The Application of SiO$_2$ Nanoparticles for Anionic Dye Removal from Aqueous Solution

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**Background & Aims of the Study:** Dyes are one of the widespread chemicals which may have many adverse effects on life cycle. Thus, this study was conducted to survey the RB19 dye removal efficacy from aqueous solution, using the SiO$_2$ nanoparticles.

**Materials and Methods:** This study was an experimental-lab study. The batch adsorption system were utilized to evaluated the RB19 dye removal efficiency under different amount of effective parameters including contact time, pH, adsorbent dosages, initial RB19 dye concentration and temperature.

**Results:** The results of this study showed that the increasing of contact time, adsorbent dosage and temperature (up to 30$^\circ$C) can positive effect on dye removal efficiency and can develop the dye removal efficiency, while the increasing of pH and RB19 dye concentration decrease the dye removal efficiency. The maximum dye removal efficiency was observed to be 95.72% at pH=5 and temperature of 30$^\circ$C. Furthermore, the equilibrium studies of the RB19 dye adsorption depicted that the Langmuir isotherm and pseudo-second-kinetic models was successfully able to describe the equilibrium data.

**Conclusion:** It can be concluded that SiO$_2$ nanoparticles are excellent adsorbent to remove the dyes from aqueous solution.


**Background**

Historically, the development of human life style has been associated with the need to large amount of energies and chemicals that might be destructive and hazardous for the environment (1-2). The dyes are of major class of the chemicals which have various target industries such as textiles, leather, paper, printing and cosmetics but the highest amount of dyes is used in textile industries (3-4). Dyes are drastically used in these industries and can generate the colorful wastewater (5). This produced wastewater which can simply release into environment and be considered as a major risk for various type of life in environments (6-7). Among various types of dyes, the reactive dyes are identified as widely used dyes to colorize the fibers (8). A large amount of these dyes (50%) is lost during dying and it is obvious that great volume of colorful wastewater is producing by this part (9). The toxicity and aesthetic risks of the dyes has been reported in various literatures. They are supposed to participate in some diseases such
as dermatitis and cancers, etc (10-11). Thus, the colorful effluents should be considered as one major risk and best methods should be applied to alleviate the dangerous effects of these chemical to save the human and environment. Different approaches such as adsorption, membrane separation, electrochemical, flocculation-coagulation, reverse osmosis, ozone oxidation, and biological treatments have been used to remove the dyes. Although, these methods was able to successfully remove the dyes; however, the popularity of these methods are reducing due to their cost and complexity (12-13). The nanotechnology and use of the nano-material is one of the effective innovations to remove the pollutants which have gained many interesting among the societies. The nanoparticles have been used in various studies to remove a number of pollutants such as dyes (14-15), antibiotics (16), heavy metals (17-18), etc. Those studies showed that the nanoparticles has considerable efficacy in removal of mentioned pollutants. This substantial efficacy is due to the unique features of these materials including high adsorption capacity, simplicity in operation, rapid adsorption process, etc (19).

**Aims of the study:**
The aim of the present work was to study the SiO$_2$ nanoparticles ability in reactive blue 19 dye removal. Also, this study was conducted to determine the effect of the contact time, pH, temperature, dye concentration and SiO$_2$ nanoparticles dosage on dye removal efficiency.

**Materials & Methods**

**Chemical material:**
The Reactive Blue 19 (RB19) dye was provided from AlvanSabet Corporation, Hamadan, Iran. The chemical characteristics and structure of RB19 dye is represented in the Table 1.

<table>
<thead>
<tr>
<th>Chemical structure</th>
<th>C$<em>{22}$H$</em>{16}$N$_2$Na$<em>2$O$</em>{11}$S$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C$<em>{22}$H$</em>{16}$N$_2$Na$<em>2$O$</em>{11}$S$_3$</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>626.54</td>
</tr>
<tr>
<td>Maximum wavelength</td>
<td>592</td>
</tr>
</tbody>
</table>

**Adsorbent properties:**
The SiO$_2$ nanoparticles were purchased from Research Institute of Petroleum Industry (RIPI), Tehran, Iran which was used to study the adsorption characteristics of RB19 dye from aqueous solutions. The outer diameter of SiO$_2$ nanoparticles used in this study was in range of 10 to 20 nm. In addition, the specific surface area of SiO$_2$ nanoparticles was reported to be greater than 210 m$^2$/g and the mass ratio of the amorphous carbon of SiO$_2$ nanoparticles was lesser than 10%. The SEM images of this adsorbent were provided, using a Philips XL30 scanning electron microscope (SEM). This image (Fig.1) shows the porous surface of this adsorbent and reveals that it can be proper adsorbent for RB19 dye removal.

**Batch adsorption studies:**
At the first, a stock solution of RB19 dye (1000mg/L) was prepared and other desired solution with different initial dye concentrations were prepared by diluting of the stock solution. The batch adsorption system was utilized to study the influence of the
A study was conducted to examine factors affecting the adsorption of RB19 dye by SiO$_2$ nanoparticles. The factors studied included contact time (10-180 min), pH (3-11), temperature (20-60°C), adsorbent dose (0.2-1.6 g/L), and initial concentration of dye (10-500 mg/L). All experiments were performed in 250 mL Erlenmeyer flasks. Dye solutions were prepared with varying concentrations and SiO$_2$ nanoparticles were added. The pH of each solution was controlled using 0.1N HC1 or 0.1N NaOH. The experiments were conducted by varying each parameter while keeping others constant to determine the optimum conditions. After mixing, samples were filtered and the final dye concentration was measured with a UV-Visible spectrophotometer (DR-4000) at a wavelength of 592 nm. The equilibrium experiments were conducted to study the effect of adsorbent dosage on the dye removal efficiency. It was observed that the RB19 dye removal efficiency increased from 44.65% to 95.63% as the SiO$_2$ nanoparticles dosage increased from 0.2 to 1.6 g/L, but the dye adsorption capacity decreased from 74.41 to 14.94 mg/g. The effect of pH on the dye removal efficiency was determined by varying the pH from 3 to 11, with the highest removal efficiency observed in the pH range of 3 to 6. Contact time and temperature also had significant effects on the dye removal efficiency, with optimal conditions being established for each factor.
The effect of these parameters was evaluated by variation of the contact time (10-180 min) and temperature (20-60°C). The results of this study are shown in figure 4. As it can be seen, the dye removal efficiency increased by increasing the contact time and temperature. The best dye removal efficiency was 95.72% at the 30. In addition, the dye removal efficiency is significant at the initial time of the adsorption process and it remains constant after 90 min.

The effect of initial RB19 dye concentration

The initial dye concentration is another parameter which can influence the adsorption process. The effect of this parameter was investigated by the variation of initial concentration of RB19 dye (10-500 mg/L), using the constant amount of other parameters. The results of this study were brought in figure 5. This figure demonstrates that increasing the dye concentration has negative effect on dye removal efficiency.

Isotherm studies

The equilibrium data of the RB19 dye adsorption were fitted on the Langmuir and Freundlich models to understand the best models to best design of the process and to optimize the use of nanoparticle.

Langmuir Isotherm:

The Langmuir isotherm is resulting on the theory of mono-layer adsorption on a homogenous surface. This equation of this isotherm can express by following equation (21-22):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$  \hspace{1cm} (3)

Where, $C_e$ (mg/L) and $q_e$ (mg/g) are the concentration of RB19 and the amount of RB19 dye adsorbed onto SiO$_2$ nanoparticles at equilibrium, respectively. $q_m$ is indicates the maximum monolayer adsorption capacity (mg/g) and $K_L$ is the Langmuir constant (L/mg).

Freundlich isotherm:

The Freundlich isotherm describes the adsorption on heterogeneous surfaces. The following equation is related to the Freundlich model isotherm (23-24):

$$\log q_e = \log C_e + \log K_f$$  \hspace{1cm} (4)

Where $q_e$ is the RB19 dye concentration on the SiO$_2$ nanoparticles (mg/g) at equilibrium, $C_e$ is
the concentration of RB19 dye in solution at equilibrium (mg/L) and $K_f$ is the Freundlich constant. The results of the isotherm studies are presented in Table 2.

**Kinetic studies:**
In this study, the pseudo-first-kinetic and pseudo-second-kinetic models were applied. These models are useful to determine the rate of the adsorption process. The pseudo-first-order rate equation is expressed as following (25-26):

$$\log(q_e - q) = \log(q_e) - k_1 t / 2.3$$  

(5)

Where; $q_e$ and $q$ are related to RB19 dye adsorption capacity (mg/g) onto the SiO$_2$ nanoparticle (mg/g) at equilibrium and at time $t$ (min), respectively; and $k_1$ is the constant rate of the pseudo-first-order kinetic model (min$^{-1}$).

The pseudo-second-order model equation is calculated by below equation (27):

$$\frac{dq}{dt} = k_2(q_e - q)^2$$  

Where; $K_2$ is the constant rate related to the second order model (g/mg/min). The plots of log ($q_e - q$) versus ($t$) are used to calculate the $k_1$ while the $k_2$ is calculated from the plots of $t/q$ against ($t$).

**Table 2** Isotherm parameters related to the reactive blue 19 dye adsorption on to SiO$_2$ nanoparticles

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Langmuir (mg/g)</th>
<th>$K_l$ (L/mg)</th>
<th>$R^2$</th>
<th>$n$</th>
<th>$K_f$ (mg/g.min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>13.4</td>
<td>0.626</td>
<td>0.945</td>
<td>3.065</td>
<td>39.38</td>
<td>0.8597</td>
</tr>
<tr>
<td>30°C</td>
<td>14.37</td>
<td>0.816</td>
<td>0.9466</td>
<td>3.82</td>
<td>34.97</td>
<td>0.8304</td>
</tr>
<tr>
<td>40°C</td>
<td>12.48</td>
<td>0.516</td>
<td>0.9407</td>
<td>2.63</td>
<td>43.54</td>
<td>0.8729</td>
</tr>
<tr>
<td>50°C</td>
<td>11.5</td>
<td>0.432</td>
<td>0.9349</td>
<td>2.28</td>
<td>48.65</td>
<td>0.8803</td>
</tr>
<tr>
<td>60°C</td>
<td>10.61</td>
<td>0.368</td>
<td>0.9297</td>
<td>2.01</td>
<td>55.03</td>
<td>0.8877</td>
</tr>
</tbody>
</table>

**Table 3** Kinetic parameters related to the adsorption of reactive blue 19 dye on to SiO$_2$ nanoparticles

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pseudo-first kinetic</th>
<th>Pseudo-second-kinetic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_e$ (mg/g)</td>
<td>0.17733</td>
<td>0.023</td>
</tr>
<tr>
<td>$K_f$ (min$^{-1}$)</td>
<td>0.763</td>
<td>0.9985</td>
</tr>
</tbody>
</table>

**Discussion**

**Effect of SiO$_2$ nanoparticles dosage:**
The adsorbent dosage has identified as most effective parameters on the adsorption of pollutants. As it was detected, although the dye removal efficiency increases by increasing the adsorbent dosage however the adsorption capacity decreases. It is expressed that the increasing of the adsorption surface site can be the logical reason for the higher dye removal efficiency. In contrast, the higher unsaturated adsorption sites on adsorbent surface are attributed to decreasing the adsorption capacity (28). Mahmoodi et al conducted a study to investigate the nanoparticles ability in direct dyes efficiency. They have found that the dye removal efficiency is developed by increasing the adsorbent dosage while the adsorption capacity decreased. They declared that the higher dye removal efficiency by increasing the adsorbent dosage can be due to increase the adsorbent surface and the accessibility of more adsorption sites. They have also reported that the declining of the adsorption capacity is due to overlapping or aggregation of adsorption sites which is led to the decrease the available total adsorbent surface area and to increase in diffusion path length (29).

**Effect of pH:**
This parameter plays an important role in adsorption processes. The above results showed that the RB19 dye removal efficiency is higher in acidic pH and the increasing of pH is led to decline the dye removal efficiency. Since the RB19 dye belongs to anionic dyes group; therefore, its molecules is negatively charged. As it is known, the surface of the adsorbent is positively charged in acidic pH; thus, the electrostatic attraction occurs between the
negatively charged molecules of dye and the surface of the adsorbent which can increase the removal efficiency. The similar results for dye removal by other adsorbents were observed in other studies (30-31). The adsorption of reactive dye was evaluated by Asadi et al; they observed that the pH has an important role in the dye removal efficiency. they has also observed that the higher dye removal efficiency is obtained at pH=3 which is in consistent with our study (32).

**Effect of contact time and temperature:**

The contact time and temperature are other parameters which are influencing the dye adsorption process. The obtained results revealed that both two parameters have direct effects on RB19 dye removal and they can enhance the dye removal that they are similar to other studies (33-34). The increasing of dye removal efficiency with temperature indicates that the RB19 dye adsorption is endothermic naturally (35). The higher dye removal efficiency at initial time of the process is related to the large number of the adsorption surface site at the start of this process. As it was observed that the dye adsorption process reached to equilibrium within 90 min (36). Ahuja et al has conducted a study to evaluate the dye from aqueous solution, using zero valent iron nanoparticles and observed that the contact time has a significant effect on dye removal efficiency. They found that dye removal efficiency, which enhanced by increasing the contact time, is agree with the results of this study (37).

**The effect of initial RB19 dye concentration:**

The study of the effect of concentration of RB19 dye indicated that the removal efficiency decreases by increasing the initial dye concentration. The dye removal efficiency is higher at the lower dye concentration but it decrease by increasing the dye concentration. The highest RB19 dye removal was observed to be 96.45% for 50mg/L dye but it is clear that the lowest dye adsorbed per adsorbent mass is 12.86mg/g. The initial dye concentration of 50mg/L was selected as an optimum concentration. The lowest dye removal and highest dye adsorbed per adsorbent mass was observed to be 68.27% and 455.133mg/g, respectively which obtained for dye concentration of 500mg/L. these results are in consistent with the results of other studies (38). Behnajady et al has surveyed the ability of TiO$_2$-P$_{25}$ nanoparticles for the adsorption of AR27 dye and they found that the dye elimination efficacy decreased from 97% to 39% with increasing of initial concentration of AR27 from 10 to 80mg/L. they reported that this event can be due to the saturation of adsorption sites onto TiO$_2$-P$_{25}$ nanoparticles (39).

**Isotherm studies:**

As it was observed in above, Langmuir and Freundlich models were applied to study the RB19 dye adsorption isotherm onto SiO$_2$ nanoparticles. The results of isotherm studies were presented in table 2. The $q_{max}$ and $k_L$ are determined from the plot of $(C_e/q_e)$ versus $C_e$ and the $K_f$ and $n$ are calculated from the plot of log $q_e$ versus log $C_e$. The higher amount of regression coefficient ($R^2$) is indicative of the better model to describe the equilibrium data. As it can be seen in table 2, the equilibrium data were studied at 20, 30, 40, 50 and 60 °C. The $R^2$ values achieved from the Langmuir model were higher than its values for Freundlich in all temperatures which indicated that the equilibrium data are best fitted on the Langmuir model. It is also observed that the amount of $R^2$ for the Langmuir model at 30 °C is greater than other $R^2$ values of this model which indicates that the highest monolayer adsorption capacity obtained from the Langmuir model in this temperature (14.37mg/g). These results are in consistent with the results of other studies (40-41).

**Kinetic studies:**

As it was observed, the studying of the kinetic of RB19 dye adsorption was performed pseudo-first-kinetic and pseudo-second-kinetic models and the results obtained from these studies were...
represented in table 3. As it can be seen, the $R^2$ obtained from the pseudo second-order kinetic model is higher than this value for the pseudo-first-kinetic which means that the uptake process follows the pseudo-second-order ($R^2 > 0.998$) and the data are best fitted on the pseudo second-kinetic models. These results are agreed with the results of other studies (42-43).

### Conclusion

In this work, RB19 dye removal efficiency by SiO$_2$ nanoparticles were evaluated in batch adsorption system. The effect of parameters including contact time, pH, adsorbent dosages, initial RB19 dye concentration and temperature were investigated and observed to be effective on the adsorption process. It was distinguished that the increasing of contact time, adsorbent dosage and temperature (up to 30°) had positive effects on dye removal efficiency and can increase the dye removal efficiency while the increasing of pH and dye concentration decrease the dye removal efficiency. The optimum amount of contact time, pH, adsorbent dosage, dye concentration and temperature was found to be 90 min, 5, 0.75g/L, 50mg/L and 30, respectively. The highest dye concentration was observed to be 95.72%. The equilibrium data were best fitted on pseudo-second kinetic and Langmuir isotherm model. The highest monolayer adsorption capacity (14.37mg/g) was obtained at 30°C. It can be concluded that SiO$_2$ nanoparticles have a significant potential for dye removal from aqueous solution.

### Footnotes

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**Conflict of Interest:**
The authors declared no conflict of interest.

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### References

