Removal of dyes from industrial wastewater by polyaniline nano-composite/ Fe$_3$O$_4$

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ABSTRACT
To supply healthy water and remove water contaminations are one of the serious concerns of modern societies. Various techniques and methods have been used to remove contaminants from industrial wastewater. The aim of this study was to remove yellow15 dye from industrial wastewater using nano-composite/Fe$_3$O$_4$. In this study, magnetic nanoparticles Fe$_3$O$_4$ were synthesized firstly by chemical precipitation. Nanoparticles synthesis was confirmed by XRD and SEM techniques. Then, by polyaniline deposition on nanoparticles, polyaniline nanocomposites were prepared and its synthesis was confirmed by TEM, SEM, and FTIR techniques. In addition, the effects of various parameters, including pH, contact time, adsorbent value, and temperature were investigated and optimized in the isolation of considered dye. Kinetics studies showed that the absorption kinetics follows a pseudo-second order equation and this dye adsorption isotherm follows a Langmuir Equation. The results showed that this method is an appropriate method for considered dye.

Keywords: nano-composite, iron magnetic nanoparticles, polyaniline, reactive yellow15 dye

INTRODUCTION
Healthy water supply is a fundamental for survival of humans. Many of the problems of developing countries are due to lack of healthy water since healthy human is at the center of sustainable development and human health depends on utilization of desirable drinking water. Without supplying healthy water, development of health and social welfare will be impossible. By increasing world population and the rapid growth of various industries and different contaminations in water, shortage of healthy water was felt gradually. Therefore, many people thought to prevent water contamination and its purification to supply healthy water. One of the important and effective industries in serious water contaminations is textile industry concerning with large quantities of dye and pigments annually. Textile industries consume large quantities of water and one of the big groups contaminating water. Total rate of pigment production in world was reached to 800,000 thousand tons per year in 1990. There are over 100,000 types of various dyes and pigments in world that 10000 types are used in textile and print industries (Will, Ishikawa, and Leder, 2000). It is important to note that about 10 to 20 percent of the dye used in various industries enters into environment through industrial waste (Sun and Yang, 2003). Dyes are first polluters that are are identified in wastes because low quantity of them in water is very evident and undesirable (Robinson, Chandran, and Nigam, 2002). In recent years, the world’s dyecontaminators laws have become stricter every
day (Sun and Yang, 2003). Therefore, these compounds must be removed before discharge into the natural environment from industrial waste, since without appropriate and sufficient water treatment, these compounds are able to remain stable in the environment for long time and disturb life thereby (Shi, Li, Wang, Feng, and Tang, 2007). For this reason, various methods have been used in recent years to remove dye materials from water. In general, water contaminations are removed using three general methods:

1. Physical methods
2. Biological methods

Several chemical methods have been used for water treatment such as electrochemical methods, burning, chlorination, ozone oxidation, ion exchange, flocculation, etc. Many biological methods have been used for water treatment, including the use of microorganisms using mushrooms, using algae, methods based on production of enzyme from microorganisms, etc. Several physical methods are also used for water treatment that some of which include: The membrane methods, aeration, radiation, surface adsorption, etc. Among the technologies used the removal of dyes and pigments, surface adsorption is a selected technology with high performance such as removal of various contaminants such as dyes. If adsorption system is developed correctly, it can purify waste with high quality (Yuh–Shan Ho and McKay, 2003). Surface adsorption process is one of the physical methods having great advantages compared to other technologies due to lower cost, easier designing, higher access, and ability to treat dyes in high concentrations. The majority of commercial systems of activated carbon as an adsorbent for removal from wastewater using an absorbent top of this is due to absorption. Activated carbon adsorption technology has been accepted as one of the best technologies, inventory control and efficiency is very good (Yuh–Shan Ho and McKay, 2003). This technique was investigated as an acceptable method with high efficiency (over 90%) for the removal of dyes in the textile industry and it is an improved method for wastewater treatment in textile industry. However, there is high willingness to use lowly cost and eco-friendly absorbents to absorb dyes from textile industries waste, due to its high cost to revive it (Robinson et al, 2002).

The newest methods are based on nanotechnology. The innovative aspect of this research is that nano-composite polyaniline Fe₃O₄ was used as absorbent that synthesis of this composite was conducted firstly at nano scale. Second, this nano-composite has magnetic properties. In addition, the effect of various parameters, including value of absorption, contact time, dye concentration and pH was examined. Finally, adsorption isotherm and dye absorption were also investigated.

**Experimental or computational methods**

**Materials needed**

1- 1 M sulfuric acid prepared from Merck Company was used to depose polymer on Fe₃O₄.
2- Potassium iodate prepared from Merck Company was used as an oxidizer in the preparation of nanocomposites.
3- Aniline prepared from Merck Company was used for the synthesis of polyaniline after distillation.
4- CTAB played the role of surfactant in deposition of polymer on Fe₃O₄.
5- Iron salt (II) of crystallized chloride prepared from Merck Company was used in the production of nanoparticles Fe₃O₄.
6- Iron salt (III) of crystallized chloride prepared from Merck Company was used in the production of nanoparticles Fe₃O₄.
7- 12 M Hydrochloric acid prepared from Merck Company was used in production of nanoparticles Fe₃O₄.
8- 1.5 M sodium hydroxide prepared by Merck Company was used in production of nanoparticles Fe₃O₄.
9- Yellow 15 dyes prepared from Dystar Company were used without any purification operations and with same business purity Fe₃O₄.
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Procedure
In this study, magnetic nanoparticles Fe₃O₄ were synthesized by chemical precipitation method. Then, aniline polymer was deposited onto Fe₃O₄ in order to optimize the level of nanoparticle, so that polyaniline nanocomposites to be formed. Certain value of synthesized nano-composite was added to dye standard solutions with certain concentration to remove dye, that their initial absorption values was read by UV-Vis device, and resulted mixture was stirred by hand made stirrer for certain time so that dye removal to be complemented. Then, the mixture containing nano-composites and absorbed dye was deposited by strong magnet (1.4 T) and after centrifugation of solution above it, the second absorption was read by UV-VIS device so that to the value of desired dye removal from solution to be determined by polyaniline nano-composite Fe₃O₄. In addition, at each stage, the value of removal of dyes by polyaniline (as absorbent) was examined and removal of dye by two types of absorbents (nanocomposites and polyaniline only) was compared.

Preparation of nanoparticle Fe₃O₄
5.2 g of crystallized salt FeCl₃·6H₂O and 2 g of crystallized salt FeCl₂·4H₂O were weighted by digital scale, and they were poured into 250-mL beaker and 25 ml of distilled water were added on them. 12 M was increased to 0.85 ml of of HCl solution to resulted solution (the reason to HCL acid in order to better dissolve of iron salts and stability of ions Fe²⁺ and Fe³⁺) and N₂ gas was passed from solution (in order to remove the gas O₂ from solution). 205ml of soda was prepared in a beaker and it N₂ was passed through it for 15 minutes. Then, soda was transferred to one Burt so that it can be entered into first beaker containing iron salts gradually in 30 minutes. During adding the soda, N₂ was also entered to beaker. Using a strong magnet 1.4 T, deposit formed Fe₃O₄ that had magnetic properties was isolated from suspension inside the beaker and it was dried at 100 °C in the oven after rinsing. Then, it was pulverized using a porcelain mortar. Photos were taken from particles Fe₃O₄ by electronic microscopes of TEM and SEM that these photos confirm the formation of particles at nano level. These photos are shown in Figure 1 and 2.

Figure 1- SEM photo of Fe₃O₄ nano particles

Figure 2- TEM photo of Fe₃O₄ nano particles

Preparation of polyaniline nanocomposite Fe₃O₄
-For depositing polymer aniline on nanoparticles on Fe₃O₄, 100 mL of 1 M sulfuric acid was poured in a beaker of 250 liters and 1 g of nanoabsorbent of Fe₃O₄ was added and resulted mixture was stirred for 15 minutes with magnet. Then, 1 g of synthesized nanoparticles Fe₃O₄ was added to mixture and it was stirred by an electric mechanical handmade stirrer for 10 minutes. Then, 0.2 g CTAB was added as surfactants added to the mixture and it was stirred for 20 minutes. Then, 1 ml of distilled aniline was added to the contents of beaker and it was stirred by hand mechanical handmade stirrer for 5 hours. Finally, after isolating the deposit formed by strong magnet, deposit was rinsed by acetone o and distilled water. It was placed in oven for 24 hours at 80 ° C put to be dried. Then, it was pulverized to be rounded. Electronic photos SEM and FTIR spectrum were taken from nano-composite that these photos and comparing polyaniline spectra and particles only confirm depositing of polymer on nanoparticles. Results are shown in Figures 6-3.
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Figure 3- SEM photo of nano composite/ Fe₃O₄

Figure 4- FTIR spectrum of polyaniline composite / Fe₃O₄

Figure 5- alone polyaniline spectrum
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RESULTS AND DISCUSSION
Effective parameters on the adsorption of the dyes, based on the results of Figures and Diagrams reported in this study show an increase in the absorption of dyes on the adsorbent. Optimizing of different parameters affecting removal of reactive yellow 15 dye
To examine the impact of pH
To examine the effect of pH, 8 solutions of yellow15 dye were poured to 100 ml beakers with equal concentration of 20 ppm and they were adjusted and stabilized at the range of 2-12. Then, the initial absorption of each of mentioned solutions was read by UV-VIS device. Then, equal values 0.03 g of polyaniline nano adsorbent Fe₃O₄ was added and it was stirred by mechanical handmade stirrer so that removal of dye process to be done. During this time, some quantity of dyestuff in solution is absorbed by nano absorbent. Then, it was deposited by strong magnet and solution above it was centrifuged for full deposition with 3500 rounds in 30 minutes. Then, secondary absorption of each of solutions was read by UV-VIS device so that value of specified dye removal and optimal value of absorbent to be determined. All of the above stages, except for deposition by magnet stage, were done by polyaniline absorbent so that dye absorption difference to be compared in two states. The results can be seen in Figure 7.
To examine the impact of contact time
To investigate this impact, 6 solutions containing yellow 15 dye in equal concentrations 20 ppm were prepared in 7 beakers of 100 ml. then, initial absorption of each of dye solutions was read by UV-Vis device. Then, 0.01, 0.02, 0.03, and 0.05, 0.07, and 0.1 g of polyaniline nanocomposite were added to mentioned solutions. Then, solutions were stirred by a handmade mechanical stirrer so that dye removal process by nano-absorbent to be done better. After 2 hours with the help of strong magnet 1.4 T, it was deposited and some quantity of residual solutions was centrifuged for complete deposition with 3500 rounds for 30 minutes. Then, secondary absorption of each of solutions was read by UV-Vis device so that value of specified dye removal and optimal value of absorbent to be determined. All of the above stages, except for deposition by magnet stage, were done by polyaniline absorbent so that dye absorption difference to be compared in two states. The results can be seen in Figure 8.
To examine the impact of nano-adsorbent value
To investigate the impact of nanocomposite, at first stage, six solutions of yellow 15 dye in equal concentrations 20 ppm were prepared in six beakers of 100 ml. then, initial absorption of each of dye solutions was read by UV-Vis device. Then, 0.01, 0.02, 0.03, and 0.05, 0.07, and 0.1 g of polyaniline nanocomposite were added to mentioned solutions. Then, solutions were stirred by a handmade mechanical stirrer so that dye removal process by nano-absorbent to be done better. After 2 hours with the help of strong magnet 1.4 T, it was deposited and some quantity of residual solutions was centrifuged for complete deposition with 3500 rounds for 30 minutes. Then, secondary absorption of each of solutions was read by UV-Vis device so that value of specified dye removal and optimal value of absorbent to be determined. All of the above stages, except for deposition by magnet stage, were done by polyaniline absorbent so that dye absorption difference to be compared in two states. The results can be seen in Figure 8.
solutions was read by UV-Vis device so that value of specified dye removal and optimal value of absorbent to be determined. In addition, to examine the impact of temperature on dye removal, this experiment was replicated at 35 and 45 temperatures. The results can be seen in Figure 8.

**Figure 7**- pH impact on dye absorption

![Figure 7](image1)

**Figure 8**- the impact of absorbent value on dye absorption

![Figure 8](image2)

**Figure 9**- contact time impact on absorption of yellow 15 reactive dye

**Adsorption isotherms:** Adsorption isotherms are useful quantitative tools to demonstrate the capacity and behavior in absorbing certain material (Mostafapoor and Kord 2000). Based on studies, various isotherm models have been proposed for absorption phenomena but only some of them can be sued for the adsorption systems of dye materials that they are referred here.

- Langmuir adsorption isotherm
Equation 1-1 shows the main form of Langmuir adsorption isotherm that is less used scientifically. 

\[ q_e = \frac{q_m C_e}{1 + K C_e} \]  

Where \( q_e \) is value of dye in absorbent in the equilibrium time (mg/g), \( C_e \) is value of dye in absorbent in the equilibrium time (mg/l), \( q_m \) is the highest value of absorption in absorbent (mg/g), and \( k \) is Langmuir constant. With some simple transformations, Equation 1-1 can be provided in the form of linear equation as 1-2 equations:

\[ \frac{1}{q_e} + \frac{C_e}{q_m} = \frac{1}{q_m k} \]

Freundlich adsorption isotherm

This equation has empirical basis stated by Freundlich as Equation 1-3.

\[ q_e = K C_e^{1/n} \]

Where \( K \) is constant and \( 1/n \) is a feature and property of investigated system depending on type of absorbent and adsorbed. Value of \( 1/n \) varies from zero to one. The equation above is the most important adsorption isotherm equation for unsmooth surfaces having great contact surface. In Freundlich Equation, we can suppose linear relationship between concentrations of adsorbed in absorbent and solution as Equation 1-4 (Cegarra, Puente, Valldeperas, 1992).

\[ \log q_e = \log K \frac{1}{n} + \frac{1}{n} \log C_e \]

Diagrams 10 and 11 and Tables 1 and 2 show that yellow 15 dye adsorption isotherm on considered nano composite follows Langmuir Equation.

**Figure 10** - Langmuir adsorption isotherm to absorb dye

**Figure 11** - Freundlich adsorption isotherm to absorb dye
Table 1- various parameters of Langmuir adsorption isotherm to absorb yellow15 reactive dye on Polyaniline nano composite / Fe$_3$O$_4$

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>K</th>
<th>$q_m$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyaniline</td>
<td>-0.31</td>
<td>166.6</td>
<td>0.980</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2- various parameters of Freundlich adsorption isotherm to absorb yellow15 reactive dye on Polyaniline nano composite / Fe$_3$O$_4$

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>K</th>
<th>n</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyaniline</td>
<td>51.05</td>
<td>10.20</td>
<td>0.955</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Absorption kinetics

Adsorption kinetics information is analyzed to understand the dynamics and rate of adsorption on the adsorbent. Adsorption kinetics of pigment or dye materials on certain absorbent has been reported and analyzed in papers in the form of pseudo-first order and pseudo-second-order models (Y-SH Ho and McKay, 1998).

Reaction equation for rate of reaction in the pseudo-first order model is based on 1-5 and 1-6 equations.

\[
\frac{dq}{dt} = k (q_e - q_t)
\]

(Equation 1-5)

\[
\ln (q_e - q_t) = \ln q_e - kt
\]

Where $q_e$ is value of dye in absorbent at the equilibrium time (mg/g), $q_t$ is the value of dye at time $t$ and $k$ is equation constant. Linearity of diagram $\ln (q_e - q_t)$ in $t$ suggests that absorbent reaction of absorbed is a pseudo-first order reaction.

Pseudo-second order kinetics model of dye is defined by Equation 1-7 and 1-8 (Min et al, 2008).

\[
k = \frac{1}{q_e} - \frac{1}{q_e^2}
\]

(Equation 1-6)

\[
\frac{q_t}{q_e} = \frac{1}{kq_e} \ln q_e
\]

Where $q_e$ is value of dye in absorbent at the equilibrium time (mg/g), $q_t$ is the value of dye at time $t$ and $k$ is equation constant. In Equation (1-10), the value $Kq_e^2$ is considered as initial absorption rate in mg min$^{-1}$. If pseudo-second order kinetics can be applied, $t/q_t$ must show a linear equation versus $t$. Investigation of diagrams 12 and 13 and Table 3 that yellow15 reactive dye kinetics follows pseudo-second order equation.

Figure 12- Pseudo-first order to absorb dye
CONCLUSION
The results of this study showed that nano-adsorbent covered with polyaniline is effective adsorbent for removal of yellow15 reactive dye from aqueous solutions. It can be explained due to an increase in absorbent surface as result of using polyaniline in the preparation of polyaniline nano composite Fe₃O₄. According to results, the optimal value of PH for removal of yellow15 dye was considered as 3. In addition, yellow 15 dye removal percentage from aqueous solution of 0.05 g of modified nano absorbent had the highest value. Optimal contact time for considered dye was considered 30 minutes according to results of study. In this study, it was revealed that the processes of yellow15 dye removal follow Langmuir equation. It was also revealed that dye absorption kinetics follows Pseudo-second order model.

REFERENCES