Adsorption of C.I. Reactive Red 228 and Congo Red dye from aqueous solution by amino-functionalized Fe$_3$O$_4$ particles: kinetics, equilibrium, and thermodynamics

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ABSTRACT

A magnetic adsorbent was synthesized by γ-aminopropyltriethoxysilane (APTES) modification of Fe$_3$O$_4$ particles using a two-step process. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and vibration sample magnetometry were used to characterize the obtained magnetic adsorbent. EDS and XPS showed that APTES polymer was successfully introduced onto the as-prepared Fe$_3$O$_4$/APTES particle surfaces. The saturation magnetization of the magnetic adsorbent was around 65 emu g$^{-1}$, which indicated that the dye can be removed fast and efficiently from aqueous solution with an external magnetic field. The maximum adsorption capacities of Fe$_3$O$_4$/APTES for C.I. Reactive Red 228 (RR 228) and Congo Red (CR) were 51.4 and 118.8 mg g$^{-1}$, respectively. The adsorption of C.I. Reactive Red 228 (RR 228) and Congo Red (CR) on Fe$_3$O$_4$/APTES particles corresponded well to the Langmuir model and the Freundlich model, respectively. The adsorption processes for RR 228 and CR followed the pseudo-second-order model. The Boyd’s film-diffusion model showed that film diffusion also played a major role in the studied adsorption processes for both dyes. Thermodynamic study indicated that both of the adsorption processes of the two dyes are spontaneous exothermic.

Key words: γ-aminopropyltriethoxysilane, adsorption, dye removal, kinetics and isotherm, magnetic adsorbent

INTRODUCTION

Large amounts of dyes are widely used and finish up in effluents (Garg 2004). In addition to unwanted colors, most of these dyes are toxic, carcinogenic and teratogenic, which may cause harm to the flora and fauna (Verma et al. 2012). Therefore, the treatment of dye effluents is urgent (Mishra & Baijai 2006). The methodologies adopted to treat dye effluents are classified into four categories: (i) physical, (ii) chemical, (iii) biological, and (iv) acoustical, radiation and electrical processes (Gupta & Suhas 2009). In chemical processes, flocculation of the reagent and residual dye results in sludge generation containing concentrated impurities, which still requires disposal (Robinson et al. 2007; Kuhad et al. 2004). Biological processes are less flexible in design and operation, and less efficient in degradation of synthetic dyes due to their complex structures, molecular size and nature (Lee et al. 2006). Acoustical, radiation, and electrical processes are usually expensive because of significant energy consumption and create large amounts of sludge and toxic intermediates (Gupta & Suhas 2009). The adsorption method is proved to be effective for the treatment of dye effluents with no unwanted by-products (Poursaberi & Has-nanisadi 2013), and has been successfully employed for removing various types of dyes (Zhai et al. 2012). Although many adsorbents such as activated carbon (Gomez et al. 2007; Rivera-Utrilla et al. 2011), clay (Gil et al. 2011), fly ash (Mall et al. 2006), and metal oxide adsorbents (Gemeay et al. 2008; Liu et al. 2012) have been investigated for dye removal, they are often difficult to separate from aqueous solution, which limits their application in dye effluents treatment.

In recent years, magnetic adsorbents such as activated carbon/Fe$_3$O$_4$ magnetic composites (Yang et al. 2008), magnetic multiwalled nanotubes filled with Fe$_2$O$_3$ particles (Qu et al. 2008), and various surface-modified Fe$_3$O$_4$ particles...
(Kamruzzaman Selim et al. 2007; Atia et al. 2009; Ebrahimi-nezhad et al. 2013) have been developed and used for dye effluents due to their rapid separation from aqueous solution. However, the preparation of such magnetic adsorbents is complicated. Aminosilane coupling agents can easily form monolayers on different surfaces to change the surface properties or introduce –NH2 groups into the modified surfaces. It has been reported that an aminosilane was used to modify the surfaces of magnetite particles for lipase immobilization (Cui et al. 2010), wear properties improvement (Park et al. 2010), and DNA purification (Pasquardini et al. 2011). In terms of dye effluents treatment, the adsorption properties of aminosilane-modified Fe3O4 particles for different dyes are still to be further studied.

The aminopropyltriethoxysilane (APTES) polymers can be used to obtain cationic amine groups on magnetic particles (Takafuji et al. 2004). Compared with most organosilanes, the grafting reaction conditions are easier and simpler (Yang et al. 2012). In this work, APTES polymers grafted on the surface of Fe3O4 particles and Fe3O4/APTES particles were obtained as a magnetic adsorbent for the removal of RR 228 and CR from aqueous solution. The Fe3O4/APTES particles were characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and vibration sample magnetometry (VSM). The adsorption of RR 228 and CR on Fe3O4/APTES particles was tested under various conditions. Kinetic, thermodynamics and isotherm parameters were also investigated.

**MATERIALS AND METHODS**

**Chemicals and reagents**

The C.I. Reactive Red 228 (RR 228), Congo Red (CR), and APTES [(C2H5O)3Si(CH2)3NH2, +97%] were obtained commercially from Ciba Company, Tianjin Bodi Chemical Co., Ltd and Nanjing Youhao Auxiliary Chemical Co., Ltd, respectively. Ferrous sulfate heptahydrate (FeSO4·7H2O), ferric chloride hexahydrate (FeCl3·6H2O), ammonium hydroxide (25% w/w), acetic acid, and ethanol were of analytical grade and obtained from commercial sources. Structures of the dyes used are listed in Figures 4(c) and 4(d). All chemicals were used without further purification. Distilled water was used in all the experiments.

**Adsorbent preparation**

FeCl3·6H2O (23.352 g) and FeSO4·7H2O (13.728 g) were dissolved in distilled water and the solution was stirred vigorously under a nitrogen atmosphere at 55 °C for 30 min. Ammonium hydroxide (25% w/w) was added dropwise until the pH value was approximately 9.5. The suspension was then stirred vigorously for another 90 min. The products were washed with distilled water, and isolated using a magnet. Finally, the products were ultrasonicated for 15 min in ethanol and then dried in an oven at 60 °C overnight for further use.

As-prepared Fe3O4 particles (10 g) were dispersed in an aqueous ethanol solution (50% v/v) by ultrasonication for 15 min under a nitrogen atmosphere. The pH was adjusted to 4.5 with acetic acid. APTES (40 mL) was added and the modification reaction was conducted under a nitrogen atmosphere, with rapid mechanical stirring, at 40 °C for 4 h. The modified Fe3O4 composite particles were washed several times with distilled water and ethanol, and then dried at 60 °C.

**Adsorbent characterization**

The surface morphologies and element composition of the products were characterized using SEM–EDS (Quanta 200) with an accelerating voltage of 15 kV. The samples were sprayed with gold prior to analysis. The modification of APTES polymer onto the surface of Fe3O4 particles was detected by using a K-Alpha XPS Analyzer (ThermoFisher Scientific Company). The magnetization properties of the samples were examined using VSM by cycling the field between −20 and 20 kOe at 298 K.

**Preparation of dye solution**

Accurate 1 g/L single solute solutions for RR 228 or CR were prepared by dissolving the dye in distilled water, respectively. Experimental solutions of various concentrations were obtained by further dilution. Ultraviolet-visible (UV-vis) absorbance measurements of the dye solutions (TU-1900 spectrometer) were used to obtain standard curves of the RR 228 and CR dye, respectively.

**Adsorption experiments**

Dye adsorption experiments were conducted in conical flasks, which were sealed and then shaken in a thermostatic oscillator at a controlled temperature. These conical flasks
contained mixtures of an accurately weighed adsorbent sample and 50.0 mL of dye solution. The pristine Fe₃O₄ for RR and CR adsorption was chosen as the reference with a dose of 20 mg, initial dye concentration of 50 mg L⁻¹, volume of 50 mL, at 30 °C for 10 h. The dye concentration of the supernatant was analyzed using a UV-vis spectrophotometer. Distilled water was chosen as the reference. The removal rate (R), adsorption capacity (qₜ, mg g⁻¹), and equilibrium adsorption capacity (qₑ, mg g⁻¹) were calculated as follows:

\[ R(\%) = \frac{(C₀ - Cₜ)}{C₀} \times 100 \]  
\[ qₜ = \frac{(C₀ - Cₜ)V}{m} \]  
\[ qₑ = \frac{(C₀ - Cₑ)V}{m} \]

where \( C₀ \), \( Cₜ \), and \( Cₑ \) (mg L⁻¹) are the dye concentration at time \( t \) (min), the initial, and equilibrium concentration in the solution, respectively; \( V \) (L) is the solution volume and \( m \) (g) is the mass of the adsorbent.

RESULTS AND DISCUSSION

Adsorbent characterization

SEM photographs of the Fe₃O₄ and Fe₃O₄/APTES particles are shown in Figures 1(a) and 1(b). It can be clearly observed that the surfaces before and after APTES modification did not change significantly. As illustrated in Figure 1(c), EDS results showed that the content of nitrogen and silicon on the adsorbent surfaces were 5.34 and 1.71 wt. %, respectively, which revealed that APTES polymer was successfully introduced on the surfaces of the Fe₃O₄ particles.

High resolution XPS spectra of Fe₂p and N₁s in the obtained adsorbent is shown in Figures 2(a) and 2(b). It can be observed that Fe 2p₃/₂ state does not have a satellite peak and the peak positions of Fe 2p₃/₂ and Fe 2p₁/₂ are 710.98 and 724.98 eV, respectively, which indicates that the obtained iron oxide is Fe₃O₄ (Descostes et al. 2000; Iram et al. 2010). The N₁s spectra can be divided into two peaks at a binding energy of 399.48 and 401.48 eV, ascribed to the neutral amino nitrogen (–NH₂) and protonated amino nitrogen (–NH₃⁺) (Wang et al. 2011). According to reference experiments, the adsorption capacities of RR 228 and CR onto modified Fe₃O₄ were 43.6 and 22 mg g⁻¹ more than that on pristine Fe₃O₄, respectively. These indicate the introduction of APTES polymer favors the adsorption.

As shown in Figure 2(c), the magnetization curves exhibited zero remanence and coercivity, which indicates superparamagnetic properties. The saturation magnetization of the Fe₃O₄/APTES particles was found to be about 65 emu g⁻¹; this is about 6 emu g⁻¹ lower than that of unmodified Fe₃O₄ particles, as a result of the presence of APTES on the surface.

Effect of adsorbent dose and initial concentration

Figures 3(a) and 3(b) give the variation of capacity and removal of adsorption versus adsorbent dose. The adsorption capacity for CR decreased from 118.9 to 39.2 mg g⁻¹ and the removal increased from 47.6 to 94.2% with increasing adsorbent dose from 200 to 1,200 mg L⁻¹. Similar trends are obtained for RR 228 solution (Figure 3(a)). This indicates that the adsorption capacity and removal depend on quantity of adsorbent used. The color of the dye solution faded obviously when the dose reached 1,000 mg L⁻¹.

The initial concentration has a significant effect on the adsorption capacity. The results are presented in Figure 3(c). As to CR, it was found that the adsorption capacity at equilibrium was lower at lower initial dye concentration due to limited number of dye molecules. However, the available active sites become fewer at higher concentration and hence the adsorption capacity of dye is dependent upon initial concentration (Basavarao & Rammohanrao 2006).
Figure 2 | High resolution XPS spectra of (a) Fe2p and (b) N1s in obtained adsorbent, and (c) magnetization and hysteresis loops at 298 K.

Figure 3 | Effect of adsorbent dose ((a), (b): temperature 303 K, initial dye concentration 50 mg L$^{-1}$, volume 50 mL, time 12 h) and initial concentration on adsorption of dyes ((c): dose 60 mg, temperature 303 K, volume 50 mL, time 12 h).
As to RR 228, similar variation trends occurred. The initial dye concentration is the main driving force for overcoming resistance to the mass transfer of dye between the aqueous and solid phases. The available adsorption sites become fully occupied with increasing initial dye concentration (Abdullah et al. 2013).

Effect of initial pH

The effect of initial pH on RR 228 and CR adsorption is shown in Figure 4. The pH of the CR solution was adjusted between 4.01 and 10.00 in the experiments because CR changed to the cationic form and the color became dark blue at pH below 4 (Acemioglu et al. 2013; Kaur et al. 2014). The removal of CR did not change obviously at various pH values, which may be related to the fact that there are coexisting –NH₂ and –SO₃⁻ groups in the CR molecule (Vimonses et al. 2009). The removal of RR 228 adsorption remained constant at pH value below 3.33, then, reduced from 95.26 to 80.47% from 3.33 to 9.73. The surfaces of the Fe₃O₄/APTES particles would be surrounded by excessive hydroxyl ions, and the Fe₃O₄/APTES particles could become negatively charged, weakening the adsorption of dye anions through higher electrostatic repulsion. Moreover, hydroxyl ions would compete with CR anions at the active adsorption sites (Wang & Wang 2008). The adsorption mechanism is shown in Figure 4(b), which indicates that the obtained adsorbent can be applied to a series of anionic dyes including RR 228 and CR.

Effect of contact time and temperature

The effect of contact time and temperature on the adsorption capacities of RR 228 and CR are shown in Figure 5. The adsorption capacity of RR 228 and CR dye rapidly increased at the initial stage of the adsorption process and completely reached equilibrium after 240 and 150 min under the given conditions, respectively. The adsorption capacities of RR 228 at equilibrium were 34.69, 31.01 and 28.13 mg g⁻¹ at 303, 323 and 333 K, respectively. It was found that lower temperature favored adsorption of RR 228 on Fe₃O₄/APTES particles. However, the effect of temperature on the adsorption capacity of CR was inconspicuous.

Adsorption isotherms

Equilibrium adsorption isotherms were used to illustrate the relationship between the equilibrium concentration of the adsorbate in the solid and liquid phases at constant temperature, and also to determine the precise interactive forces involved in the process (Baek et al. 2010).

The Langmuir equation (Langmuir 1916) is given in linear Equation (4) to provide an insight into the mechanism
of the adsorption.

\[
\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0}
\]  \hspace{1cm} (4)

where \(Q_0\) (mg g\(^{-1}\)) and \(b\) (L mg\(^{-1}\)) are Langmuir constants related to the maximum adsorption capacity and energy of adsorption, respectively. Likewise, the Freundlich model suggests a multilayer adsorption. The Freundlich equation (Freundlich 1906) is given in linear Equation (5).

\[
\ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e
\]  \hspace{1cm} (5)

where \(K_f\) (L g\(^{-1}\)) is the Freundlich constant and \(1/n\) is the heterogeneity factor.

The isotherm parameters are listed in Table 1. According to the \(R^2\) values, the Langmuir isotherm therefore gives a better fit to the experimental data, indicating that the adsorption of RR 228 on Fe\(_3\)O\(_4\)/APTES particles was more compatible with the Langmuir hypothesis, i.e. that the adsorption capacity was represented by a monolayer of adsorbed molecules without interactions. The adsorption of CR on Fe\(_3\)O\(_4\)/APTES particles was more compatible with the Freundlich model because of higher \(R^2\) values than that of the Langmuir isotherm. The \(n\) value of this study was found higher than 1.72, indicating that adsorption of CR onto Fe\(_3\)O\(_4\)/APTES particles is a favorable adsorption process (Yan & Wang 2013). The different isotherms for RR 228 and CR may be attributed to their structures. The –NH\(_2\) groups of CR were positively charged in aqueous solution and transformed to –NH\(_3^+\), which can attract –SO\(_3^-\) on other CR dye molecules. Therefore, a multilayer CR adsorption occurred on the surface of the Fe\(_3\)O\(_4\)/APTES particles.

**Adsorption kinetics**

Pseudo-first-order (Ho & McKay 1998), pseudo-second-order (Bulut & Aydın 2006) and Boyd’s film-diffusion models (Boyd et al. 1971) were used to evaluate the adsorption kinetics of RR 228 and CR on Fe\(_3\)O\(_4\)/APTES particles.

The pseudo-first-order kinetic model and the pseudo-second-order kinetic model are represented by Equations (6) and (7), respectively.

\[
\ln (q_e - q_t) = \ln q_e - k_1t
\]  \hspace{1cm} (6)

\[
t/q_t = 1/(k_2q_e^2) + t/q_e
\]  \hspace{1cm} (7)

where \(q_e\) (mg g\(^{-1}\)) and \(q_t\) (mg g\(^{-1}\)) are the adsorption capacity at equilibrium and \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) is the rate constant for the pseudo-second-order model.

**Table 1** | Isotherm parameters for sorption of C.I. Reactive Red 228 and Congo Red on Fe\(_3\)O\(_4\)/APTES particles

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Isotherms</th>
<th>Parameters</th>
<th>303 K</th>
<th>313 K</th>
<th>323 K</th>
<th>333 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.I. Reactive Red 228</td>
<td>Langmuir isotherm</td>
<td>(b) (L mg(^{-1}))</td>
<td>0.120</td>
<td>0.072</td>
<td>0.048</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Q_0) (mg g(^{-1}))</td>
<td>63.29</td>
<td>65.36</td>
<td>67.11</td>
<td>63.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(R^2)</td>
<td>0.984</td>
<td>0.991</td>
<td>0.979</td>
<td>0.969</td>
</tr>
<tr>
<td>Congo Red</td>
<td>Freundlich isotherm</td>
<td>(K_f) (L g(^{-1}))</td>
<td>23.65</td>
<td>13.64</td>
<td>17.16</td>
<td>14.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(n)</td>
<td>1.93</td>
<td>1.72</td>
<td>2.18</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(R^2)</td>
<td>0.945</td>
<td>0.966</td>
<td>0.990</td>
<td>0.994</td>
</tr>
</tbody>
</table>
The values of \( \ln(q_e - qt) \) and \( t/qt \) were calculated using Equations (6) and (7). Straight-line plots of \( \ln(q_e - qt) \) and \( t/qt \) against time were obtained at different temperatures, as shown in Figure 6. The kinetic parameters are listed in Table 2. The results indicated that the pseudo-second-order kinetic model described the adsorption processes well. The \( q_{e,\text{cal}} \) and \( q_{e,\text{exp}} \) values were closer to each other in the case of the pseudo-second-order model, and all the values of \( R^2 \) reached 1, which showed that the adsorption processes accurately followed the pseudo-second-order kinetic model, indicating the overall rate of the adsorption processes appear to be controlled by more than one step i.e. surface adsorption and diffusion phenomena. The values of \( q_{e,\text{cal}} \) differed greatly from those of \( q_{e,\text{exp}} \), and the \( R^2 \) values were not satisfactory for the pseudo-first-order model.

The Boyd's film-diffusion model was employed to investigate the contribution of film resistance to the kinetics of RR 228 and CR adsorption. The linear equation is described as follows:

\[
B_t = -0.4977 - \ln(1 - F(t))
\]

\[
F(t) = qt/q_e
\]

where \( q_e \) (mg g\(^{-1}\)) and \( qt \) (mg g\(^{-1}\)) are the adsorption capacity at equilibrium and at time \( t \) (min), respectively. \( F(t) \) represents the fraction of solute adsorbed at any time \( t \) (min), and \( B_t \) is a mathematical function of \( F(t) \). The Boyd plots for the adsorption of RR 228 and CR are shown in Figures 6(c) and 6(d). The Boyd parameters are listed in Table 2. The experiment data of RR 228 and CR are fitted by the Boyd model with correlation coefficients \( (R^2) \) higher than 0.914. The intercepts of the plots of RR 228 and CR adsorption are significantly different from zero, indicating the rate of both RR 228 and CR adsorption are both controlled by film diffusion, i.e. the rate-determining step is the external mass transfer since the plots are linear and does not pass through the origin.

**Adsorption thermodynamics**

Thermodynamic parameters are often used to determine the spontaneity of an adsorption process and can be estimated by the following equations:

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0 = -RT \ln k_c
\]

\[
k_c = (C_0 - C_e)/C_e
\]
of the sorption of RR 228 and CR on Fe3O4/APTES particles. The Freundlich isotherm gave a better fit to the experimental data of the CR adsorption. The rate of both RR 228 and CR adsorption are controlled by film diffusion. Thermodynamic studies showed that the adsorption of the two dyes was a spontaneous and exothermic process. The saturation magnetization value, 65 emu g⁻¹, indicates that Fe₃O₄/APTES particles are easily separated from aqueous solutions with an external magnetic field.

\[ \ln k_t = -\Delta H^0/(RT) + \Delta S^0/R \]  \hspace{1cm} (10)

The values of \(\Delta H^0\) and \(\Delta S^0\) were obtained from the slope and intercept of the linear form of the Van’t Hoff equation. The thermodynamic parameters of RR 228 were as follows: \(\Delta H^0 = -19.44 \text{ kJ mol}^{-1}\), \(\Delta S^0 = -53.73 \text{ J mol}^{-1} \text{ K}^{-1}\), and \(\Delta G^0 = -25.61 \text{ kJ mol}^{-1}\), \(-2.62 \text{ kJ mol}^{-1}\), \(-2.08 \text{ kJ mol}^{-1}\), \(-1.55 \text{ kJ mol}^{-1}\) at 303, 313, 323, and 333 K, respectively. The thermodynamic parameters of CR were as follows: \(\Delta H^0 = -62.25 \text{ kJ mol}^{-1}\), \(\Delta S^0 = -62.25 \text{ J mol}^{-1} \text{ K}^{-1}\), and \(\Delta G^0 = -6.75 \text{ kJ mol}^{-1}\), \(-6.13 \text{ kJ mol}^{-1}\), \(-5.51 \text{ kJ mol}^{-1}\), \(-4.89 \text{ kJ mol}^{-1}\) at 303, 313, 323, and 333 K, respectively. The negative values of free energy change (\(\Delta G^0\)) suggest the spontaneous nature of the sorption of RR 228 and CR on Fe₃O₄/APTES particles. Additionally, the value of \(\Delta G^0\) for CR was approximately twice as high as that for RR 228 and the same phenomenon occurred in the maximum adsorption capacities for RR 228 and CR, confirming \(\Delta G^0\) is a good indicator for adsorption capacity. The negative value of standard enthalpy changes (\(\Delta H^0\)) reflected that the adsorption was an exothermic process. The negative value of entropy (\(\Delta S^0\)) confirmed the decrease in randomness at the interface during the sorption process.

**CONCLUSION**

A new magnetic adsorbent, Fe₃O₄/APTES particles, was prepared and characterized. An investigation of the removal of RR 228 and CR from aqueous solution was conducted. The adsorption of RR 228 and CR increased with increasing adsorbent dose and initial concentration of dye solution. The maximum adsorption capacity of RR 228 and CR reached 51.4 and 118.8 mg g⁻¹, respectively. The adsorption of the two dyes followed the pseudo-second-order kinetic model well. The Langmuir isotherm provided the best correlation of the experimental data for the adsorption of RR 228 on Fe₃O₄/APTES particles. The Freundlich isotherm gave a better fit to the experimental data of the CR adsorption. The rate of both RR 228 and CR adsorption are controlled by film diffusion. Thermodynamic studies showed that the adsorption of the two dyes was a spontaneous and exothermic process. The saturation magnetization value, 65 emu g⁻¹, indicates that Fe₃O₄/APTES particles are easily separated from aqueous solutions with an external magnetic field.

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First received 1 April 2013; accepted in revised form 4 November 2013. Available online 23 November 2013