Adsorption behavior of Azo Dye C. I. Acid Red 14 in aqueous solution on surface soils

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Abstract

Azo dyes have received considerable attention because of their association with various human health problems. The aim of the investigation is to determine the adsorption behavior of azo dyes in aqueous solution on DG06, GSE17200, and GSE17201 soils using C. I. Acid Red 14 (AR14) as example. The experimental results indicate that the Freundlich model expresses the adsorption isotherm better than the Langmuir model and the pseudo-second-order model achieves adsorption of AR14 on the three soils well. Based on the pseudo-second-order model, the adsorption thermodynamic of AR14 on DG06 soil have been studied and the thermodynamics parameter of \( \Delta G^0 \) is determined and \( \Delta G^0 \) value shows the adsorption process of AR14 on DG06 is mainly physical in nature. Furthermore, the effects of temperature, pH and salinity (NaCl) on adsorption have been investigated. The decrease in pH or the increase in salinity enhances the adsorption of AR14 by DG06, GSE17200, and GSE17201.

Key words: soil; azo dyes; C. I. Acid Red 14 (AR14); adsorption isotherm; adsorption kinetics; adsorption thermodynamics

Introduction

Azo dyes are widely used in many industrial fields, such as textile, leather, paper, plastics, rubber, etc. They have been considered as an extremely important pollutant in environment due to their complex composition, high toxicity, poor degradability and great solubility in water (Ramakrishna et al., 1997; Vandevivere et al., 1998; Robinson et al., 2002). At present, owing to wide usage of azo dyes in China, the water and soil have been contaminated widely (Liu et al., 2001; Zhou, 2001).

It is well-recognized that organic pollutants adsorption process can affect their other environmental behaviors such as transport, degradation, volatilization, bioaccumulation, consequently, influence the final fate of these pollutants in environment (Gao et al., 1998). Much research has been done on the adsorption behaviors of azo dyes in aqueous solution by adsorbents such as activated carbon, activated sludge, chitosan and resin (El-Geundi, 1991; Yoshida et al., 1993; Al-Degs et al., 2000; Aksu, 2001; Yu et al., 2004). These studies on adsorption behaviors contribute to the treatment of dye-contaminated wastewater (Robinson et al., 2001). However, reports on the adsorption behaviors of azo dyes in aqueous solution by soils are very few (Ketelsen and Meyer-Windel, 1999). Since the average concentration of total organic dyes in surface soils adjacent to printing, dyeing or synthetic dying enterprises, has been up to 12.3–3114.0 mg/kg (dry weight) in China (Zhou, 2001), it’s very necessary to develop a knowledge base of azo dye’s adsorption behaviors on surface soil to evaluate the extents to which soils are contaminated by them and the environmental conditions which affect the adsorption amount by soils.

The objective of this investigation is to determine the adsorption behavior of azo dye in aqueous solution on three kinds of surface soils using C. I. Acid Red 14 (AR14) as sample. Two kinetic models, pseudo-first-order equation and pseudo-second-order equation were used to describe the sorption mechanism of AR14 on the three soils (Lagergren and Svenska, 1898; Ho and McKay, 1999a, 1999b). The Langmuir isotherm and the Freundlich isotherm of AR14 on the three soils were determined respectively. Based on the pseudo-second-order equation, the thermodynamics parameter, \( \Delta G^0 \) of AR14 on DG06 soil was studied and the adsorption process of AR14 on DG06 has been pointed out. In addition, the effects of pH and salinity (NaCl) on adsorption have been also investigated.

1 Materials and methods

1.1 Materials

The azo dye, C.I. Acid Red 14 (Color Index NO.14720), was obtained from Tianjin Shengda Chemical Factory.
(China) and the purity was above 97%. The molecular weight of AR14 was 502.42 and the structure of AR14 is shown in Fig.1.

![Chemical structure of C. I. Acid Red 14.](image)

Selected soils GSE17200 and GSE17201 soils were obtained from Bayer Landwirtschaftszentrum, Monheim, Germany. DG06 soil was sampled in the surface layers (0–20 cm) located in Dalian, Liaoning Province, China. Three kinds of soils were air-dried, sieved to 2 mm and stored in dark at a room temperature (20 ± 1°C). The physical and chemical properties of the three soils are shown in Table 1.

### 1.2 Adsorption isotherm and kinetics studies

Adsorption isotherm and kinetics studies on DG06, GSE17201 and GSE17200 soils were performed in batch experiments. An exactly known amount of the adsorbent (10 g soil) was weighed into a 250-ml glass stoppered conical flask. Different concentrations of 100 ml AR14 solutions (from 100 to 800 mg/L at six different concentrations) were added to the flasks with the soil. The flasks were then shaken (200 r/min) for 48 h for equilibration at 20±0.5°C. Samples were withdrawn periodically for AR14 concentration analysis. Before analysis samples were separated by centrifugation (10000 r/min, 15 min). After membrane filtration (cellulose acetate, 0.22 µm), the filtrate was analyzed using HPLC. All determinations were performed against a soil blank to correct for possible interferences in the measurement of the dye. All samples were in triplicate.

### 1.3 Adsorption thermodynamics studies

DG06 soil was selected for study of adsorption thermodynamics. Each conical flask was supplemented with 100 ml AR14 solution (300 mg/L). These conical flasks were placed on a rotary shaker (200 r/min) at different temperature (10 ± 0.5°C, 20 ± 0.5°C, 30 ± 0.5°C). Samples were withdrawn periodically for AR14 concentration analysis. The adsorption kinetics at different temperatures (10 ± 0.5°C, 20 ± 0.5°C, 30 ± 0.5°C) was studied especially.

### 1.4 Effects of pH and salinity on the adsorption isotherm

To test the effect of pH on the adsorption isotherms of the three soils, each conical flask was supplemented with 100 ml AR14 solution (300 mg/L). The pH value of AR14 solution varied from 2.0 to 10.0. The pH of each solution was adjusted to the required value with diluted or concentrated HCI and NaOH solutions before mixing the soils. These conical flasks were placed on a rotary shaker (200 r/min) at 20 ± 0.5°C. At the equilibrium time, samples were withdrawn for AR14 concentration analysis. The effect of initial pH (from 2.0 to 10.0) of AR14 solution (300 mg/L) on pH of the systems (AR14 solution + soil) was determined. The same setup was also used for testing the effect of salinity (specially, NaCl) on the adsorption isotherms of the three soils. The quality concentration of NaCl in AR14 solution were 0.2%, 0.5%, 1%, 2%, and 4%.

### 1.5 Analytical methods

The concentration of AR14 in aqueous solution was monitored with HPLC (1100-FLD, Agilent Technologies, USA). The column is Waters Bondpak C18 (4.6 mm × 250 mm). The mobile phase was methanol/water (40:60, V/V) and the flow rate was 1 ml/min. The detector wavelength was set at 516 nm.

The amounts of AR14 adsorbed by the three soils, $q_e$ (mg/g), were calculated by the following equation:

$$q_e = \left(\frac{C_0 - C_f}{M}\right) \times V$$  

where, $C_0$ and $C_f$ are the initial and equilibrium concentrations of AR14 in solution (mg/L), respectively. $V$ is the total volume of the AR14 solution (L), and $M$ is the mass of soils used (g).

### 2 Results and discussion

#### 2.1 Effect of initial dye concentration on AR14 adsorption

Initial concentration has an important effect on adsorption, which can give a driving force to overcome all mass transfer resistances of the dye between the liquid and solid phases. Hence a higher initial concentration of dye will enhance the sorption process. In this study, the effect of initial dye concentration on the dye adsorption capacity was investigated between 100 and 800 mg/L at 20 ± 0.5°C, the results are presented in Table 2. As listed in Table 2, when initial dye concentration is 100 mg/L, the dye uptake efficiencies of AR14 on DG06, GSE17200, and GSE17201 soils are high, and they are 21.9%, 10.4%, and 8.0%, respectively. With the increase in initial concentration, although the equilibrium adsorption amount ($q_e$) significantly increases, the dye uptake efficiency takes on a decrease trend. When the initial dye concentration reaches 800 mg/L, the dye uptake efficiency has the lowest values

<table>
<thead>
<tr>
<th>Soil</th>
<th>pH (0.01 mol/L)</th>
<th>OC (%)</th>
<th>CEC (cmol/kg)</th>
<th>Clay (%)</th>
<th>Silt (%)</th>
<th>Sand (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DG06</td>
<td>7.0</td>
<td>3.62</td>
<td>18.5</td>
<td>26.40</td>
<td>34.95</td>
<td>38.65</td>
</tr>
<tr>
<td>GSE17200</td>
<td>7.3</td>
<td>0.86</td>
<td>8</td>
<td>12.00</td>
<td>51.10</td>
<td>36.90</td>
</tr>
<tr>
<td>GSE17201</td>
<td>6.3</td>
<td>2.48</td>
<td>10</td>
<td>7.20</td>
<td>12.30</td>
<td>80.50</td>
</tr>
</tbody>
</table>

OC: organic carbon; CEC: cation exchange capacity.
that are 10.2%, 6.1%, and 4.5% for DG06, GSE17200, and GSE17201, respectively. This may result from the saturation of the sorption sites on the soils as the dye concentration increases.

### 2.2 Adsorption Isotherm

The Langmuir model equation is (Benefield et al., 1982; Mall et al., 2005):

\[
\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0}
\]

where, \(q_e\) (mg/g) is the amount of dye adsorbed at the point of equilibrium, \(C_e\) (mg/L) is the equilibrium dye concentration in solution, \(Q_0\) (mg/g) is the monolayer saturation capacity of the adsorbent, and \(K_L\) (L/mg) is the Langmuir adsorption constant. A plot of \(C_e/q_e\) vs \(C_e\) gives a straight sloping line \(1/Q_0\) and intercept \(1/K_L Q_0\).

The Freundlich equation is (Adamson, 1990):

\[
\log q_e = \log K_F + \left(\frac{1}{n}\right) \times \log C_e
\]

where, \(q_e\) (mg/g) is the amount of dye adsorbed at the point of equilibrium, \(C_e\) (mg/L) is the equilibrium dye concentration in solution, and \(K_F\) (L/mg) and \(n\) are Freundlich constants which can be calculated from the logarithmic plot of \(q_e\) vs \(C_e\).

Table 3 shows the values of \(Q_0\), \(K_L\), \(K_F\), \(1/n\) and the correlation coefficients for Langmuir (\(R^2_L\)) and for Freundlich (\(R^2_F\)). In Table 3, the values of \(K_F\) for soils of DG06, GSE17200, and GSE17201 are 0.9869, 0.9448, and 0.9216 respectively, which are higher than the corresponding \(R^2_L\) values (0.9392, 0.8561, and 0.7151). The experimental data of the adsorption isotherm are correlated by the Freundlich equation better than by the Langmuir equation. So the Freundlich equation expresses the adsorption isotherms of AR14 on the three soils better than the Langmuir equation over the entire range of concentrations.

Figure 2 shows the adsorption isotherm of AR14 adsorbed by DG06, GSE17200, and GSE17201 soils. Based on the Freundlich equation, when \(C_e = 1\), the value of \(K_F\) coincides with the adsorbed concentration \(q_e\), and hence can be used to compare the relative adsorption capacity on different adsorbents. The relative soil adsorption capacity of AR14 on the three soils could be obtained through the comparison of their corresponding \(K_F\) values. As shown in Table 3, the \(K_F\) values of AR14 on DG06, GSE17200, and GSE17201 soils are 7.1×10^{-3}, 4.8×10^{-3}, and 3.2×10^{-3} respectively. These results indicate DG06 has the highest adsorption capacity among the three soils. In addition, according to the classification of Giles et al. (1960) adsorption isotherms of the AR14 on the three soils follow L-type (\(n > 1\)) curves, which indicate that the adsorption firstly occurs on the high energy sites of adsorbents, follows by the low energy sites (Alok and Xu, 2001). Furthermore, the adsorption affinity of the dye appears to be positively correlated with the clay content of the soils and adsorption increases in the following order: GSE17201 (7.20% clay), GSE17200 (12.00% clay), and DG06 (26.40% clay). This finding is agreement with Ketelsen and Meyer-Windel (1999) who reported a strong positive correlation between Brilliant Blue FCF (dye tracer) and clay contents of soils.

### 2.3 Adsorption Kinetics

To study the process of AR14 adsorption by the surface soil, two kinetic models, pseudo-first order equation and pseudo-second order equation are used to describe the mechanism of adsorption.

### Table 3 Adsorption isotherm data described the adsorption of AR14 by the three soils

<table>
<thead>
<tr>
<th>Soil</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Q_0)</td>
<td>(K_L)</td>
</tr>
<tr>
<td>DG06</td>
<td>1.38</td>
<td>2.1×10^{-3}</td>
</tr>
<tr>
<td>GSE17200</td>
<td>0.98</td>
<td>1.5×10^{-3}</td>
</tr>
<tr>
<td>GSE17201</td>
<td>0.83</td>
<td>1.2×10^{-3}</td>
</tr>
</tbody>
</table>
The expression of the pseudo-first-order model is:

$$\log(q_t - q_e) = \log(q_1) - \frac{K_1}{2.303} t$$  \(4\)

where, \(q_1\) (mg/g) is the amount of dye adsorbed at the point of equilibrium, \(q_t\) (mg/g) is the amount of dye adsorbed at time \(t\), and \(K_1\) (min\(^{-1}\)) is the rate constant which can be calculated from the straight-line plot of \(\log(q_1 - q_t)\) vs \(t\).

The pseudo-second-order model equation is:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$  \(5\)

where, \(q_2\) (mg/g) is the amount of dye adsorbed at the equilibrium time, \(q_t\) (mg/g) is the amount of dye adsorbed at time \(t\), and \(K_2\) (min\(^{-1}\)) is the rate constant which can be calculated from the straight-line plot of \(t/q_t\) vs \(t\).

Figure 3 shows the adsorption kinetics of AR14 by the three soils at 300 mg/L initial dye concentration. The adsorption kinetic parameters of the two models determined are shown in Table 4. The correlation coefficients \(R^2\) of the pseudo-first-order model for DG06, GSE17200, and GSE17201 soils are 0.9370, 0.9246, and 0.9186, respectively. The correlation coefficients \(R^2\) of the pseudo-second-order model are 0.9991, 0.9904, and 0.9946, respectively (insert in Fig.3). So the pseudo-second-order model is more significant than the pseudo-first-order model. In addition, the calculated \(q_1\) values from the pseudo-first-order model do not give reasonable values, which are too low compared to experimental \(q_e\) values. However, the calculated \(q_2\) values from the pseudo-second-order model are basically same as the experimental \(q_e\) values. Therefore, these results demonstrate that the pseudo-second-order kinetic model describes the adsorption process of AR14 by the three soils better than pseudo-first-order model. Furthermore, based on the pseudo-second-order model, the initial adsorption rates (mg/(g-min)) of AR14 on the three soils are calculated by the following equation (Ho and McKay, 1999b) \(v = K_2 q_e^2\), which are also listed in Table 4. Comparing these determined kinetic parameters shown in Table 4, AR14 on DG06 soil has the highest rate constant \((K_2 = 0.078)\) and the initial adsorption rate \((v = 0.0130)\) among the three soils. Therefore, AR14 is more quickly adsorbed by DG06 soil than by the other two soils.

### 2.4 Adsorption thermodynamics

As described above, DG06 soil has higher adsorption capacity and can more quickly adsorb AR14 than GSE17200 and GSE17201 soils, so DG06 soil was used to further study adsorption thermodynamics of AR14, based on the pseudo-second-order model. Fig.4 shows at different temperatures the variation of AR14 adsorption kinetics with DG06 soil.

The adsorption kinetic parameters of AR14 by DG06 at 10, 20, and 30°C are measured and shown in Table 5. The correlation coefficients at three different temperatures are higher than 0.99, which means the adsorption process can be expressed well by the pseudo-second-order adsorption equation at the temperature range from 10 to 30°C. According to these kinetic parameters determined, the thermodynamic parameters of standard free energy \((\Delta G^0)\), enthalpy \((\Delta H^0)\), and entropy \((\Delta S^0)\) are measured by using the following equations (Catena and Bright, 1989; Namasivayam and Yamuna, 1995):

\[
K_C = \frac{q_e}{C_e} \quad (6)
\]

\[
\Delta G^0 = -RT \ln K_C \quad (7)
\]

\[
\log K_C = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (8)
\]

![Fig. 3](image-url) Variation of AR14 adsorption kinetics with DG06, GSE17200, and GSE17201 soils; the insert figure shows the Pseudo-second-order sorption kinetics used for the fitting. Initial dye concentration: 300 mg/L, 20 ± 0.5°C, significance at \(P < 0.05\).

![Fig. 4](image-url) Effect of temperature on the adsorption kinetics of AR14 on DG06 soil. Initial dye concentration: 300 mg/L, significance at \(P < 0.05\).

<table>
<thead>
<tr>
<th>Soil</th>
<th>(K_1)</th>
<th>(q_1)</th>
<th>(R^2)</th>
<th>(K_2)</th>
<th>(q_2)</th>
<th>(\Delta H^0)</th>
<th>(\Delta S^0)</th>
<th>(\Delta G^0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DG06</td>
<td>0.0020</td>
<td>0.126</td>
<td>0.9370</td>
<td>0.078</td>
<td>0.410</td>
<td>0.0130</td>
<td>0.9991</td>
<td>0.407</td>
</tr>
<tr>
<td>GSE17200</td>
<td>0.0010</td>
<td>0.152</td>
<td>0.9246</td>
<td>0.035</td>
<td>0.306</td>
<td>0.0033</td>
<td>0.9904</td>
<td>0.500</td>
</tr>
<tr>
<td>GSE17201</td>
<td>0.0014</td>
<td>0.166</td>
<td>0.9186</td>
<td>0.038</td>
<td>0.281</td>
<td>0.0030</td>
<td>0.9946</td>
<td>0.278</td>
</tr>
</tbody>
</table>
where, $K_C$ is the equilibrium constant, $q_e$ is the amount of dye (mg) adsorbed on the adsorbent medium per dm$^3$ of the solution at equilibrium, and $C_e$ (mg/dm$^3$) is the equilibrium concentration of the dye in the solution. $T$ (K) is the solution temperature and $R$ is the gas constant.

It is well known that the absolute magnitude of the change in free energy for physisorption is between $-20$ and $0$ kJ/mol; chemisorption has a range of $-80$ to $-400$ kJ/mol (Jaycock and Parfitt, 1981). As shown in Table 5, the values of $\Delta G^0$ at 10, 20, and 30°C are $-1.52$, $-1.66$, and $-1.76$ kJ/mol respectively. Based on the values of $\Delta G^0$, it can be concluded that the adsorption process of AR14 by DG06 is mainly physical in nature. The positive value of the standard enthalpy change ($\Delta H^0$), of 1.88 kJ/mol, indicates that the interaction of AR14 with DG06 is an endothermic reaction.

### 2.5 Effect of pH

Figure 5 shows the effect of initial solution pH on the adsorption of AR14 by DG06, GSE17200, and GSE17201 at 20 ± 0.5°C. The initial concentration of AR14 is 300 mg/L. When the initial AR14 solution pH ranges from 10.0 to 4.0, due to pH buffer capacity of the soils, the pH of the systems (AR14 solution + soil) decreased slightly. However, when the initial AR14 solution pH is lower than 4.0, since the pH buffer capacity of the soils are damaged, pH of the systems decreases significantly, and the adsorption of AR14 on the three soils increases significantly. These results suggest that an acidic condition is helpful in adsorption of AR14 on these three soils.

### 2.6 Effect of salinity

Industrial dyeing-wastewater usually has high inorganic salt level (specially, NaCl) (Low and Lee, 1997). It is necessary to investigate the adsorption of AR14 by DG06, GSE17200, and GSE17201 soils in the presence of NaCl. Fig.6 shows the effect of salinity (NaCl) on the adsorption of AR14 by the three soils. The concentration of NaCl ranges from 0.2% to 4%. As shown in Fig.6, the amount of equilibrium adsorption increases with the increase in salinity. Generally, there are negative charges in surface soil. Under higher NaCl concentrations, more Na$^+$ can react with negative charges, which results in the reduction of electrostatic repulsion between RSO$_3$– anion and negatively charged surface soils. Thus, the amount of AR14 adsorbed by the three soils will increase with the increase in salinity.

According to the above formula, positive charges and hydroxyl groups will increase with the decrease in pH. So the decrease of pH in solutions increases the electrostatic bonding between the soils and AR14; consequently, increases the adsorption of AR14 on the three soils. When the initial AR14 solution pH ranges from 10.0 to 4.0, due to pH buffer capacity of the soils, the pH of the systems (AR14 solution + soil) decreased slightly. However, when the initial AR14 solution pH is lower than 4.0, since the pH buffer capacity of the soils are damaged, pH of the systems decreases significantly, and the adsorption of AR14 on the three soils increases significantly. These results suggest that an acidic condition is helpful in adsorption of AR14 on these three soils.

### Table 5

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Kinetic parameters of the pseudo-second-order</th>
<th>Thermodynamic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_2$</td>
<td>$q_2$</td>
</tr>
<tr>
<td>10</td>
<td>0.049</td>
<td>0.398</td>
</tr>
<tr>
<td>20</td>
<td>0.078</td>
<td>0.410</td>
</tr>
<tr>
<td>30</td>
<td>0.220</td>
<td>0.416</td>
</tr>
</tbody>
</table>

*Fig. 5* Effect of initial solution pH on the adsorption of AR14 by DG06, GSE17200 and GSE17201 as well as on pH of the systems (AR14 solution + soil). Initial dye concentration: 300 mg/L, 20±0.5°C.

*Fig. 6* Effect of salinity (NaCl) on the adsorption of AR14 by DG06, GSE17200 and GSE17201. Initial dye concentration: 300 mg/L, 20±0.5°C, significance at $P < 0.05$. 
3 Conclusions

This paper reports on the adsorption of azo dye AR14 by DG06, GSE17200, and GSE17201 soils. Adsorption isotherm, adsorption kinetic and adsorption thermodynamics were systematically studied for AR14 on the three soils. The adsorption isotherm indicates that the Freundlich model expresses the adsorption behavior better than the Langmuir model. Among the three soils, DG06 has the highest $K_F$. The pseudo-second-order model expresses the adsorption kinetics well. DG06 has the higher values of $q_e$, $K_2$, and $v$ than the other two soils. These results demonstrate that compared to GSE17200 and GSE17201, DG06 has the higher initial adsorption rate and higher adsorption capacity, which is easier to be polluted by AR14. The thermodynamic parameter of $\Delta G^0$ suggests that the adsorption process of AR14 by DG06 is mainly physical in nature. In addition, the effect of pH and salinity (NaCl) on the adsorption was also investigated and the results showed that pH and salinity can influence the amount of adsorption at the point of equilibrium. The decrease of pH or the increase of salinity can enhance the adsorption of AR14, thus increase the extent to which the three soils are polluted by AR14.

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References


