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Removal of Congo red from aqueous solution by anilinepropylsilica xerogel

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Abstract

The hybrid anilinepropylsilica xerogel (SiAn) was synthesized by sol−gel method and it was used as adsorbent for removing Congo red from aqueous solutions. The dye adsorption experiments were carried out by using bath procedure. The pH effects, the contact time and the initial dye concentration were changed to obtain the best experimental conditions. The dye adsorption equilibrium was rapidly attained after 20 min of contact time. The experimental data were best fitted to Sips and Redlich−Peterson isotherm models, attaining a maximum adsorption capacity of 22.62 mg g^{-1} of Congo red.
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Keywords: Congo red; Dye adsorption; Hybrid organic−inorganic xerogels; Silica based materials; Isotherm models

1. Introduction

The removal of color from aquatic systems caused by presence of synthetic dyes that usually contains azo-aromatic groups is extremely important from the environmental viewpoint because most of these dyes are toxic, mutagenic and carcinogenic [1−2]. Colored waters are objectionable on aesthetic grounds for drinking purpose and other uses. Additionally, the dye presence on natural water systems inhibits sunlight diffusion into the water, consequently reducing the photosynthetic process of aquatic plants [3]. Therefore, it is very important to develop new systems that can be used for removing dyes from waters.

The major problem in the treatment of waters that contain azo-dyes is due to the high stability of these species. Dyes are resistant to light and oxidation agents moderately, thus they cannot be completely treated by conventional methods of anaerobic digestion [4]. Some procedures can be used for treating waters containing dyes, for instance, coagulation and flotation [5], ozonization [6,7], membrane separation [8] and adsorption by activated carbon [9]. The adsorption process at solid/liquid interface has been extensively employed for several reasons, mainly due to its efficiency and economy [10,11].

Different adsorbent materials have been used to remove dyes from waters. The use of clays, fly ash, agricultural byproducts, microorganisms, activated carbon and sands was reported [12−19]. However, to the best of our knowledge, this is the first paper dealing with the use of hybrid silica based xerogels used as adsorbents for dye removal from aqueous solution. The possibility of monitoring the physical−chemical properties of hybrid materials, prepared by the sol−gel method, makes possible the use of these systems in different environmental applications [20−22]. In this work, the hybrid anilinepropylsilica xerogel was used as adsorbent to remove Congo red (CR) from aqueous solution. CR is an anionic dye widely used in textiles, paper, rubber and plastic industries. The pH, contact time and initial dye concentration effects were studied aiming to obtain the best adsorption capacity by the hybrid xerogel.

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2. Experimental

2.1. Preparation of anionic dye solutions

De-ionized water was used throughout for solution preparations.

The anionic dye, Congo red (CR) was obtained from Sigma Chemical Co., USA, with analytical grade and it was used without further purification. The stock solution was prepared by dissolving accurately weighted dye in double-distilled water in the concentration of 500 mg l^{-1}. The working solutions were obtained by diluting the dye stock solution to the required concentrations. In order to adjust the acidity of the solutions, 0.10 mol l^{-1} sodium hydroxide or hydrochloric acid solutions were used, using a pH meter Digimed Model DM 20 for the pH measurements.

2.2. Synthesis of hybrid anilinepropylsilica xerogel

The preparation of the anilinepropylsilica xerogel, designated as SiAn, was prepared according to the following procedure: aniline (1 ml) was activated for 30 min with sodium hydride (0.32 g) in 10.0 ml of an aprotic solvent mixture (toluene/tetrahydrofuran, 1:1 v/v) and 0.8 ml of 3-chloropropyltrimethoxysilane (CPTMS) was added. The mixture was stirred vigorously for 5 h under an argon atmosphere at reflux temperature. The solution was centrifuged at 5000 rpm for 20 min and the supernatant containing the product anilinepropyltrimethoxysilane (APTMS) was used as organic precursor in the gelation process. To this solution was added, under stirring, tetraethylorthosilicate (TEOS) (5.0 ml), ethanol (5.0 ml), water (2.1 ml) and the catalyst hydrofluoric acid (0.1 ml). The solution was stored for five days for gelation. The resulting xerogel was then exhaustively washed with ethanol and water and finally dried for 30 min in an oven at 100 °C.

2.3. Elemental analysis

The amount of organics present in the xerogel was determined by using a CHN Perkin–Elmer M CHNS/O analyzer, model 2400. The analyses were made in triplicate, previously heating the material at 100 °C, under vacuum, for 60 min.

2.4. Infrared analysis

Self-supporting disks of the samples were prepared with 5 cm^2 area, weighing *ca*. 100 mg. The disks were heated at 200 °C, under vacuum (10^{-2} Torr), for 2 h. The self-supporting disks were analyzed in the infrared region using a Shimadzu FTIR, model 8300. The spectra were obtained at room temperature with a resolution of 4 cm^{-1}, with 100 scans.

2.5. Surface area and pore size distribution

The specific surface areas of the materials were determined by the BET (Brunauer, Emmett and Teller) multipoint technique in a volumetric apparatus using nitrogen as probe [23]. Pore size distribution was obtained by nitrogen adsorption–desorption isotherms, determined at the liquid nitrogen boiling point, using the BJH (Barret, Joyner, and Halenda) method [24].

2.6. Adsorption studies

For this experiment, it was used sodic anionic Congo red, $CR^- Na^+$ that in this work was simply designated as CR. A fixed amount of SiAn adsorbent, 0.1 g, was placed in a 100 ml Erlenmeyer flask containing 50.0 ml of dye solution (4.0–120 mg l^{-1}) at pH ranging from 2.0 to 12.0. Then, the Erlenmeyer flasks were shaken in a rotary orbital shaker at 60 rpm and 25 °C for 5–120 min. The adsorbent was separated from the liquid phase by centrifugation at 3000 rpm for 20 min and then, the dye remained in the solution was determined by spectrophotometry using a UV–VIS spectrophotometer (Shimadzu Model TCC240-A) with 1.0 cm length-path cell. Absorbance measurements were made at the maximum wavelength of CR at 500 nm. The amount of dye uptaken by the SiAn adsorbent was calculated by applying the equation:

$$q = \frac{C_0 - C_e}{m} V \tag{1}$$

where q is the amount of dye uptaken by the adsorbent (mg g^{-1}); C_0 is the initial CR concentration put in contact with the adsorbent (mg l^{-1}), C_e is the CR concentrations (mg l^{-1}) after the batch adsorption procedure, m is the mass of adsorbent (g) and V is the volume of dye put in contact with the adsorbent (l).

2.7. Isotherm modeling

The isotherm models of Langmuir [25], Freundlich [25], Sips [25] and Redlich–Peterson [9] were fitted to describe the equilibrium adsorption. These equations of isotherms were given below:

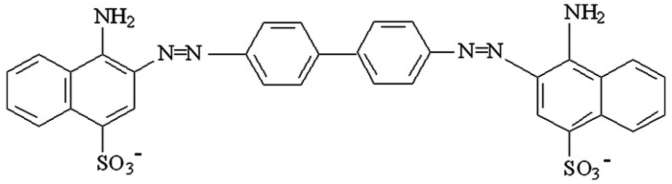
$$\text{Langmuir isotherm} \quad q = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \tag{2}$$

where C_e is the supernatant concentration at the equilibrium state of the system (mg l^{-1}), K_L is the Langmuir affinity constant (l mg^{-1}), and Q_{max} is the maximum adsorption capacity of the material (mg g^{-1}) assuming a monolayer of adsorbate uptaken by the adsorbent.

$$\text{Freundlich isotherm} \quad q = K_F C_e^{1/n} \tag{3}$$

where K_F is the Freundlich constant related with adsorption capacity [mg g^{-1} (mg $l^{-1})^{-1/n}$] and n is the Freundlich exponent (dimensionless).

$$\text{Sips isotherm} \quad q = \frac{Q_{max} K_S C_e^{1/n}}{1 + K_S C_e^{1/n}} \tag{4}$$



Scheme 1.

where K_S is the Sips constant related with affinity constant $(\mathrm{mg\,l^{-1}})^{-1/n}$ and $Q_{\max}$ is the Sips maximum adsorption capacity $(\mathrm{mg\,g^{-1}})$.

$$\text{Redlich–Peterson isotherm} \quad q = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{\beta}} \tag{5}$$

where K_{RP} and a_{RP} are Redlich–Peterson constants, with the respective units: $\mathrm{l\,g^{-1}}$ and $(\mathrm{mg\,l^{-1}})^{-\beta}$ and β is the Redlich–Peterson exponent (dimensionless).

In this work, the Langmuir, Freundlich, Sips and Redlich–Peterson isotherms were fitted employing the non-linear fitting method using the software Microcal Origin 7.0. In addition, the models were also evaluated by average relative error function [26], which measures the differences of the amount of dye uptaken by the adsorbent predicted by the models and the actual q measured experimentally.

$$\text{Average relative error} \quad F_{\text{error}} = \frac{100\%}{n} \sum_{i}^{n} \left| \frac{q_{\text{i cal}} - q_{\text{i exp}}}{q_{\text{i exp}}} \right| \tag{6}$$

where $q_{\text{i model}}$ is each value of q predicted by the fitted model and $q_{\text{i experimental}}$ is each value of q measured experimentally, and n is the number of experiments performed.

2.8. Adsorption kinetic study

In order to investigate the adsorption processes of CR on the SiAn adsorbent, the pseudo-first order and pseudo second-order kinetic models [9] were experimented.

$$\text{Pseudo first-order equation} \quad \ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

where q_e is the adsorption capacity in equilibrium $(\mathrm{mg\,g^{-1}})$, q_t is the amount of adsorbate adsorbed at time t $(\mathrm{mg\,g^{-1}})$, and k_1 is the pseudo first-order rate constant $(\mathrm{min^{-1}})$.

$$\text{Pseudo second-order equation} \quad q_t = \frac{t k_2 q_e^2}{1 + t k_2 q_e} \tag{8}$$

where k_2 is the pseudo second-order rate constant $(\mathrm{g\,mg^{-1}\,min^{-1}})$.

Table 1
Physical–chemical characteristics of anilinepropylsilica xerogel

Specific surface area	$150\ \mathrm{m^2\,g^{-1}}$ [a]
Pore diameter average	4.5 nm [b]
Organic content	$1.10\ \mathrm{mmol\,g^{-1}}$ [c]

[a] BET method.
[b] BJH method.
[c] Elemental CHN analysis.

3. Results and discussion

3.1. Synthesis and characterization of the adsorbent

CR is an anionic dye, very stable in aqueous medium. It is moderately resistant to light and oxidation agents, thus, it is very difficult to be biodegraded. The chemical structure of the CR dye contains NH_2 and SO_3 functional groups (see Scheme 1).

In previous papers, it was shown that the CR dye can be adsorbed on the surface of the hybrid anilinepropylsilica xerogel by electrostatic interaction, and this system was used as electrochemical sensor for the determination of ascorbic acid in commercial Vitamin C tablets [27]. Additionally, the hybrid anilinepropylsilica xerogel has shown interesting metal sorbent properties [28,29]. It was successfully used as selective metal sorbent [30].

The physical–chemical characteristic of anilinepropylsilica xerogel is presented in the Table 1. It is possible to see that the SiAn adsorbent presents an elevated concentration of aniline groups estimated as $7.3\ \mathrm{\mu mol\,m^2}$ available to CR adsorption. Besides this, SiAn presents a remarkable surface area and it is a mesoporous material that allows CR diffusion into the pores.

The immobilization of the aniline groups chemically attached on the xerogel material was also confirmed by infrared spectroscopy analysis. Fig. 1 shows a typical spectrum of pure silica and that of SiAn xerogel. The organic component can be identified by the bands at 1600 and 1500 $\mathrm{cm^{-1}}$ corresponding to the aniline ring modes [31], while the inorganic matrix is identified by the broad band near 1870 $\mathrm{cm^{-1}}$, due to the typical overtone bands of the silica [32].

3.2. Use of SiAn as adsorbent for CR removal from aqueous solution

Fig. 2 shows the efficiency of the SiAn xerogel on the dye adsorption, in relation to the pH medium. It was observed that

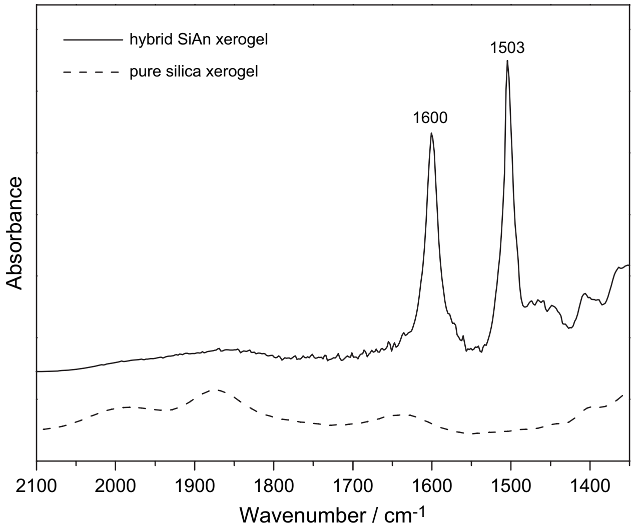


Fig. 1. Infrared adsorption spectra of pure silica and SiAn adsorbent, obtained at room temperature after heating treatment at 200 °C, in vacuum, for 1 h.

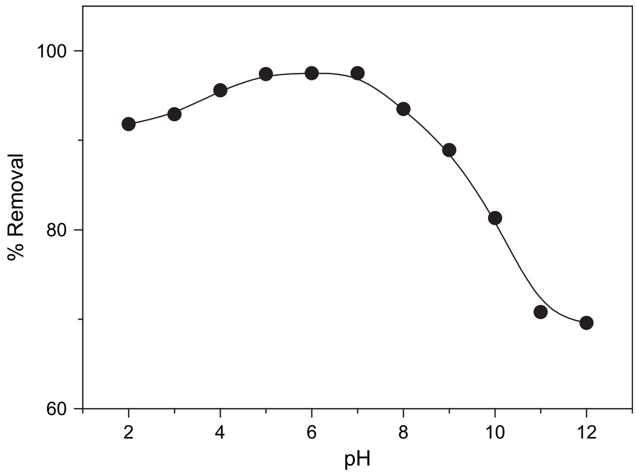


Fig. 2. Percent dye removal *vs* pH, obtained at 25 °C.

the pH medium affects the adsorption capacity of SiAn adsorbent. The higher percent removal was obtained in pH between 5 and 7. It was previoulsy reported that the pK_a of aniline immobilized on silica surfaces is lower than that of free aniline [33],the value being 3.73. It was expected that for pH lower than 3.7 the aniline groups were protonated. In this situation the electrostatic interaction would be favored. However, for pH values ranging from 4.0 to 7.0, the adsorption could be explained taking into account other adsorption mechanisms, such as hydrogen bonds or π–π stacking interactions [34]. At elevated pH values, the CR adsorption decreases, and this result was interpreted taking into account the formation OH^- ions that compete with the dye anionic species for the adsorption sites. Therefore, considering the adsorption capacity, the best pH values were obtained in the range from 5.0 to 7.0. Thus, in the further experiments, the pH was kept at 5.0.

The effect of contact time between CR and SiAn was carried out. It was observed that a rapid adsorption took place attaining the saturation with a contact time of 20 min. Further experiments were carried out using 40 min of contact time to guarantee a complete equilibrium condition using more concentrated solutions. Pseudo first-order and pseudo second-order kinetic models were tested [9], however, the results were better fitted to pseudo second-order kinetic model indicating that the sorption process depends on the adsorbent and adsorbate (see Fig. 3). The values of the pseudo second-order rate constant obtained are given in Table 2.

Table 2
Pseudo second-order rate constant at different Congo red concentrations

C_{CR} (mg l^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
4.5	5.21	0.9970
10.0	1.53	0.9958
18.3	0.916	0.9973

Non-linear curve fitting was employed (Fig. 3).

Isotherm of adsorption of CR on SiAn xerogel was performed using the best experimental conditions: pH 5.0, contact time of 40 min, and temperature fixed at 25 °C. The adsorption experiments were fitted to Langmuir, Freundlich, Sips and Redlich–Peterson isotherm models [25,9] (see Fig. 4). The data of the fitted models are presented in Table 3. As can be seen, the best isotherm model that fits the experimental data with lower error was the Sips and Redlich–Peterson isotherm models. The average relative error measures how close is the q fitted by the model to the actual q measured experimentally [26]. From the values of Table 3, it can be inferred that the maximum adsorption capacity of the hybrid SiAn xerogel for CR removal from aqueous solution was 22.62 mg g^{-1} which is a more suitable value when compared with the Langmuir maximum adsorption capacity.

4. Conclusion

The present work shows that the hybrid anilinepropylsilica xerogel can be used as an effective adsorbent for removing Congo red from aqueous solution. The best pH values for

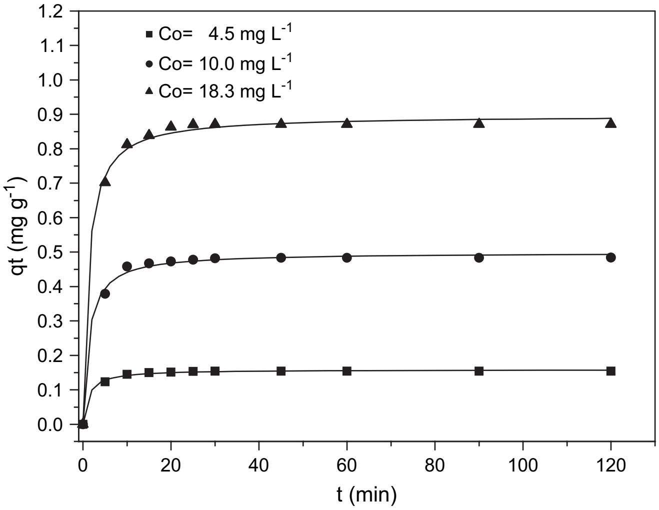


Fig. 3. Non-linear pseudo second-order adsorption kinetics of Congo red on SiAn.

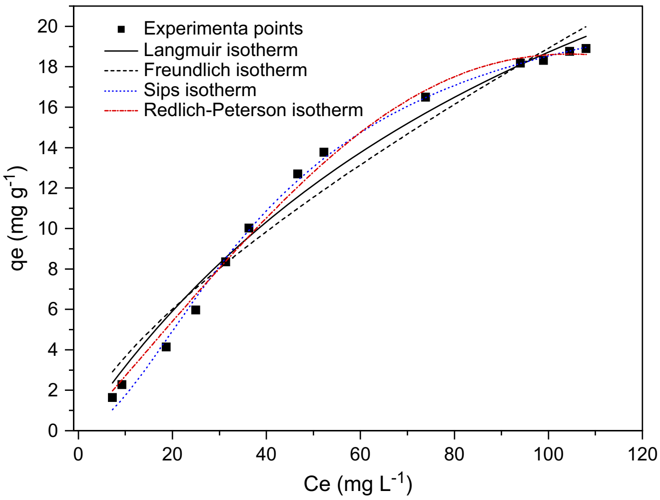


Fig. 4. Adsorption isotherm of Congo red from aqueous solution on SiAn, obtained at 25 °C, at pH 5 and 30 min of contact time.

Table 3
Isotherm parameters

Isotherm	Value
Langmuir	
$Q_{\max}$ (mg g^{-1})	40.86
K_L (l mg^{-1})	0.0085
R^2	0.9829
Average relative error (%)	12.73
Freundlich	
K_F (mg g^{-1} (mg l^{-1})$^{-1/n}$)	0.7103
N	1.403
R^2	0.966
Average relative error (%)	18.68
Sips	
$Q_{\max}$ (mg g^{-1})	22.62
K_S ((mg l^{-1})$^{-1/n}$)	0.00155
N	0.5769
R^2	0.9968
Average relative error (%)	7.43
Redlich–Peterson	
K_{RP} (l g^{-1})	0.2714
a_{RP} (mg l^{-1})$^{-\beta}$	6.83×10^{-7}
β	2.914
R^2	0.9946
Average relative error (%)	6.55

favorable dye adsorption were between 5.0 and 7.0. The dye adsorption equilibrium was attained after 20 min and the maximum adsorption capacity obtained was 22.62 mg of dye per gram of hybrid xerogel.

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