Algorithms and statistics for municipal wastewater treatment using nano zero valent iron (nZVI)

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ORIGINAL RESEARCH ARTICLE

ABSTRACT

Nano Zero Valent Iron (nZVI), one of magnetic nanosorbents, was successfully prepared which is used in the removal of different wastewater contaminants simultaneously without adding any surfactant. The prepared nZVI was characterized by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Ultraviolet spectrophotometer. The prepared nZVI was tested for domestic wastewater treatment at different operating parameter for pH, nZVI dosage, contact time and stirring rate. The efficiency of treatment was evaluated according to the reduction in turbidity, total nitrogen (TN), total phosphorus (TP), chemical oxygen demand (COD), biological oxygen demand (BOD), ammonia, total suspended solids (TSS), and total dissolved solids (TDS). The optimum conditions for the effective removal was appeared at neutral pH using nZVI with 0.4 g/L dosage for 30 min with fixed stirring rate 150 rpm and the removal percentages was between 13 and 93% for the above mentioned parameter. Statistical analysis using Response surface methodology, Artificial neural networks was studied using linear regression and nonlinear Multi-Layer Perceptron algorithms, respectively, to predict the model’s significance, R2, standard error, probability, accuracy and importance of different covariables. The statistic models can describe the removal behavior of each contaminant in the separate step and estimate individual removal equation for any application.

KEYWORDS
Artificial Neural Networks (ANN); magnetic nanosorbents; Multilayer Perceptron (MLP); nZVI; Response Surface Methodology (RSM); wastewater treatment

1 INTRODUCTION

One of the main challenges in the field of water supply chain is continuous contamination of freshwater resources by different types pollutants (Schwarzenbach et al., 2006). This issue can be solved by focusing on the treatment of wastewater and drinking water (Ferroudj et al., 2013). However, the traditional methods of treatment such as adsorption, ion exchange, reverse osmosis chemical precipitation, electro-deposition, photocatalysis reduction, and solvent extraction are not efficient enough to completely remove the emerging contaminants and meet the strict water quality standards (Qu et al., 2012, Mostafa and Peters, 2016). But these traditional methods involve several disadvantages such as high energy requirement, incomplete pollutant removal and generation of toxic sludge (Burkhard et al., 2000). Hence, new processes are required to decontaminate selected pollutants and this can be achieved either by the development of completely new methods or by improving the existing methods through some interventions.

One of the existing technology is nanotechnology, nanomaterials have proved to be promising tools for treating wastewater and various other environmental problems (Sadegh et al., 2014, Gupta et al., 2015). It can be classified into three types: nano-adsorbents, nano-catalysts and nano-membranes. Wastewater treatment by adsorption
process increased gradually using different types of nanomaterials (Amin et al., 2014, Zhang et al., 2014, Shamsizadeh et al., 2014, Kyzas and Matis, 2015). It can be produced using the atoms of elements like clay materials, activated carbon, silica, or their composites (Kyzas and Matis, 2015). In the recent years, nanoscale metallic zero valent iron (nZVI) is studied as an adsorbent for contaminated water and soil. The technology has reached a commercial status in many countries worldwide. However, it is yet to gain universal acceptance abilities (O’Carroll et al., 2013, Boparai et al., 2011).

Nano zero valent iron (nZVI) has become a valuable material for its environmental remediation abilities. The specific character of nZVI refers to particle has an average size between 10 to 100 nm and a specific surface area of 20-25 m$^2$/g. Iron in zero oxidation state is very unstable and have strong reducer’s property (Lv et al., 2013).

Linear models describe a relationship between the target and one or more predictors. Enter (Regression); A procedure for variable selection in which all variables in a block are entered in a single step. Ghafari et al. (2009) has studied the application of response surface methodology (RSM) to optimize coagulation-flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum to apply and optimize the operating variables viz. coagulant dosage and pH using Quadratic models (Ghafari et al., 2009).

Neural networks are new tools to build predictive models (Salchenberger et al., 1992, Lek and Guégan, 1999). This module can discover the complex relationships in the data and expect better performing predictive models (Samarasinghe, 2016, Hansen and Salamon, 1990). A computational neural network is a set of non-linear data modeling tools consisting of input and output layers plus one or two hidden layers like human brain contain billions of neurons that connected together to process a variety of different information (Lek and Guégan, 1999, Agatonovic-Kustrin and Beresford, 2000). The connections between neurons in each layer have associated weights, which are iteratively adjusted by the training algorithm to minimize error and provide accurate predictions (Dietterich, 2000; Coulibaly et al., 2000). Neural networks programs can let the user set the conditions under which the network “learns” and can control the stopping rules and network architecture, or this process can occur automatically. Kim et al. (1988) explored Artificial Intelligence for U.S. Army Wastewater Treatment Plant Operation (WWTP) and Maintenance and focus their study was to increase performance and reduce the cost of army WWTP throughout by monitoring the operating system and detect the reasons leading to decrease the performance of the plant. Hamoda et al. (1999) studied integrated wastewater treatment plant performance evaluation using artificial neural networks for municipal wastewater treatment plant using backpropagation model. Aleboyeh et al. (2008) predicted azo dye decolorization by UV/H$_2$O$_2$ using artificial neural networks using multilayer feedforward networks and trained by 114 sets of input-output using a backpropagation algorithm and can expect the importance of H$_2$O$_2$ was 48 % (Aleboyeh et al., 2008). Bhatti et al. (2011) studied RSM and ANN modeling for electrocoagulation of copper from simulated wastewater as well as multi objective optimization using genetic algorithm approach (Bhatti et al., 2011).

The aim of this study is to assess the potential of magnetic nanosorbents such as nZVI in the removal of different wastewater contaminants. The effect of the solution pH, contact time, stirring rate and adsorbent doses on the removal of contaminant ions was studied. The surface characteristics of nZVI were studied.

Statistical analysis using RSM was studied using linear regression and the ANN was studied using nonlinear multilayer perceptron algorithms, respectively, to predict the model’s significance, $R^2$, standard error, parameter probability, accuracy and importance of covariables and independent parameters.

## 2. MATERIALS AND METHODS

### 2.1. Chemicals and Reagents

The following chemicals were used in this study: Ferric chloride hexahydrate (FeCl$_3$.6H$_2$O, 98.5% pure, Arabic lab.), Sodium borohydride (NaBH$_4$, 99% pure, Win lab.), Ethanol (C$_2$H$_6$O, 95% pure, World Co.), Sodium hydroxide (NaOH, 99% pure, Oxford Co.), Sulfuric acid (H$_2$SO$_4$, 95-97%, Honeywell Co.).

### 2.2. Preparation of nZVI

To prepare (nZVI) of size between 10 and 40 nm using drop by drop method, 1.0812 g of FeCl$_3$.6H$_2$O was dissolved in 60 mL of 4/1 (v/v) ethanol/deionized water mixture and well mixed. Also, reducing agent was prepared by adding 0.7564 g NaBH$_4$ in 200 mL
of deionized water to produce 0.1 molar NaBH₄ solutions. To ensure the better formation of nZVI excess borohydride solution about 10 mL was added. The NaBH₄ solution was poured in a burette and added drop by drop into the FeCl₃·6H₂O solution placed on a magnetic stirrer as shown in Figure 1. Black solid particles appeared immediately after the first drop of NaBH₄ solution as shown in equation 1. The chemical reaction between FeCl₃·6H₂O and NaBH₄ to form nZVI (Cumbal and SenGupta, 2005, Abdel-Gawad et al., 2016). The mixture was stirred for another 10 min after adding the whole NaBH₄ solution. Then, the vacuum filtration technique was applied to separate the black iron nanoparticles from the liquid solution. Two sheets of Whatman filter papers (42 circles, diameter 150 mm) were used in filtration. The filtrated black iron nanoparticles were then washed with 50 mL of absolute ethanol three times to prevent the rapid oxidation of nZVI. Finally, the synthesized iron nanoparticles were dried in the oven at 80 °C overnight. For storage, the nano iron particles were protected against oxidation by adding a thin layer of ethanol (Yuvakkumar et al., 2011).

\[
2\text{FeCl}_3 + 6\text{NaBH}_4 + 18\text{H}_2\text{O} \rightarrow 2\text{FeO} + 21\text{H}_2 + 6\text{B(OH)}_3 + 6\text{NaCl}
\]

(1)

2.3. Characterization of nZVI

The prepared nZVI sample was analyzed using XRD, magnetic properties and UV spectrophotometer. After placing the nZVI in a stainless steel sample holder, the XRD patterns were recorded at a radiation wavelength (Cu K-alpha = 1.5418 A°). The X-Ray current and voltage values were 40 kV and 40 mA, respectively. The diffraction angle (2θ) ranged from 5° to 70° at a step size of 0.0167° (Xi et al., 2010). The UV scanning spectrum was examined for prepared nZVI after adding absolute alcohol (0.1 nZVI/20 mL ethanol) from wavelength 190 to 1000 with rate 50 nm/min (Abdel-Gawad et al., 2016).

2.4. Wastewater sample

The sample was collected from Abo-Said wastewater treatment plant (WWTP) which is located at Helwan Governorate, Egypt. Samples were collected using 1-liter brown plastic bottles at 50 cm below the water surface. Samples were stored in the ice box for 4 hours before analyzing also storage reagent (Sulfuric acid, Nitric acid) were added according to ASTM 21 edition 2005. The samples were analyzed for pH, dissolved oxygen (DO), total dissolved solids (TDS), turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD), and total phosphate (PO₄³⁻), and then compared with the limits specified in ministerial decree No. 44 of 2000 (advanced) (Jamil et al., 2013, WHO, 2006). HORIBA instrument enabled measurement of pH, DO, TDS, and turbidity in the field. The acidified brown glass bottles were placed in an ice box for transportation to the laboratory. The samples were tested after 8 hours of collection. Analysis of the other parameters took place in the Egyptian Housing Building Research Center (HBRC) laboratory, Egypt. The 5-day BOD Test 5210B enabled determination of the BOD concentration in the samples. The closed reflux, titrimetric method 5220C was used to determine COD concentration in the samples. Persulfate method 4500-P J enabled determination of the PO₄³⁻ concentration in the samples. All the calculated parameters are presented in Table 1.

2.5. Batch Experimental System

The effect of pH for different wastewater contaminant removal was studied at pH below and above the Point of Zero Charge (PZC). The PZC for nZVI is around 7.7 (Diallo et al., 2013). The removal efficiency was studied at pH 3, 5, 7 and 9. The pH was adjusted using NaOH or H₂SO₄. The adsorption and degradation processes of different wastewater contaminants were studied using nZVI by batch technique. A known weight of nZVI (0.02, 0.04, 0.06, and 0.08 g/L) was equilibrated with 100 mL of wastewater sample of known wastewater contaminants in 250 mL Erlenmeyer flasks and agitated at 150 rpm at room temperature of 25±2°C for a 30 min. After equilibration, the suspension of the adsorbent was separated from the solution by filtration using Whatman filter paper No. 42 and the concentration of contaminants remaining in solution.
were measured using UV-Visible spectrophotometer (T70+ spectrophotometer, China at wavelength 690, 600 and 410 nm) according to the standard methods for water and wastewater (Federation and Association, 2005). The percentage removal efficiency was calculated using Equation 2. The amount of different wastewater contaminants sorbed by nZVI was calculated using Equation 3.

\[
\text{Sorption(\%)} = \frac{C_o - C_e}{C_o} \times 100
\]

\[
q_e (mg/g) = \frac{(C_o - C_e)V}{m}
\]

where \(C_o\) is the initial concentration of row wastewater sample (mg/L) and \(C_e\) is the equilibrium concentration after treatment for each parameter individually, \(q_e\) is the equilibrium adsorption capacity (mg/g), \(V\) is the volume of aqueous solution (L), and \(m\) is the dry weight of the adsorbent (g).

**2.6. Effect of operating parameters**

The effect of operating parameter for wastewater treatment using nZVI was studied using different operating parameter including adsorbent dose, pH, contact time, and the stirring rate at constant temperature 25 ± 3 °C as shown Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Row sample</th>
<th>Tested sample</th>
<th>Ministerial Resolution No. 44 of year 2000 (advanced)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO, mg/L</td>
<td>1.8</td>
<td>2.66</td>
<td>≥4 mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>6.8</td>
<td>7.8</td>
<td>6-9</td>
</tr>
<tr>
<td>Turbidity, NTU</td>
<td>32</td>
<td>17</td>
<td>≤20</td>
</tr>
<tr>
<td>COD, mg/L</td>
<td>167</td>
<td>22</td>
<td>≤40 mg/L</td>
</tr>
<tr>
<td>BOD₅, mg/L</td>
<td>96</td>
<td>17</td>
<td>≤20 mg/L</td>
</tr>
<tr>
<td>TN, mg/L</td>
<td>27.6</td>
<td>23.1</td>
<td>≤15 mg/L</td>
</tr>
<tr>
<td>TP, mg/L</td>
<td>4.1</td>
<td>3.65</td>
<td>&lt; 2 mg/L</td>
</tr>
<tr>
<td>TDS, mg/L</td>
<td>492</td>
<td>424</td>
<td>≤500 mg/L</td>
</tr>
<tr>
<td>TSS, mg/L</td>
<td>113</td>
<td>18</td>
<td>≤20 mg/L</td>
</tr>
</tbody>
</table>

**Table 1.** The comparison calculated parameters values between row samples and Ministerial Resolution No. 44 of the year 2000 (advanced).

**Table 2.** The effect of adsorbent dose of nZVI, pH, contact time, and stirring rate at temperature 25 ± 3 °C.

<table>
<thead>
<tr>
<th>Effect of parameter</th>
<th>Adsorbent dose (g)</th>
<th>Contact time (min)</th>
<th>pH</th>
<th>Stirring rate (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect of pH</td>
<td>0.4</td>
<td>30</td>
<td>3, 5, 7, and 9</td>
<td>150</td>
</tr>
<tr>
<td>Effect of adsorbent dose</td>
<td>0.2, 0.4, 0.6, &amp; 0.8</td>
<td>30</td>
<td>3.0±0.2</td>
<td>150</td>
</tr>
<tr>
<td>Effect of contact time</td>
<td>0.4</td>
<td>15, 30, 45 &amp; 60</td>
<td>7.0±0.2</td>
<td>150</td>
</tr>
<tr>
<td>Effect of stirring rate</td>
<td>0.4</td>
<td>30</td>
<td>7.0±0.2</td>
<td>150, 200, 250 &amp; 300</td>
</tr>
</tbody>
</table>

2.7. Statistical and algorithms analysis (RSM, ANN)

### 2.7.1. RSM by using linear modeling, statistics and algorithms (Enter method):

Notation:
- \(n\) is the number of distinct records in the dataset (\(n ≥ 1\)).
- \(P\) is the number of dummy variables but excluding the intercept in the model (\(P = 1\)).
- \(p^*\) is the number of non-redundant parameters but excluding the intercept in the model (\(p ≥ p^* ≥ 0\)).
- \(p^\) is the number of effects excluding the intercept (\(0 ≤ p ≤ p^\)).
- \(Y\) is the target vector with elements \(y_i\). \(f\) is the frequency weight vector. \(g\) is the regression weight vector.

The rows represent the
records and the columns represent the parameters. $\epsilon_{nx1}$ vector of unobserved errors. $\beta(p+1)x1$ vector of unknown parameters; $\beta = (\beta_0, \beta_1, \ldots, \beta_p)$. $\beta_0$ is the intercept. $\hat{\beta}(p+1) \times 1$ vector of parameter estimates. $b(p+1)x1$ vector of standardized parameter estimates. It is the result of a sweep operation on matrix $R$. $b_0$ is the standardized estimate of the intercept and is equal to 0. $\hat{\gamma}n \times 1$ vector of predicted target values. $\hat{\gamma}_j$ is the weighted sample mean for $x_j$, $j = 1, 2, \ldots, p$. $\hat{\gamma}$ Weighted sample mean for $y$. $S^i_{xy}$ weighted sample covariance between $X^i$ and $y$. $S^i_{yy}$ weighted sample variance for $y$. $R(p+1) \times (p+1)$ weighted sample correlation matrix for $X$ (excluding the intercept, if it exists) and $y$. $\hat{\gamma}$ is the resulting matrix after a sweep operation whose elements are $\hat{\gamma}_j$.

Model:

$$y = X\beta + \epsilon$$

(4)

where, $\epsilon$ follows a normal distribution with mean 0 and variance $\sigma^2 D^{-1}$, where $D^{-1} = \text{diag}(1/g_1, \ldots, 1/g_n)$ and the elements of $\epsilon$ are independent with respect to each other.

F statistics and their corresponding p-values:

$$F(\text{enter})_j = \frac{(SSe_p - SS_{e+p})/(N - p)}{SS_{e+p}/(N - p - r)}$$

(5)

$$F(\text{remove})_j = \frac{(SSe_{p-1} - SS_{e+p})/(N - p - r)}{SS_{e+p}/(N - p - r)}$$

(6)

$$p(\text{enter})_j = P(F_{r',N-r'} \geq F(\text{enter})_j) = 1 - P(F_{r',N-r'} \leq F(\text{enter})_j)$$

(7)

$$p(\text{remove})_j = P(F_{r',N-r'} \geq F(\text{remove})_j) = 1 - P(F_{r',N-r'} \leq F(\text{remove})_j)$$

(8)

Adjusted R-squared:

The adjusted $R^2$ value for entering or removing an effect from the current model is:

$$adj. R^2 = 1 - \frac{(N - 1)\hat{\gamma}y}{N - p - r}$$

(9)

Model evaluation:

A) Standard errors of regression coefficients:

$$\hat{\sigma}_{\hat{\beta}_j} = \sqrt{\text{var}(\hat{\beta}_j)} = \sqrt{\frac{\hat{\gamma}_j \hat{\gamma}_{yy} S_{yy}}{S_{dfe}}}$$

(10)

B) t statistics for regression coefficients:

$$t = \frac{\hat{\beta}_j}{\hat{\sigma}_{\hat{\beta}_j}} = \frac{\hat{\gamma}_j}{\sqrt{\hat{\gamma}_{yy} \hat{\gamma}_{jj}}}$$

(11)

C) F statistic:

for corrected model:

$$F = \frac{SS_{r}/df_r}{SS_{e}/df_e} = \frac{SS_{r}}{SS_{e}} \cdot \frac{df_r}{df_e}$$

(12)

for each effect:

The SS for the effect $j$ is also used to compute the F statistic for the hypothesis test $H_0$: as follows:

$$F_j = \frac{S_j/r_j}{SS_e/df_e}$$

(13)

D) Intercept estimation:

$$\hat{\beta}_0 = \bar{y} - \sum_{j=1}^{p} \hat{\beta}_j x_j$$

(14)

The RSM plots show simultaneous confidence band for the fitted response surface. A chart was plotted that displays a contour of RSM for different wastewater contaminants removal efficiency against the independent variables, pH, time, adsorbent dose, and stirring rate. A pure-linear regression model (equation 15) was employed to describe the RSM plots by fitting the experimental data.

$$Y = \hat{\beta}_0 + \hat{\beta}_1 x_1 + \hat{\beta}_2 x_2 + \hat{\beta}_3 x_3 + \hat{\beta}_4 x_4$$

(15)

where $Y$ is the predicted response of different wastewater contaminants removal efficiency (%); $x_i$ is contact time (5 – 60 min); $x_2$ is adsorbent dose (0.2 – 0.8 g); $x_3$ is pH (3 – 7); $x_4$ is stirring rate (150 – 300 rpm); $\hat{\beta}_0$ is the model intercept; $\hat{\beta}_1, \hat{\beta}_2, \hat{\beta}_3$ and $\hat{\beta}_4$ are the linear coefficients of $x_1, x_2, x_3$ and $x_4$, respectively.

2.7.2. Artificial Neural Networks by using MLP (Multi-Layer Perceptron) statistical algorithms:

Procedure fits a particular kind of neural network called a multilayer perceptron. The multilayer perceptron uses a feed forward architecture and can have multiple hidden layers. It is one of the most commonly used neural network architectures.

Notation:

$X^m = (x_1^m, \ldots, x^m_n)$ Input vector, pattern m, $m = 1, \ldots, M$. $Y^m = (y_1^m, \ldots, y_R^m)$ Target vector, pattern m. I Number of layers, discounting the input layer. $J_0 = P$, $J_i = R$, discounting the bias unit. $r$ Set of categorical outputs. $c$ Set of scale outputs.
h Set of subvectors of $Y_m$ containing 1-of-c coded hth categorical variable. $a_{m_{ij}}^i$ Unit j of layer i, pattern m, $J=0, \ldots, J_{ij}$ ; $i=0, \ldots, I$. $W_{m_{ij}}^i,k$ Weight leading from layer $i-1$, unit j to layer i, unit k. No weights connect $a_{m_{ij}}^{i-1}$ and the bias $a_{m_{10}}^1$ that is, there is no $w_{0j,0}$ for any j. $C_{m_{ij},ki}^i$ $\sum_{j=0}^{J_{ij}} W_{m_{ij},ki}^i a_{m_{ij}}^{i-1}$, $i=1, \ldots, I$ $\gamma_i(c)$ Activation function for layer i. $W$ is the weight vector containing all weights.

Architecture:
The general architecture for MLP networks is:
a) Input layer: $j_0 = p$ units, $a_{0,0}, \ldots, a_{0,j_0}$; with $a_{0,j} = x_j$.
b) $i$th hidden layer
c) $j_i$ units, $a_{i,1}, \ldots, a_{i,j_i}$; with $a_{i,k} = \gamma_i(c_{i,k})$ and $c_{i,k} = \sum_{j=0}^{J_{ij}} W_{m_{ij}}^i,j,k a_{m_{ij}}^{i-1}$, $i=1, \ldots, I$.
d) Output-layer: $j_I = R$ units, $a_{I,1}, \ldots, a_{I,j_I}$; with $a_{I,k} = \gamma_I(c_{I,k})$ and $c_{I,k} = \sum_{j=0}^{J_{ij}} W_{m_{ij}}^{I,j,k} a_{m_{ij}}^{I-1}$, $i=1, \ldots, I$.

Error Functions:
a) Sum-of-Squares: $E_r(w) = \sum_{m=1}^{M} E_m(w)$
\begin{equation}
E_m(w) = \frac{1}{2} \sum_{r=1}^{R} (y_r^m - a_{m,ir})^2
\end{equation}
and
\begin{equation}
E_m(w) = \frac{1}{2} \sum_{r=1}^{R} (y_r^m - \tilde{y}_r^m)^2
\end{equation}
b) Cross-Entropy: $E_r(w) = \sum_{m=1}^{M} E_m(w)$
\begin{equation}
E_m(w) = -\sum_{r \in \gamma} y_r^m \log \left( \frac{a_{m,ir}}{\tilde{y}_r^m} \right)
\end{equation}

This is only available if all output layer units correspond to categorical variables and the softmax activation function is used.

Output Statistics:
a) Sum-of-Squares or Cross Entropy Error: described in equations (16, 17 and 18).
b) Relative Error for each scale target r:
\begin{equation}
\frac{\sum_{m=1}^{M} (y_r^m - \tilde{y}_r^m)^2}{\sum_{m=1}^{M} (y_r^m - \bar{y}_r)^2}
\end{equation}
c) Average Overall Relative Error:
\begin{equation}
\frac{\sum_{m=1}^{M} \sum_{r=1}^{R} (y_r^m - \tilde{y}_r^m)^2}{\sum_{m=1}^{M} \sum_{r=1}^{R} (y_r^m - \bar{y}_r)^2}
\end{equation}
d) Sensitivity Analysis: For each predictor p and each input pattern m, compute:
\begin{equation}
d_{pm} = \max_{x_{p1},x_{p2}} \in s_p\|y_{p1}^m - y_{p2}^m\|
\end{equation}

3. RESULTS AND DISCUSSION

3.1. Characterization of nZVI

Figure 2A shows the UV–vis absorption spectrum of the prepared nZVI sample in ethanol solution dissolved in ethanol solution in the region between 195 and 1000 nm with rate of 25 nm/min. In this spectrum, the absorption peaks appeared at 192 and 195 nm confirmed the formation of nano iron particles with the particle size from 10-100 nm (Farahmandjou and Soflaee, 2015). Also, there was a small hump peak at 370 and 910 nm. A small hump at 370 nm confirmed the presence Fe$^{2+}$ ions with OH to form Fe(OH)$_2$ and another beak at 910 nm indicates the presence of some oxides (Parveen et al., 2010). This optical phenomenon of blue shift indicates that the prepared nZVI in the nanoscale range and this is in a good agreement with the literature reviews (Yuvakkumar et al., 2011).

Figure 2. UV-scanning spectrum (A) and XRD (B) and SEM (C) of nZVI.
Figure 2B shows the XRD patterns of prepared nZVI material in zero valent states. The position of the diffraction peaks fit well with the body-centered structure of Fe mineral (JCPDS card No.87-0722). In this figure, the intense peaks at the diffraction angles of 44.713° and 64.9° are attributed to (110) and (200) planes, respectively (Mahmoud, 2017). Figure 2b clearly indicated that the characteristic peaks of iron oxide have high intensities which imply that the prepared sample is of crystalline structure and no peaks for other impurities or oxides are found in all powder samples. By applying Scherer equation to estimate nZVI crystal size the results were between 23 and 60 nm showed agreement with SEM results. The crystallite size D of main peaks are summarized in Table 3 (Mostafa et al., 2017, Darwish et al., 2015).

Figure 2c shows SEM images at low and high resolution provided detailed information about sample surface and topography. We can understand from the SEM images whether NPs aggregate or not. These images have been taken in 2 days after synthesis and it is clear that they have just started to aggregate. From Figure 2c, it is clear that nZVI appeared as a semi-spherical shape with an average size of 40 nm.

3.2. Effect of operating parameters

3.2.1. Effect of pH

The effect of pH on the performance of nZVI was studied using different pH values (3, 5, 7 and 9) on the basis of different wastewater parameters (DO, Color, Turbidity, COD, BOD, TN, TP, TDS and TSS). The obtained results showed that there is no significant effect on DO at different pH. The effect of pH on wastewater color was studied at pH (3, 5, 7 and 9) and the obtained results were (Yellowish, Grayish yellow, faint gray and faint gray color) indicated that some of nZVI was dissolved in the acidic medium until pH 7. At pH values of 3, 5, 7 and 9, the decrease in turbidity values were 45, 51, 66 and 19 %, respectively. On the other hand, nZVI decreased 85, 89, 92 and 73 % of COD values at pH 3, 5, 7 and 9, respectively. Also, nZVI significantly decreased BOD values about 94, 92, 94 and 72 %, whereas TN about 30, 33, 32 and 29 % and TP about 34, 29, 23 and 4 % at pH 3, 5, 7 and 9, respectively. In the case of TDS values 9, 10, 13 and 8 % were recorded at pH 3, 5, 7 and 9, respectively and TSS values were 88, 90, 93 and 73 %., respectively. Finally, the average removal efficiency of treated wastewater sample using nZVI was 50, 53, 56 and 37 % at pH 3, 5, 7 and 9, respectively as shown Figure 3. From the obtained results, it was

![Figure 3](image-url)

**Figure 3.** Effect of operating parameter on the removal efficiency. A) effect of pH on the removal efficiency using nZVI, B) effect of dose on the removal efficiency using nZVI, C) effect of stirring rate on the removal efficiency using nZVI, D) effect of contact time on the removal efficiency using nZVI.
observed that pH 7 was found to be the optimum pH for the removal of different wastewater contaminants. The pH depends on the charge on the surface of the iron as shown Figure 4. The adsorption of negative and positive aqueous species depends also on the surface charge. When the surface charge is neutral it is called point of zero charge (PZC). The PZC of unmodified ZVI is typically within pH 6 to 8 (Bezbaruah et al., 2009, Kosmulski, 2004). Above this value the surface of nZVI is negatively charged causing repulsion of negative and electrostatic attraction of positive species, and vice versa. The particles aggregation increases at the PZC and decreases above and below the PZC due to the electrostatic repulsion between particles. Aggregation may affect particle reactivity and mobility due to decreasing the surface area for reaction (Kröger and Law, 2005, Watts, 2014). The excess of free electrons that comes from nZVI can also degrade most hazardous pollutants such as contaminants which increase the amount of COD, BOD, and TSS. nZVI can also degrade pesticides and radiations at neutral medium.

\[
\begin{align*}
\text{Fe}^0 + O_2 + 2H_2O & \rightarrow 2\text{Fe}^{2+} + 4OH^- \\
6\text{Fe}^{2+} + O_2 + 6H_2O & \rightarrow 2\text{Fe}_3O_4 \text{[magnetite]} + 12H^+ 
\end{align*}
\]

3.2.2. Effect of nZVI dose

The effect of nZVI dosage was studied using 0.2, 0.4, 0.6 and 0.8 g/L on different wastewater parameters (DO, Color, Turbidity, COD, BOD, TN, TP, TDS and TSS). The obtained results showed that there was no significant effect on DO and color on varying nZVI dosage. At different nZVI doses namely 0.2, 0.4, 0.6 and 0.8g, the decrease in turbidity values were 44, 66, 72 and 84 %, respectively. On the other hand, nZVI decreased 74, 92, 95 and 96 % of COD values, and BOD values of 73, 94, 96 and 96 %, whereas TN values of 28, 32, 37 and 42 % and TP values of 20, 23, 29 and 42 %, at dosages of 0.2, 0.4, 0.6 and 0.8g, respectively. On the other hand, TDS values were 12, 13, 12 and 9 % and TSS values were 75, 93, 95 and 96 %., at dosages of 0.2, 0.4, 0.6 and 0.8g, respectively. Finally, the average removal efficiency of treated wastewater sample using nZVI was 44, 56, 60 and 65 % at 0.2, 0.4, 0.6 and 0.8 g nZVI dosages, respectively as shown in Figure 3. From the obtained result the optimum nZVI dosage for the removal of different wastewater contaminants was observed to be 0.4 g/L.

3.2.3. Effect of contact time

The effect of contact time was studied at 5, 15, 30, 45 and 60 min on different wastewater parameters (DO, Color, Turbidity, COD, BOD, TN, TP, TDS and TSS). The obtained results showed that there is no significant effect on DO and color of wastewater. At different contact times of 5, 15, 30, 45 and 60 min, the decrease in turbidity values were 22, 47, 66, 69 and 69 %, respectively. On the other hand, nZVI decreased 65, 87, 92, 93 and 93 % of COD values. and  BOD values of 64, 80, 94, 95 and 95 %, whereas TN values of 4, 16, 32, 37 and 45 % and TP values of 4, 11, 23, 30 and 34 %, at contact times of 5, 15, 30, 45 and 60 min, respectively. On the other hand, TDS values were 13, 14, 13, 13 % and TSS values were 66, 87, 93, 95 and 96 %, at contact times of 5, 15, 30, 45 and 60 min, respectively. Finally, the average removal efficiency of treated wastewater sample using nZVI was 30, 43, 56, 37

Table 3. nZVI size calculation at positions 44.713° and 65.1° using Scherer equation

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Table 4. t statistics and p-values for coefficients of the pure-linear regression model

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58 and 60% at contact time 5, 15, 30, 45 and 60 min, respectively as shown in Figure 3. From the obtained results the minimum effective time was 30 min.

3.2.4. Effect of stirring rate
The effect of stirring rate was studied at 150, 200, 250 and 300 rpm on different wastewater parameters (DO, Color, Turbidity, COD, BOD, TN, TP, TDS and TSS). The obtained results showed that there is no significant effect on DO and color results. At different stirring rate 150, 200, 250 and 300 rpm, the decrease in turbidity values were 66, 69, 69 and 69%, respectively. On the other hand, nZVI decreased 92, 92, 92 and 92% of COD values and BOD values of 94, 94, 94 and 95%, whereas TN values of 32, 32, 33 and 34% and TP values of 23, 29, 30 and 32%, at stirring rates of 150, 200, 250 and 300 rpm, respectively. On the other hand, TDS values were 13, 13, 12 and 11%, and TSS values were 93, 94, 94 and 95%, at stirring rates of 150, 200, 250 and 300 rpm, respectively. Finally, the average removal efficiency of treated wastewater sample using nZVI was 56, 57, 58 and 58% at stirring rate 150, 200, 250 and 300 rpm, respectively as shown Figure 3. From the obtained results the effective stirring rate for the removal of different wastewater contaminants was observed to be 150 rpm.

3.3. Statistical Analysis

3.3.1. RSM
The effect of pH, dose, contact time and stirring rate on the removal of different wastewater contaminants was illustrated as listed in Table 4. In case of removal of COD, BOD, Turbidity, Total Nitrogen (TN) and TSS from municipal wastewater by using nZVI, the positive linear effect of the independent variables “time” and “dose” were observed to be significant (p < 0.05). However, insignificant effect (p > 0.05) was determined for the linear term of “pH” and “stirring rate”. While the effect of nZVI on TP removal showed positive linear effect of the all independent variables. The effect of nZVI on TDS removal, positive linear effect of the independent variables “time”, “dose” and “pH” were observed to be significant (p < 0.05). However, insignificant effect (p > 0.05) was determined for the linear term of “pH”. The coefficient of determination between measured data and simulated results (R²), adjusted R², F factor, standard error and P value of each contaminant model were placed in Table 4. The high R² value suggested the reliability of the proposed model. Equation 15 showed all regression models (significant and insignificant).

% (Turbidity) = -19.634 + 0.795 x₁ + 69.923 x₂ + 2.714 x₃ + 0.032 x₄

% (COD) = 52.229 + 0.819 x₁ + 35.170 x₂ - 0.281 x₃ + 0.057 x₄

% (BOD) = 59.326 + 0.532 x₁ + 37.518 x₂ - 2.503 x₃ + 0.082 x₄

% (TP) = -0.556 + 0.554 x₁ + 40.712 x₂ - 3.078 x₃ + 0.075 x₄

% (TN) = -6.075 + 0.720 x₁ + 30.006 x₂ - 0.751 x₃ + 0.041 x₄

% (TDS) = 187.479 - 0.038 x₁ - 26.361 x₂ - 19.155 x₃ - 0.113 x₄

% (TSS) = 53.793 + 0.465 x₁ + 32.562 x₂ - 0.661 x₃ + 0.069 x₄

% (average) = 16.071 + 0.479 x₁ + 42.762 x₂ - 0.047 x₃ + 0.064 x₄

where, Y is the predicted response of different wastewater contaminants removal efficiency (%); x₁ is contact time (5 – 60 min); x₂ is adsorbent dose (0.2 – 0.8 g); x₃ is pH (3 – 7); x₄ is stirring rate (150 – 300 rpm); β₀ is the model intercept; β₁, β₂, β₃ and β₄ are the linear coefficients of x₁, x₂, x₃ and x₄, respectively.

Abbreviations; Std Error, the standard error of the estimated difference between the means; DF, the degrees of freedom used in constructing the confidence interval; t Ratio, the t ratio for the test of whether the estimated difference between the means is zero; Prob>|t|, the p-value for the test.

3.3.2. ANNs
All ANNs were trained using the back-propagation algorithm. Network training is a process by which the connection weight and bias on the ANN are adapted through a continuous process of simulation by the environment in which the network is embedded. Each wastewater contaminant was studied using sample training and testing as explained in Table 5. the parameters (COD, BOD, TN and TDS) have the same
Figure 5. Neural network models for different wastewater contaminant.

Figure 6. The relationship between predictive value and actual removal value.
**Figure 7.** The relation between residual and predicted removal value.

**Figure 8.** Normalized importance for each covariable.
Table 5. Case processing summary

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Turbidity and average</th>
<th>COD, BOD, TN and TDS</th>
<th>TP</th>
<th>TSS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>%</td>
<td>N</td>
<td>%</td>
</tr>
<tr>
<td>Sample training</td>
<td>8</td>
<td>61.5</td>
<td>10</td>
<td>76.9</td>
</tr>
<tr>
<td>Sample testing</td>
<td>5</td>
<td>38.5</td>
<td>3</td>
<td>23.1</td>
</tr>
<tr>
<td>Valid</td>
<td>13</td>
<td>100</td>
<td>13</td>
<td>100</td>
</tr>
<tr>
<td>Excluded</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>13</td>
<td>100</td>
<td>13</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 6. Network information

<table>
<thead>
<tr>
<th></th>
<th>Turbidity, BOD, average</th>
<th>COD, TN</th>
<th>TP, TDS, TSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input Layer</td>
<td></td>
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</tr>
<tr>
<td>Covariates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of Units</td>
<td></td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Rescaling Method for Covariates</td>
<td></td>
<td>Normalized</td>
<td></td>
</tr>
<tr>
<td>Hidden Layer(s)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Number of Hidden Layers</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Number of Units in Hidden Layer 1</td>
<td></td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Activation Function</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dependent Variables</td>
<td></td>
<td></td>
<td>Removal</td>
</tr>
<tr>
<td>Number of Units</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Rescaling Method for Scale Dependen-</td>
<td></td>
<td>Standardized</td>
<td></td>
</tr>
<tr>
<td>ts</td>
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<td></td>
</tr>
<tr>
<td>Output Layer</td>
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<td></td>
</tr>
<tr>
<td>Error Function</td>
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<td></td>
<td></td>
<td>Identity</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sum of Squares</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7. Summary of ANNs results for testing and training

<table>
<thead>
<tr>
<th></th>
<th>Turbidity</th>
<th>COD</th>
<th>BOD</th>
<th>TP</th>
<th>TN</th>
<th>TDS</th>
<th>TSS</th>
<th>average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Training</td>
<td>Sum of Squares Error</td>
<td>.309</td>
<td>2.376</td>
<td>.009</td>
<td>.749</td>
<td>.081</td>
<td>2.532</td>
<td>.986</td>
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<tr>
<td></td>
<td>Relative Error</td>
<td>.088</td>
<td>.528</td>
<td>.002</td>
<td>.136</td>
<td>.018</td>
<td>.563</td>
<td>.271</td>
</tr>
<tr>
<td></td>
<td>Stopping Rule Used</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Testing</td>
<td>Sum of Squares Error</td>
<td>.167</td>
<td>.078</td>
<td>.005</td>
<td>1.415E-5</td>
<td>.001</td>
<td>.046</td>
<td>.726</td>
</tr>
<tr>
<td></td>
<td>Relative Error</td>
<td>.251</td>
<td>.463</td>
<td>2.154</td>
<td>0.0</td>
<td>.020</td>
<td>.027</td>
<td>.512</td>
</tr>
</tbody>
</table>

Table 8. Summary of ANNs results for testing and training

<table>
<thead>
<tr>
<th>Importance</th>
<th>Turbidity</th>
<th>COD</th>
<th>BOD</th>
<th>TP</th>
<th>TN</th>
<th>TDS</th>
<th>TSS</th>
<th>average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time</td>
<td>.648</td>
<td>.479</td>
<td>.512</td>
<td>.363</td>
<td>.720</td>
<td>.046</td>
<td>.670</td>
</tr>
<tr>
<td></td>
<td>Dose</td>
<td>.235</td>
<td>.293</td>
<td>.430</td>
<td>.325</td>
<td>.211</td>
<td>.042</td>
<td>.172</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>.115</td>
<td>.033</td>
<td>.007</td>
<td>.172</td>
<td>.049</td>
<td>.844</td>
<td>.039</td>
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<tr>
<td></td>
<td>Stirring</td>
<td>.002</td>
<td>.195</td>
<td>.052</td>
<td>.141</td>
<td>.020</td>
<td>.069</td>
<td>.119</td>
</tr>
<tr>
<td>Normalized importance</td>
<td>Time</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>100.0%</td>
<td>5.4%</td>
<td>100.0%</td>
<td>100.0%</td>
</tr>
<tr>
<td></td>
<td>Dose</td>
<td>36.3%</td>
<td>61.1%</td>
<td>84.0%</td>
<td>89.4%</td>
<td>29.3%</td>
<td>4.9%</td>
<td>25.6%</td>
</tr>
<tr>
<td></td>
<td>pH</td>
<td>17.7%</td>
<td>7.0%</td>
<td>1.4%</td>
<td>47.4%</td>
<td>6.8%</td>
<td>100.0%</td>
<td>5.8%</td>
</tr>
<tr>
<td></td>
<td>Stirring</td>
<td>0.3%</td>
<td>40.6%</td>
<td>10.1%</td>
<td>38.7%</td>
<td>2.8%</td>
<td>8.1%</td>
<td>17.7%</td>
</tr>
</tbody>
</table>
sample training and testing number, TP and TSS each of them has unique training and testing number, also turbidity and average have the same training and testing numbers without any excluded values for mentioned parameters. Table 6 shows the statistical environment for input, hidden and output layers indicated that all wastewater contaminant parameters run at the same calculation method for covariables except the number of unit in hidden layers. Figure 5 shows the neural network models for different wastewater contaminant including 4 covariables (Time, Dose, pH and stirring) as input layers was connected together in hidden layer and bias to proceed the artificial intelligence of output layer (removal %). Table 7 shows the obtained ANNs of testing and training results indicating that the SSE for all parameter was acceptable except TDS the SSE was 2.532 for training and this result agree with RSM results and chemical explanation of TDS removal from wastewater using nZVI. Figure 6 and 7, shows the relation of predictive with actual removal value and residual for different wastewater contaminant parameters. It has appeared that there is no significant difference between predictive and actual value for all parameter especially for the average of all parameter except TDS. The relation between residual and predictive act as better example indicate that the difference between predictive and actual against predictive lays between (-10,+10) for turbidity, (-20,+5) for COD, (-10,+5) for BOD, (-10,+5) for TP, (-3,+3) for TN, (-20,+60) for TDS, (-15,+10) for TSS and (-4, +4) for average of removal percentages of the above mentioned parameters. Table 8 and Figure 8 showed the importance and normalized importance for each co-variable that affects the wastewater treatment using nZVI. The normalized importance agrees with previous discussions of the effect of the operating parameter and RSM statistic algom.

### 4. CONCLUSIONS

In this study, nZVI was prepared in an economical and fast way. The prepared nZVI showed high potential to decontaminate wastewater through removal of turbidity, COD, BOD and TSS with removal percentages of 66, 92, 94 and 93 %, respectively; whereas exhibited moderate effect of the removal of TP and TN with removal percentages of 23 and 32 %, respectively and poor effect towards TDS removal (less than 13 %). Statistical analysis using RSM showed that all models were significant with a p value less than 0.05 and R2 between 0.690 and 0.908 except the TDS model p value equal 0.054 and R2 0.536 indicated the reality of the models and agreement with experimental data. Also, the RSM analysis showed the significant, insignificant results for each co-variable as well as predicted the removal equations for each wastewater contaminant. ANNs models using the back-propagation provide the relationship between trained and tested values also provide the importance and normalized importance of each co-variable. The results of ANNs showed agreement with RSM results and experimental data.

### ACKNOWLEDGEMENTS

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### REFERENCES


