Enhanced decolorization of dyes by an iron modified clay and thermodynamic parameters

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ABSTRACT

The sorption processes of red 5 (R5) and yellow 5 (Y5) dyes by iron modified and sodium bentonite in aqueous solutions was evaluated. The modified clay was prepared, conditioned and characterized. The sodium clay did not remove any of either dye. The sorption kinetics and isotherms of R5 and Y5 dyes by iron modified clay were determined. The maximum removal percentages achieved were 97% and 98% for R5 and Y5, respectively, and a contact time of 72 h; the experimental data were best adjusted to Ho model. The isotherms of both dyes were best adjusted to the Langmuir model and the maximum adsorption capacities of the modified clay were 11.26 mg/g and 5.28 mg/g for R5 and Y5, respectively. These results indicate that adsorption processes have a high probability to be described as chemisorption on a homogeneous material. Temperature range between 283 and 213 K does not affect the adsorption of Y5 by the iron modified clay, but the adsorption process of R5 was affected, and the thermodynamic parameters could be calculated, which indicate a chemisorption mechanism.

Key words | adsorption, bentonite, iron, red 5, thermodynamics, yellow 5

INTRODUCTION

Among the substances that provide color, there are two groups: dyes and pigments (San Andrés et al. 2010). Although the structure of the dyes is organic in nature, degradation is slow and difficult because the organisms in nature do not have adequate mechanisms for its rapid decomposition and they accumulate in the ecosystem. So it is important to have efficient removal methods to treat those ecosystems (Chamagore et al. 2010).

The dyes have a high persistence in the environment, are resistant to chemicals and are poorly degradable. Industries such as textile and food use large volumes of water in their processes; therefore, large amounts of wastewater containing dyes are generated. There are more than 100,000 commercial dyes, and about 700,000 tons per year are produced; it is estimated that 2% of annual production is discharged in effluents from manufacturing operations, while 10% of the discharges are associated with the textile industry (Allen & Koumanova 2005; Arunachalam et al. 2012).

The activated carbon treatment is one of the most commonly used, producing high quality effluents; dye adsorption with activated carbon is regarded as one of the best technologies available to remove contaminants as dyes. However, it is important to search for alternative cheaper adsorbents because of the high cost of this material (Lazo et al. 2007).

The best known standard methods for the removal of dyes from wastewater are chemical precipitation (Belhachemi & Addoun 2011), coagulation-flocculation (Allen & Koumanova 2005), aerobic and anaerobic biological treatment (Morales & Melgoza 2009) and adsorption on activated carbon (Belhachemi & Addoun 2011).

Unconventional methods have also been developed for the removal of dyes, such as photocatalysis, ozonation, reverse osmosis, electrocoagulation, ultrafiltration and adsorption on novel materials of natural (Arango et al. 2007) or synthetic origin (Allen & Koumanova 2005).

Adsorption treatments are used for the removal of contaminants or toxic organic impurities, which are often more economical, simple and efficient compared with biological methods. Adsorption can produce high quality water that can be reused in industrial processes, providing economic benefits (Allen & Koumanova 2005). Different adsorbents have been proposed to remove different dyes from water, such as zeolites (Salinas-Hernández et al. 2012), clays (Hernández-Hernández et al. 2013), activated carbon, hydrogels, etc.
Most adsorption phenomena take place by a combination of physical, chemical and ion exchange mechanisms, and it is not so easy to distinguish between physical and chemical mechanism, (Perry & Green 2001).

Clay minerals are very important because of their adsorptive properties, such as the particle size of about 2 micrometers, and their structure. These minerals are diverse in terms of their chemical composition and inorganic nature; they are composed primarily of Si$^{4+}$, Al$^{3+}$, Fe$^{3+}$, H$_2$O and often alkali and alkaline earth metals in small quantities, amorphous organic matter and other compounds.

The aim of this research was to compare the adsorption processes of red 5 (R5) and yellow 5 (Y5) by untreated and iron modified clay mineral.

**EXPERIMENTAL**

**Materials**

The clay obtained from SUD Chemie of Mexico, which is a sodic bentonite with 70% of montmorillonite, was dried at 333 K for 4 h, milled and sieved. The grain size used was 100 meshes (0.08 mm). One hundred grams of clay were treated with one liter of a 0.1M FeCl$_3$ solution and refluxed for 3 h. This procedure was repeated twice. Afterwards, the material was washed with distilled water until no presence of chloride ions was indicated in the washing solution using AgNO$_3$ test. Finally the clay was dried at 333 K for 4 h.

**Dyes**

R5 (disodium 4 hydroxy-3-(4-sulfonatone 1-naphylazo) naphthalene-1-sulfonate) and Y5 (tartrazine) (trisodium 1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-5-pyrazolone-3-carboxylate) were obtained as commercial dyes from SENSIENT Co., USA. R5 molar mass is 502.45 gmol$^{-1}$ and CAS 3567-69-9, and for Y5 molar mass 534.36 gmol$^{-1}$ and CAS 1934-21-0.

**Characterization**

**Scanning electron microscopy**

For scanning electron microscopy observations, the samples were mounted directly on the holders then observed at 10 and 20 kV in a JEOL JSM-5900-LD electron microscope (JEOL, USA). The microanalysis was done with an energy X-ray dispersive spectroscopy system.

**Surface areas, Brunauer–Emmett–Teller ($S_{BET}$)**

The Brunauer–Emmett–Teller (BET)-specific surface areas were determined by standard multipoint techniques of nitrogen adsorption, using a BELSORP Max Japan Inc., BELSORP, USA. The samples were heated at 473 K for 24 h before the specific surface areas were measured.

**Zero charge point determination**

The experiments were carried out using unmodified and iron modified clays and 0.1 M NaNO$_3$ solution with pH values previously adjusted between 1 and 11, with intervals of 1 unit, by adding 0.1 M HCl or NaOH solutions. After 72 h of shaking at 303 K and 120 rpm, the samples were centrifuged and decanted; pH was measured in the final liquid phases with a potentiometer Orion Research model 901, Orion Research, USA.

**Sorption kinetic experiments**

The kinetic removal of dyes by unmodified and iron-modified clays was performed as follows: 100 mg of adsorbent and 10 mL aliquots of a 10 mg/L solution were placed in vials and shaken for different times (15, 30 and 45 min, and 1, 2, 3, 5, 8, 12, 18, 24, 36, 48, 60 and 72 h) at 100 rpm at 283, 293, 303 and 313 K; later, the samples were centrifuged and decanted. The dye concentrations in the solutions were determined by using an ultraviolet-visible spectrophotometer analyzer UV/VIS Perkin Elmer Lambda 10 (Perkin Elmer, USA) at $\lambda_{max} = 516$ nm for R5 and $\lambda_{max} = 426$ nm for Y5. The pH of each solution was measured before and after treatments and all experiments were done in duplicate.

**Sorption isotherms**

One hundred milligram samples of adsorbent were put in contact with 10 mL of different concentrations of dye solutions (5, 10, 20, 30, 40, 50, 60, 70 and 80 mg/L) for 72 h at 283, 293, 303 and 313 K in a shaker at 100 rpm. Later the samples were centrifuged and decanted, dye concentrations were determined in the liquid phases, and also the pH was measured in each solution.
RESULTS AND DISCUSSION

Characterization

Scanning electron microscopy

The morphologies of the unmodified and iron modified clays are heterogeneous, grains of different sizes and shapes; this shows porosity on the surface of the material and they are similar to a natural montmorillonite from Shandong, China (Wang & Wang 2008). The images of the materials treated with R5 and Y5 are similar, with a smooth surface.

The elemental chemical compositions of the unmodified clay, the iron modified clay and the saturated materials with R5 and Y5 dyes are shown in Table 1. The main elements, Si, Al and O, corresponding to aluminosilicates, were identified (Tuesta et al. 2005); magnesium, calcium, chlorine and iron were also found in the materials; the elemental percentages found are similar to those reported by Hernández-Hernández et al. (2013) for a bentonite. Iron increased nine times in the clay after it was treated with iron chloride and magnesium content decreased, which indicates that it was exchanged by iron. The presence of chlorine could be due to the treatment of the natural clay with FeCl₃; similar results have been reported elsewhere (Hernández-Hernández et al. 2013).

Surface areas, BET (S_{BET})

The BET specific surface areas were 76 m²/g and 96 m²/g; the total pore volumes were 0.14 cm³/g and 0.17 cm³/g and the mean pore diameters were 7.5 nm and 7.1 nm for the untreated and iron modified clay samples, respectively. The specific surface area increased when the material was treated with FeCl₃ solution; this behavior could be attributed to the ion exchange of calcium by iron, the ionic radius of calcium is bigger than the one of iron (III) and then the pores are opened during modifications of the clay. A similar behavior was reported elsewhere with zeolitic and clay tuffs (Salinas-Hernández et al. 2012; Hernández-Hernández et al. 2013). The specific areas found are similar to those reported in the literature, which are between 62 and 96 m²/g. It is important to note that the specific surface area of the natural clay increased after the modification.

Zero charge point

The zero charge points for the unmodified and iron modified clays were determined when the equilibrium pH values were equal or quite similar to the initial pH; they were 7.5 and 2.5 for the untreated and iron modified clay, respectively. These behaviors show that the charge of the clay changes with iron modification. When the pH is below the zero charge point, the charge of the surface of the material is positive, and it is negative when the pH is above. Similar results have been reported for natural clays; Hernández-Hernández et al. (2013) reported a value of pH 8 for a natural clay and Rozalén et al. (2009) reported a value of pH 7.73 for a montmorillonite. The value found for the iron modified clay is similar to the one reported by Hernández-Hernández et al. (2013), which was pH 2.8, and Boonfueng et al. (2005) reported that the zero charge points for montmorillonite samples are between pH 2 and 10.

Sorption kinetics

R5

Figure 1 shows the relationship between contact time and the sorption capacities of the iron modified clay for R5 dye at 283, 293, 303 and 313 K. According to this figure,
the sorption capacities increase as the temperature increases, the highest removal was observed at 313 K, and it shows that the adsorption process is endothermic; Almeida et al. (2013) reported that on increasing the temperature, the diffusion increases, then the viscosity decreases and the sorption process is more efficient; the equilibrium time was reached between 18 and 36 h and the pH during the process was 7.6 ± 0.3. It is important to note that the untreated clay did not remove any quantity of R5 from the aqueous solutions.

Dogan et al. (2009) reported that the temperature is inversely proportional to the sorption capacity for yellow maxilon and red maxilon by a kaolinite, and they concluded that the sorption mechanism was physisorption.

Y5

The removal of Y5 by the iron modified clay at 283, 293, 303 and 313 K from 0.25 to 72 h is shown in Figure 2. The figure shows that the process is endothermic from 283 to 303 K and the adsorption is similar at 303 and 313 K. Similar results were reported by Al-Ghouti et al. (2005), who observed that by increasing the temperature from 293.15 to 333 K, the sorption capacities of a modified diatomite increase for some dyes. The equilibriums at different temperatures were reached between 48 and 72 h, the pH was 7.9 ± 0.3 during the adsorption process, and the maximum adsorption rate was between 0.25 and 24 h. It is important to note that the unmodified clay does not remove any Y5 dye in the same experimental conditions.

It is difficult to compare the adsorption capacity obtained with the data from the literature because the experimental conditions are different, such as pH, mass/volume ratio, temperature, concentration, etc. Adsorption capacities of clays for different dyes have been reported; for example, Roula & Vassiliadis (2008) reported a high q_e value of 798.10 mg/g for the removal of blue basic 41 by a bentonite and Georgieva et al. (2005) reported a low q_e value of 0.17 mg/g for the removal of acid yellow II by a bentonite. Acemioglu (2005) reported an adsorption capacity of 1.01 mg/g of perlite for methylene blue, which is equal to the value obtained for Y5.

The experimental results were adjusted to the following kinetic models with the help of Statistica® v.7.

**Pseudo first order model (Lagergren)**

This model is commonly used for homogeneous sorbents and physical sorption; the sorption rate is proportional to the solute concentration. If the sorption behavior is of the first order, then the experimental results could be adjusted to the following equation:

\[ q_t = q_e \left(1 - e^{-Kt}\right) \]  

where \(q_t\) and \(q_e\) are the amounts of adsorbed dye (mg/g) in the equilibrium and at time \(t\) (h), respectively, and \(K\) (h\(^{-1}\)) is the sorption constant of Lagergren (Ho et al. 2004).

**Second order model (Elovich)**

This model has been used suitably in chemisorptions on highly heterogeneous materials (Cortés et al. 2004) and it is represented by the following equation:

\[ q_t = \left(\frac{1}{\beta}\right) \ln(1 + \alpha \beta t) \]  

where \(\alpha\) and \(\beta\) are the initial rate constants (mg/g h\(^{-1}\)) and (mg/g h\(^{-1}\)), respectively.
where \( q_t \) is the amount of adsorbed dye at time \( t \), \( \alpha \) is the sorption constant of the dye (mg/g) and \( \beta \) is the desorption constant (mg/g).

**Pseudo second order model**

The pseudo second order model, proposed by Ho & McKay (2002), is based on the assumption that the rate-limiting step may be chemisorption involving valence forces through the sharing or exchange of electrons between adsorbent and adsorbate. This model can be represented in the following form:

\[
q_t = \frac{kq_e^2t}{1 + kq_et}
\]  

where \( q_t \) and \( q_e \) are the amount adsorbed at time \( t \) and at equilibrium (mg/g), respectively, and \( k \) is the pseudo second order rate constant for the sorption process (g/mg h).

Tables 2 and 3 show the parameters obtained by applying the second order and pseudo second order models to experimental data for R5 and Y5, respectively; the data could not be adjusted to the pseudo first order model that describes a physisorption processes.

The data were best adjusted to the pseudo second order model because in general the determination coefficients were the highest and the experimental adsorption capacities were similar to the values calculated by this model; these results indicate that the adsorption mechanism is chemisorption. Wang & Wang (2008) reported a similar mechanism for the removal of Congo red by montmorillonite.

Table 4 shows the results reported in the literature for dyes and similar adsorbents. However, the results depend on the experimental conditions, like concentration of dye, adsorbent mass, temperature, pH, etc. In general, it is observed that the removal of dyes by clay material follows the pseudo second order model.

**Sorption isotherms**

Figure 3 shows the adsorption isotherms of R5 by the clay at different temperatures (283, 293, 303 and 313 K). The adsorption of dye is higher at low concentrations and 313 K, and then a plateau was reached, and it seems that the temperature does not affect the sorption capacity of the modified clay. A similar behavior is observed for yellow 6 (Figure 4).

The experimental results were adjusted to the Langmuir, Freundlich and Langmuir–Freundlich models.

**Langmuir model**

This model considers that maximum sorption corresponds to a monolayer saturated with dye molecules on the sorbent...
surface (Otero et al. 2003). The Langmuir isotherm is represented by the following equation:

$$q_e = \frac{q_0 b C_e}{1 + b C_e}$$

(4)

where $q_e$ is the amount of dye adsorbed per unit weight of the adsorbent in forming a complete monolayer on the surface (mg/g), $q_0$ is amount of dye adsorbed (mg/g), $C_e$ is the concentration of the dye in the solution at equilibrium (mg/L) and $b$ is the constant related to the energy or net enthalpy of sorption.

**Freundlich model**

The Freundlich model, which has been applied to adsorbents with heterogeneous surfaces, considering multilayer sorption (Torres-Pérez et al. 2008), is given by the following formula:

$$q = K_f C_e^{1/n}$$

(5)

where $q$ is the amount of dye adsorbed per unit weight of adsorbent (mg/g), $C_e$ is the equilibrium concentration of the dye in the solution (mg/L), $K_f$ is the equilibrium constant indicative of adsorption capacity and $n$ is the adsorption equilibrium constant, whose reciprocal is indicative of the heterogeneity of surface sorbent.

**Langmuir–Freundlich model**

The Langmuir–Freundlich model is a combination of Langmuir and Freundlich models (Torres-Pérez et al. 2008) and
can be represented by the following equation:

\[
q_e = \frac{K_f C_e^{1/n}}{1 + a C^{1/n}}
\]  

(6)

where \(q_e\) is the amount of dye adsorbed per unit weight of adsorbent (mg/g), \(C_e\) is the equilibrium concentration of dye in solution, \(K_f\) and \(a\) are empirical constants.

Tables 5 and 6 show the parameters obtained for R5 and Y5. Most data could be adjusted to the Langmuir model, which is used for homogeneous materials and describes ideal sorption processes (Vimonses et al., 2009); the adsorption of R5 was higher than Y5. The data of R5 could be adjusted to the Freundlich model, which describes adsorption for heterogeneous surfaces, and for the case of the Langmuir–Freundlich model only the data at 303 for R5 and 283 K for Y5 could be adjusted. Although the clay is a

<table>
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<th>Table 5</th>
<th>Isotherms parameters for the adsorption of R5 by iron modified clay at different temperatures</th>
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</thead>
<tbody>
<tr>
<td>Temperature K</td>
<td>(R^2)</td>
</tr>
<tr>
<td>283</td>
<td>0.984</td>
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<tr>
<td>293</td>
<td>0.955</td>
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<tr>
<td>303</td>
<td>0.983</td>
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<td>313</td>
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<th>Table 6</th>
<th>Isotherms parameters for the adsorption of Y5 by iron modified clay at different temperatures</th>
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<td>Temperature K</td>
<td>(R^2)</td>
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<td>283</td>
<td>0.944</td>
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<tr>
<td>293</td>
<td>0.959</td>
</tr>
<tr>
<td>303</td>
<td>0.977</td>
</tr>
<tr>
<td>313</td>
<td>0.776</td>
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<th>Table 7</th>
<th>Comparison of the adsorption found in this work with others from the literature</th>
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<tr>
<td>Reference</td>
<td>Dye</td>
</tr>
<tr>
<td>This work</td>
<td>R5</td>
</tr>
<tr>
<td></td>
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<tr>
<td>This work</td>
<td>Y5</td>
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<tr>
<td>Auta &amp; Hameed (2012)</td>
<td>Methylene blue</td>
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<tr>
<td>Eren (2009)</td>
<td>Crystal violet</td>
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<tr>
<td>Elsherbiny (2013)</td>
<td>Fuchsinic acid</td>
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<tr>
<td>Nandi et al. (2009)</td>
<td>Brilliant green</td>
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<tr>
<td>Tehrani-bagha et al. (2011)</td>
<td>Basic yellow</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td>Vimonses et al. (2009)</td>
<td>Congo red</td>
</tr>
</tbody>
</table>
natural material, the results indicate that the iron modified clay is a homogeneous material.

Table 7 shows a comparison of the sorption capacities found in this work with those reported in the literature for other clays and different dyes. The adsorption capacity for Y5 is similar to the value reported by Vimoneses et al. (2009) for Congo red and kaolin; the value at 303 K for R5 is similar to the value reported by Tehrani-Bagha et al. (2011) for basic yellow and kaolin. Unuabonah et al. (2008) reported the lowest capacity, and the highest was reported by Eren (2009) for violet crystal by a modified bentonite.

## Thermodynamic parameters

### R5

Thermodynamic parameters, like heat of sorption, ΔH, entropy, ΔS, and free energy of activation, ΔG, play an important role in predicting the adsorption behaviors because they are strongly dependent on temperature.

According to Al-Ghouti et al. (2009), the thermodynamic parameters can be calculated from the kinetic data, using the K2 calculated from the pseudo second order model at different temperatures (283, 293, and 303 K).

The activation energy was calculated from the Arrhenius equation (Al-Ghouti et al. 2005).

\[
\ln k = \ln k_0 - \frac{E_a}{R \left( \frac{1}{T} \right)}
\]

where k is the pseudo second order constant (q/mg min), k0 is the adsorption constant (q/mg min) and E_a is the adsorption activation energy in the external surface of an adsorbent (kJ/mol). The activation energy was calculated from the slope and the value is shown in Table 8.

Other useful relationships (Eyring equation) to calculate ΔH and ΔS are the following (Al-Ghouti et al. 2005):

\[
\ln \left( \frac{k_2}{T} \right) = \ln \left( \frac{k_B}{h} \right) + \left( \frac{\Delta S}{R} \right) - \left( \frac{\Delta H}{R} \right) \left( \frac{1}{T} \right)
\]

where \( k_B \) is the Boltzmann constant (1.3807 \( \times \) 10\(^{-23} \) J/K) and \( h \) is the Planck constant (6.6261 \( \times \) 10\(^{-34} \) J s).

The thermodynamic parameters were calculated considering the adsorption kinetics shown in Figure 1 for the modified clay. Figure 5 shows ln(k/T) vs. 1/T, and ΔH and ΔS were calculated and the values are shown in Table 8.

The free energy of Gibbs was calculated at 283, 293, 303 and 313 K; Table 8 shows the equation and values determined.

Low activation energy values (5–40 kJ/mol) indicate a physisorption processes, and higher values (40–800 kJ/mol) indicate chemisorption processes; then the process in this work is chemisorption (Errais et al. 2011; Elsherbiny 2003). Furthermore, activation energy values lower than 42 kJ/mol indicate diffusion control processes (Eren 2009). Then, the activation energy found for the adsorption of R5 dye by the clay (Table 8) indicates chemisorption and that the process is not spontaneous.

### Table 8

<table>
<thead>
<tr>
<th>Equation</th>
<th>Parameter</th>
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<tr>
<td>Arrhenius ( \ln k_2 = \ln k_0 - \frac{E_a}{R \left( \frac{1}{T} \right)} )</td>
<td>Ea</td>
</tr>
<tr>
<td>Equation of Eyring ( \ln \left( \frac{k_2}{T} \right) = \ln \left( \frac{k_B}{h} \right) + \left( \frac{\Delta S}{R} \right) - \left( \frac{\Delta H}{R} \right) \left( \frac{1}{T} \right) )</td>
<td>ΔH ΔS</td>
</tr>
</tbody>
</table>

| \( \Delta G = \Delta H - T \Delta S \) | ΔG (kJ/mol) |
| 283 | 67.67 |
| 293 | 72.97 |
| 303 | 78.27 |
| 313 | 83.56 |

Figure 5 | ln(k/T) vs. 1/T.
Negative values of $\Delta H$ indicate an exothermic process and positive values an endothermic process. The value obtained ($\sim -82.33$ kJ/mol) indicates that the adsorption process of R5 by the iron modified clay is endothermic. $\Delta H$ values higher than 42 kJ/mol indicate chemisorption process (Errais et al. 2011). A positive change in the entropy indicates a disorder increment in the system and a negative change indicates chemical bond between the dye and the adsorbent. Positive values of $\Delta G$ show that the adsorption is not spontaneous.

The thermodynamic parameters of the adsorption of Y5 by the iron modified clay could not be calculated because the kinetic and isotherms adsorption data at different temperatures were similar.

**CONCLUSIONS**

The morphology of the clay did not change after modification with FeCl3 and the content of iron increased nine times in comparison to the content of iron in the unmodified material. The unmodified clay did not remove the dyes in the experimental conditions considered and the iron modified clay removed more than 90% of both dyes from solution. The data were best adjusted to the pseudo second order model; this behavior indicated that the adsorption of dyes by the iron modified clay takes place by chemisorption. Temperature range between 283 and 315 K does not affect the adsorption of Y5 by the iron modified clay, but the adsorption process of R5 was affected and the thermodynamic parameters could be calculated for this last dye.

The activation energy for the adsorption of R5 by the iron modified clay indicates that the process takes place by chemisorption. The negative value of $\Delta H$ indicates that the process is endothermic and the values of $\Delta G$ indicate that the adsorption is not spontaneous.

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**CONFLICT OF INTEREST**

NCO received a research grant no. 494191 from CONACYT and the authors declare that they have no conflict of interest.

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