by reduction with a strong reducing agent. Among the different methods for reducing vat dyes, use of NZVI as a strong reducing agent affect efficiency. Because of its small particle size, large specific surface area, high density and great intrinsic reactivity of reactive surface sites, NZVI has gained prominence for applications in environmental remediation\(^30,31\). Based on these characteristics, the NZVI technology could become a promising approach for treating dyestuff wastewater. The present study is undertaken to

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evaluate the efficiency of NZVI for removal of dye in wastewater. In order to design on adsorption treatment system, knowledge of the kinetic and mass transfer processes is essential. In this paper, we report the applicability of thermodynamic for the adsorption of vat green 1.

Experimental Procedure

Materials
Sodium borohydride (NaBH₄) and ferric chloride (FeCl₃.6H₂O) were purchased from Merck. Vat green 1 (C₃₆H₄₀O₄, C.I. 59825) 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.

Preparation of NZVI particles
NZVI particles were prepared by liquid phase reduction method. All solvents were degassed and saturated for 30 min with N₂ before use. Nano zero-valent iron was synthesized by adding 1M NaBH₄ solution into 0.5 M FeCl₃ solution during vigorously stirring under N₂ atmosphere. 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 grain particles in the three-neck flask. Ferric iron (Fe³⁺) was reduced and zero-valent iron particles precipitated instantly according to the following reaction:

\[ 4\text{Fe}^{3+} + 3\text{BH}_4^- + 9\text{H}_2\text{O} \rightarrow 4\text{Fe}^0 (s) + 3\text{H}_2\text{BO}_3^- (aq) + 12\text{H}^+ + 6\text{H}_2 \] (1)

Then black NZVI particles were vacuum-filtered and washed with deionized water and 1:1 (v/v) ethanol/acetone. This prevented the NZVI from oxidizing, and then the resulting gray-black solid was dried under nitrogen atmosphere before use. A scanning electron microscope (JEOL JSM-5600 Digital) was used to characterize the NZVI for its morphological information.

Adsorption studies
Adsorption of vat green 1 by NZVI was carried out by batch method and the influence of various parameters such as contact time (15-120 s), adsorbent dosage (0.1-0.9 g/L), pH (1.5-9), initial dye concentration (20, 30, 40, 50 and 60 mg/L), temperature (298, 308 and 318K) were studied. The adsorption measurements were conducted by mixing various amounts of NZVI in glass Erlenmeyer flasks containing 50 mL of dye solution of known concentration. The pH of the solution was adjusted to the desired value by adding small amount of HCl or NaOH (0.1M). At the end of determined time intervals, the samples were taken out and the supernatant solution was separated from the NZVI by centrifugation at 3500 rpm for 10 min and the adsorption capacity of dye on adsorbent was calculated using the following relationship:

\[ q_e = \frac{(C_a - C_c)V}{W} \] (2)

where \( C_a \) and \( C_c \) are the dye concentrations (mg/L) initially and at a given time \( t \) respectively; \( V \), the volume of dye solutions (L); and \( W \), the weight of adsorbent (g). To evaluate the fitness of kinetic and isotherm equations to the experimental data, the average relative error (ARE) was used to measure the kinetic and isotherm constants. ARE can be defined as:

\[ \text{ARE} = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{q_{\text{cal}} - q_{\text{Exp}}}{q_{\text{Exp}}} \right| \] (3)

where \( n \) is the number of data points. Each experiment was conducted in triplicate under identical conditions to confirm the results, and was found reproducible (experimental error within 3%).

Results and Discussion
Characterization of adsorbent
Figure 1a shows the SEM image of freshly synthesized iron nanoparticles. It can be observed that the iron particles are in the form of nanospheres, which exist in contact with each other and form chains having diameters of 50-100 nm. Figure 1b shows that the Vat green 1 molecules onto the NZVI surface are covered.

Effect of contact time
Figure 2a shows that the adsorption of Vat green 1 increases with increasing time and attains saturation in about 1 min. At this time, due to saturation of adsorption sites on adsorbent, the dye removal efficiency does not change. Basically, the removal of adsorbate is rapid, but it gradually decreases with time until it reaches equilibrium. To investigate the kinetics of adsorption, initial concentration of dye is chosen as 30 mg/L.

Effect of initial concentration
The dye uptake mechanism is particularly dependent on the initial Vat green 1 concentration.
As the initial dye concentration increases, the adsorption efficiency by NZVI decreases. This is due to increase in dye concentration, surface area, and saturated active sites of the adsorbent, and hence the adsorption efficiency is decreased. Similar trends have been observed for the reduction of azo dye Acid Black 24, Methyl Orange, Orange I, Orange II and Reactive Blue 4 by NZVI.

Effect of pH

The effect of pH was investigated by employing 30 mg/L initial concentration of dye and 0.5 g of NZVI. The initial pH values are adjusted with 0.1M HCl and 0.1M NaOH to form a series of pH from 1.5 to 9 (Fig. 2b). The adsorption capacity of Vat green 1 at low pH is better than that at higher pH. This result may also attributed to a $pH_{zpc}$ (zero point charge) of NZVI. Lie et al. indicated that the $pH_{zpc}$ of NZVI is at around 8. At low pH ($<pH_{zpc}$), the NZVI surface has positive charge, and the dye molecules have a negative charge, so the adsorption of dye into the iron surface is improved. At a high pH, the NZVI surface could be coated by the corrosion products containing Fe(II)- or Fe(III) hydroxides and oxides, which inhibits further reaction. Thus, acidic conditions are favorable for this process. Similarly, Chang et al. reported that reducing the pH to 2.1, 3.0 and 4.0 for Acid Black 24 (AB 24), the removal by NZVI particles results in a significant increase in decolorization efficiency and elevating the pH of dye wastewater to 9.0, 10.2 and 10.9 results in a lower decolorization efficiency of Acid Black 24 over the original pH of 6.4. This trend of slower destruction kinetics with increasing pH has previously been observed while treating other chemicals with NZVI, such as chlorinated etanes, atrazine and antibiotic metronidazole.

Effect of adsorbent dosage

The effect of adsorbent dose is studied at room temperature by varying the NZVI amounts from 0.1 g to 0.9 g. For all these runs, initial concentration of Vat green 1 is fixed as 30 mg/L. Figure 2c shows that the adsorption of Vat green 1 increases rapidly with increase in the amount of NZVI up to a certain limit and then it remains almost constant. Increase in adsorption with adsorbent dosage can be attributed to increased adsorbent surface area and availability of more adsorption sites. Shih et al. and Fan et al. observed the same trend in degradation of azo dyes using various amount of NZVI. The maximum adsorption of Vat green 1 is obtained using the adsorbent dosage of 0.5 g L$^{-1}$.
Effect of temperature

To study the effect of temperature on the removal of dye, the experiments were carried out at temperature varying from 298 K to 318 K (Fig. 2d). The adsorption capacity of Vat green 1 onto NZVI is found to increase with a rise in temperature, indicating that the process is endothermic. The enhancement in the adsorption capacity might be due to the enhancement of adsorptive interaction between the active sites of adsorbent and adsorbate ions.

Adsorption isotherms

The equilibrium adsorption isotherm is one of the most important data to understand the mechanism of the adsorption systems. Langmuir, Freundlich and Temkin isotherm equations were used to interpret the experimental data.

Langmuir isotherm

Langmuir isotherm theory is based on the assumption that adsorption on a homogeneous surface, i.e., the surface consists of identical sites, equally available for adsorption and with equal energies of adsorption and that the adsorbent is saturated after one layer of adsorbate molecules forms onto surface. The linearized form of the Langmuir adsorption isotherm equation is

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m}$$

... (4)

The Langmuir constants, ($q_m$ and $K_L$) can be calculated from the plot $\frac{c_e}{q_e}$ versus $C_e$. Figure 3a shows the Langmuir adsorption isotherm of the Vat green 1 onto NZVI. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter $R_L$, which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_e}$$

... (5)

The $R_L$ value indicates the type of the isotherm to be either irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). All of the isotherm model parameters for the dye onto NZVI are listed in Table 1.

Freundlich isotherm

The linearized Freundlich isotherm equation that corresponds to the adsorption on heterogeneous surface is given as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

... (6)

where $C_e$ is the equilibrium concentration of solute (mg/L); and $q_e$, the equilibrium adsorption capacity (mg/g). The Freundlich isotherm constants $K_F$ and $(1/n)$ can be calculated from the plot of $\ln q_e$ versus

Table 1 — Isotherm constants for adsorption of Vat green 1 on NZVI

<table>
<thead>
<tr>
<th>Isotherm constants</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir isotherm</td>
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<tr>
<td>$q_m$, mg/g</td>
<td>70.92</td>
</tr>
<tr>
<td>$K_L$, L/mg</td>
<td>0.033</td>
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<tr>
<td>$R_L$</td>
<td>0.82</td>
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<tr>
<td>$R^2$</td>
<td>0.9976</td>
</tr>
<tr>
<td>ARE</td>
<td>1.7</td>
</tr>
<tr>
<td>Freundlich isotherm</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>1.457</td>
</tr>
<tr>
<td>$K_F$, mg/g</td>
<td>3.852</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9970</td>
</tr>
<tr>
<td>ARE</td>
<td>1.9</td>
</tr>
<tr>
<td>Temkin isotherm</td>
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</tr>
<tr>
<td>$B$</td>
<td>163.34</td>
</tr>
<tr>
<td>$K_T$, L/mg</td>
<td>0.3315</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9830</td>
</tr>
<tr>
<td>ARE</td>
<td>3.6</td>
</tr>
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</table>

Fig. 3 — Plots of (a) Langmuir isotherm (b) Freundlich isotherm and (c) Temkin isotherm for Vat green 1 adsorption on NZVI
$lnC_e$ (Fig. 3b). The slope $(1/n)$ measures the surface heterogeneity. Heterogeneity becomes more prevalent as $1/n$ gets closer to zero.

**Temkin isotherm**

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. The linearized equation is:

$$q_e = B \ln K_T + B \ln C_e$$ \hspace{1cm} \ldots (7)

where $B = \frac{RT}{b}$ and $K_T$ is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy and constant $B$ is related to the heat of adsorption ($b$ and $K_T$ are the constants). A plot of $q_e$ versus $lnC_e$ (Fig. 3c) enables the determination of the isotherm constants and $B$. Values of $K_T$ and $B$ as obtained are shown in Table 1 along with the values of the correlation coefficients and average relative error.

**Adsorption kinetics**

In order to analyze the adsorption kinetics of Vat green 1, the pseudo-first and pseudo second order and intra-particle diffusion models are applied to data.

**Pseudo-first order model**

The first order rate equation of Lagergren is one of the most widely used for the sorption of a solute from liquid solution \cite{49} and is represented as:

$$ln(q_e - q_t) = ln(q_e) - k_1 t$$ \hspace{1cm} \ldots (8)

where $q_e$ is the mass of metal adsorbed at equilibrium (mg/g); $q_t$, the mass of dye adsorbed at time $t$ (mg/g); and $k_1$, the first-order reaction rate constant (l/s). The pseudo-first order considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites. A straight line of $ln(q_e - q_t)$ versus $t$ indicates the application of the first-order kinetic model (Fig. 4a).

**Pseudo-second order model**

The adsorption kinetics may also be described by a pseudo second-order equation \cite{50-53}. The differential equation is given below:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$ \hspace{1cm} \ldots (9)

where $q_e$ and $q$ are defined as in the pseudo first-order model; and $k_2$, the rate constant of the pseudo second-order model for adsorption (g/mg s) (ref. 54). The slope and intercept of the linear plot of $\frac{t}{q_t}$ against $t$ yield the values of $q_e$ and $k_2$. Figure 4b shows a plot of linearization form of pseudo first-order model at all concentrations studied.

**Intra-particle diffusion model**

The intra-particle diffusion model is expressed as \cite{55}:

$$q = \frac{1}{2} K_1 t^{1/2} + C$$ \hspace{1cm} \ldots (10)

where $C$ is the intercept which gives an idea about the boundary layer thickness; and $k_1$, the intra-particle diffusion rate constant (mg/g s^{0.5}), which can be evaluated from the slope of the linear plot of $q$ versus $t^{1/2}$ (ref. 56). Figure 5 shows linearized form of the intra-particle diffusion model at all concentrations studied. Table 2 shows the coefficients of the pseudo-first and second order adsorption kinetic models, and the intra-particle diffusion model.

**Thermodynamic studies**

Spontaneity of a process can be determined by thermodynamic parameters such as enthalpy

![Fig. 4](image_url) — (a) Pseudo-first order plot and (b) pseudo-second order plot for adsorption of Vat green 1 by NZVI

![Fig. 5](image_url) — Intra-particle diffusion plot for adsorption of Vat green 1 by NZVI
change ($\Delta H^o$), free energy change ($\Delta G^o$) and entropy change ($\Delta S^o$). A spontaneous process will show a decrease in $\Delta G^o$ value with increasing temperature. The thermodynamic parameters such as change in free energy ($\Delta G^o$) (J mol$^{-1}$), enthalpy ($\Delta H^o$) (J mol$^{-1}$) and entropy ($\Delta S^o$) (J K$^{-1}$ mol$^{-1}$) are determined using the following relationships:

$$\Delta G^o = -RT \ln K^o$$  \hspace{1cm} (12)

$$K^o = \frac{q_e}{c_e}$$  \hspace{1cm} (13)

$$\ln K^o = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$  \hspace{1cm} (14)

where $K^o$ is equilibrium constant; $T$, absolute temperature (K); and $R$, gas constant. $\Delta H^o$ and $\Delta S^o$ values are obtained from the slope and intercept of plot $\ln K^o$ against $1/T$. Figure 6 shows effect of temperature on adsorption of vat green 1 onto NZVI (Van’t Hoff plot). The observed thermodynamic values are listed in Table 3.

The pseudo-first order model is identified as the best kinetic model for the adsorption of Vat green 1 on NZVI surface. Accordingly, the rate constants ($k_2$) of the pseudo-first order model are adopted to calculate the activation energy of the adsorption process using the following Arrhenius equation:

$$ln k_1 = ln A - \frac{E_a}{RT}$$  \hspace{1cm} (15)

where $k_1, A, E_a, R$ and $T$ are the rate constants of the pseudo-first order model (1/s), the Arrhenius factor, the activation energy (kJ/mol), the gas constant (8.314 J/mol K) and the temperature (K) respectively. The activation energy could be determined from the slope of the plot of $ln k_1$ versus $1/T$. The activation energy is found to be 73.10 kJ mol$^{-1}$ at 298 K and pH 4 for Vat green 1 adsorption on NZVI surface. The magnitude of the activation energy yields information on whether the adsorption is mainly physical or chemical. The physiosorption process usually has energies in the range 5–40 kJ mol$^{-1}$, while higher activation energies (40–800 kJ mol$^{-1}$) suggest chemisorption. The value of activation energy given confirms the nature of the chemisorptions process of Vat green 1 onto NZVI adsorbent.

### Table 2 — Adsorption kinetic model rate constants for Vat green 1 removal

<table>
<thead>
<tr>
<th>Rate constants</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
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</tr>
<tr>
<td>$q_e$, mg/g</td>
<td>22.47</td>
</tr>
<tr>
<td>$k_1$, 1/s</td>
<td>0.0523</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9941</td>
</tr>
<tr>
<td>ARE</td>
<td>1.3</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td></td>
</tr>
<tr>
<td>$q_e$, mg/g</td>
<td>33.55</td>
</tr>
<tr>
<td>$k_2$, g/mg s</td>
<td>0.0008</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9937</td>
</tr>
<tr>
<td>ARE</td>
<td>1.35</td>
</tr>
<tr>
<td>Intra-particle diffusion</td>
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</tr>
<tr>
<td>$k_i$, mg/g s$^{0.5}$</td>
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</tr>
<tr>
<td>$C$</td>
<td>0.4244</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9776</td>
</tr>
<tr>
<td>ARE</td>
<td>3.25</td>
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</table>

### Table 3—Thermodynamic parameters for adsorption of Vat green 1 on NZVI

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta G^o$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^o$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^o$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-1.641</td>
<td>42.50</td>
<td>148.13</td>
<td>0.9909</td>
</tr>
<tr>
<td>308</td>
<td>-3.360</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>318</td>
<td>-4.582</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 6 — Van’t Hoff plot for the adsorption of Vat green 1 on NZVI
16 and 1, which confirms that the prepared NZVI is favorable for adsorption of Vat green 1 dye. Kinetics of Vat green 1 adsorption onto NZVI follow the pseudo-first order model. Thermodynamics parameters indicate spontaneous and endothermic process.

References
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52 Ho Y S & Chiang C C, Adsorption, 7 (2001) 139.