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# **Technical Article**

# Adsorption of congo red dye from aqueous solution onto amino-functionalized silica gel

Adsorção do corante vermelho congo em solução aquosa com sílica aminofuncionalizada

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#### **ABSTRACT**

This study investigates the potential use of amino-functionalized silica gel as an adsorbent for the recovering of congo red dye from aqueous solution. The effects of pH, contact time, and temperature were determined and evaluated. Equilibrium isotherms were also studied. The adsorption kinetics was modeled by pseudo-first order and pseudo-second order. Furthermore, desorption of congo red was preliminarily studied. The pH range from 4.5 to 7.0 was favorable for the adsorption of congo red onto amine modified silica at 25°C. Higher adsorption capacity was obtained at 50°C. Langmuir and Freundlich models were fitted to the adsorption equilibrium data. The best fittings were obtained with the pseudo-second order and Langmuir model for kinetics and equilibrium, respectively. Desorption studies suggest that ion exchange might be the major mode of adsorption. KOH solution was the best desorbing agent for recovering the adsorbed dye.

**Keywords:** 3-aminopropyltriethoxysilane; anionic dye; color removal; arafted silica.

#### **RESUMO**

Este estudo investiga o potencial uso de sílica gel aminofuncionalizada como adsorvente para a recuperação de corante vermelho congo em solução aquosa. Efeitos do pH, do tempo de contato e da temperatura foram determinados e avaliados. As isotermas de equilíbrio também foram estudadas. A cinética de adsorção foi modelada por pseudoprimeira ordem e pseudossegunda ordem. Além disso, a dessorção do vermelho congo foi preliminarmente estudada. O intervalo de pH de 4,5 a 7,0 foi favorável para a adsorção do corante pela sílica modificada com amina a 25°C. Obteve-se maior capacidade de adsorção a 50°C. Modelos de Langmuir e Freundlich foram ajustados aos dados de equilíbrio de adsorção. Os melhores resultados foram obtidos com a pseudossegunda ordem e o modelo de Langmuir para cinética e equilíbrio, respectivamente. Estudos de dessorção sugerem que a troca iônica pode ser o principal modo de adsorção. O hidróxido de potássio foi o melhor agente de dessorção para recuperar o corante adsorvido.

**Palavras-chave:** 3-aminopropiltrietoxisilano; corante aniônico; remoção de cor: sílica modificada.

#### INTRODUCTION

In recent decades, contamination of ground and surface water by heavy metals and organic pollutants is a crucial factor of environmental problems. Among these contaminants are the dyes, which are discharged into water resources from many industries such as textile, pulp and paper, leather, cosmetics, plastics, paints, food and petrochemicals. Most of the dyes can cause damage not only to aquatic life, but also to human beings as they or their metabolites are toxic, mutagenic or carcinogenic (WANG & WANG, 2008; DONIA *et al.*, 2009; AHMAD & KUMAR, 2010; COTORUELO *et al.*, 2010; XIA *et al.*, 2011). Therefore, the removal of dyes from industrial wastewater is an important environmental issue and has motivated

many researches (FORGACS; CSERHÁTI; OROS, 2004; AKSU, 2005; LORENC-GRABOWSKA & GRYGLEWICZ, 2007; CHOWDHURY & VIRARAGHAVAN, 2009; GUPTA & SUHAS, 2009; ALI, 2010; AHMED et al., 2011; WAN NGAH; TEONG; HANAFIAH, 2011; SALLEH et al., 2011).

Adsorption has been recognized as the most popular technique for the removal of non-biodegradable pollutants, including dyes, from wastewater, mainly due to its effectiveness, versatility and reliability compared to other conventional methods (AKSU, 2005; TOR & CENGELOGLU, 2006; LORENC-GRABOWSKA & GRYGLEWICZ, 2007; DONIA *et al.*, 2009; MITTAL *et al.*, 2009; AHMAD & KUMAR, 2010; SHARMA *et al.*, 2011). The major advantages of the adsorptive

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treatment of dye effluents are low investments in terms of the initial development cost, the simplicity of design and operation, the fact that it is free from generating toxic substances, and the easiness and safety on the recovering of the adsorbent as well as the adsorbate materials (MITTAL *et al.*, 2009; SHARMA *et al.*, 2011).

Most industrial wastewater treatment plants utilize activated carbon as adsorbent to remove dyes and other organic pollutants, in reason of its considerable adsorption capacity for these contaminants. However, its widespread use is still limited, mainly due to the often prohibitive cost, besides the difficulty in regeneration and final disposal (TOR & CENGELOGLU, 2006; SHARMA et al., 2011; WANG et al., 2011; XIA et al., 2011; ZHU et al., 2011). For this reason, the number of studies on the viability of low-cost alternative adsorbents for dye removal, such as waste and biomass-based materials, has increased over recent years (AKSU, 2005; GUPTA & SUHAS, 2009; MITTAL et al., 2009; AHMAD & KUMAR, 2010; SALLEH et al., 2011; SHARMA et al., 2011; ZHU et al., 2011). Unfortunately, the adsorption capacities of these materials are generally non-attractive (XIA et al., 2011). Thus, high-capacity and low-cost adsorbents are still under development toward reducing the adsorbent amount and minimizing disposal problems in dye wastewater treatment systems (YIĞITOĞLU & TEMOÇIN, 2010; XIA et al., 2011).

In this context, silica gel functionalized superficially with different active moieties is of particular interest. Silica gel is an amorphous inorganic support well known by its high surface area, high thermal and chemical stability, mechanical and swelling resistance, possibility of repeated use and inexpensive cost (ATIA; DONIA; AL-AMRANI, 2009; DONIA *et al.*, 2009; MAHMOODI; KHORRAMFAR; NAJAFI, 2011). This material is able to interact with various organic substances when it is grafted with organosilyl compounds, making it a promising adsorbent for selective adsorption. Recently, silica gel modified with aminoorganosilanes has successfully been applied for the removal of dyes (ANDRZEJEWSKA; KRYSZTAFKIEWICZ; JESIONOWSKI, 2007; CESTARI *et al.*, 2009; DONIA *et al.*, 2009), including azo dyes, the most widely used class of industrial dyes, constituting 60% to 70% of all produced dyestuffs (YIĞITOĞLU & TEMOÇIN, 2010).

The present study deals with the adsorptive removal of dye congo red (CR) from aqueous solutions by aminopropyl functionalized silica gel. CR is a benzidine-based anionic disazo dye, highly water-soluble and difficult to biodegrade and photodegrade due to its structural stability. It is also a known human carcinogen and toxic chemical to animals and plants. It has been widely used in textile, tannery, printing and dyeing, paper, rubber and plastics industries, and consequently found in their wastewaters (PURKAIT; MAITI; DASGUPTA, 2007; MITTAL *et al.*, 2009; AHMAD & KUMAR, 2010; WANG *et al.*, 2011). Thus, knowledge of the behavior of congo red on modified silica may contribute to the development of more economic and effective adsorptive processes for treatment of effluents containing this and other azo dyes.

#### **MATERIALS AND METHODS**

## Reagents and solutions

Congo red dye (C. I. 22120) and commercial white silica gel (CSG) were purchased from Vetec, Brazil. 3-aminopropyltriethoxysilane (APTES) was purchased from Acros Organics, Belgium. The structural formulas of CR and APTES are shown in Figure 1. These reagents were used without further purification. All the other chemicals used were of analytical grade.

A 400 mg  $L^{-1}$  congo red stock solution was prepared and storaged in the dark at 4°C. The working dye solutions were obtained by buffering and diluting aliquots of the stock solution to the pH and concentrations desired. The stock solution was also used to prepare buffered calibration solutions. All solutions were prepared with deionized water.

The determination of the prepared dye solution concentrations was performed on a double beam Uv-vis spectrophotometer (UV-1601PC Shimadzu, Japan), at a wavelength of 490 nm. Moreover, a pH meter Bel Model W3B was used in the pH measurements of solutions in the different experimental stages.

# Synthesis of modified silica

Aminomodified silica (AMS) was prepared by the reaction of commercial silica gel with APTES as silylating agent, according to Donia *et al.* (2009). A scheme of the amine grafted silica surface is presented in Figure 2.

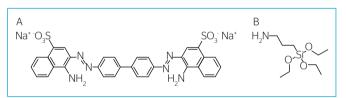


Figure 1 - Structures of: (A) congo red, pH>5.5; (B) APTES.

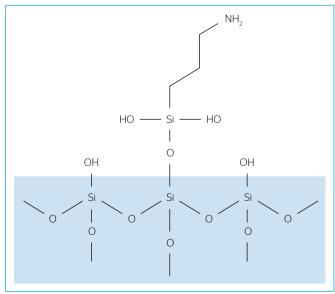


Figure 2 - Schematic illustration of the AMS surface.

## Effect of pH on adsorption

The adsorption of dyes is highly dependent on the pH of the adsorptive solution, as it influences the chemistry of both the dye molecule and the adsorbent surface in aqueous solution (TOR & CENGELOGLU, 2006; AHMED & KUMAR, 2010; SALLEH *et al.*, 2011). Hence, the effect of the pH solution on the adsorption of congo red was studied by buffering the adsorptive solutions in the pH range from 2 to 10 in an initial dye concentration of 0.050 g L<sup>-1</sup>, and for a contact time of 72 h. These tests were carried out similarly to the adsorption experiments, and the percentage of CR removal at different pH values was calculated. Furthermore, tests were conducted to evaluate the influence of the buffers on the adsorption of congo red by adjusting the pH with a HCl or NaOH solution or with buffer.

#### Adsorption experiments

Batch experiments were carried out to measure the adsorption kinetics and equilibrium of congo red onto AMS at different temperatures. Initially, 25°C was established as it is the ambient temperature of the study site. Considering this, a variation of 10 to 15°C or above was chosen, since our equipment does not refrigerate. The maximum study temperature took into consideration the boiling point of the water to minimize errors due to the evaporation of the solution.

For purposes of comparison, kinetic studies of adsorption of CR on unmodified commercial silica gel (CSG) were also performed. For each experimental point in these tests, 0.1 g of the used adsorbent was initially immersed in 5 mL of deionized water, buffered to pH 7.0 within a borosilicate culture tube  $20\times150$  mm, with PTFE lined screw cap. The mixture was then allowed to stand for 24 hours without agitation at the temperature of the experiment. Subsequently, 10 mL of working dye solution was added to each tube. The concentration and temperature of the added dye solution depended on the desired experimental conditions.

In the kinetic tests, each tube was agitated in a temperature-controlled air bath shaker at 150 rpm, promptly after addition of the working solution, and after a predetermined interval, a 10 mL aliquot of supernatant solution was withdrawn and centrifuged. The centrifuged samples were again buffered to pH 7.0 and analyzed using a double beam Uv-vis spectrophotometer (UV-1601PC Shimadzu, Japan) at 490 nm for quantifying the variation of solution concentration with time.

In the equilibrium tests, the tubes were agitated in a temperature-controlled air bath shaker at 150 rpm for 4 hours. After shaking, they were kept at rest for a period of 68 hours to ensure that the adsorption equilibrium was reached. A 10 mL aliquot of supernatant solution was also withdrawn, centrifuged and rebuffered to pH 7.0. The resultant sample was then analyzed using a double beam Uv-vis spectrophotometer (UV-1601PC Shimadzu, Japan) at 490 nm for determining the concentrations of the remaining dye solution and consequently the amount of adsorbed dye at equilibrium.

The amount of congo red adsorbed q (mg g<sup>-1</sup>) in a time t was calculated by the following the Equation 1.

$$q = \frac{(C_o - C_i)V}{M} \tag{1}$$

In which:

 $C_{\rm o}$  = the initial concentration of congo red (mg L<sup>-1</sup>) in adsorption;

 $C_{\bullet}$  = the concentration of congo red in adsorption after time t (mg L<sup>-1</sup>);

V = the volume of the dye solution (L);

M = the mass of the dry adsorbent used (g).

## **Desorption** experiments

Desorption is also a key role for the practical application of adsorptive processes to wastewater treatment. A high efficient desorption can reduce costs because the spent adsorbent and the recuperated adsorbate can be reused. Hence, preliminary desorption studies were conducted by mixing 0,15 g of CR-saturated AMS dried with 10 mL of desorbing solutions in culture tubes previously mentioned and shaking for 2 hours at 150 rpm and 25°C. The saturation of the adsorbent was carried out by contacting 3 g of AMS with 200 mL of 50 mg/L congo red solution for 6 hours. Considering the electrostatic repulsion between the adsorbent surface and congo red at alkaline environment, some basic aqueous solutions at different concentrations (0.01 eq L<sup>-1</sup>, 0.05 eq L<sup>-1</sup>, and 0.1 eq L<sup>-1</sup>) were examined as desorbing solutions for CR on AMS: NaOH, KOH, NaCO<sub>3</sub> and NaHCO<sub>3</sub>.

For determining the concentrations of congo red desorbed, a 7 mL aliquot of adsorbing solution after shaking was withdrawn, centrifuged and buffered to pH 7.0. The resultant sample was spectrophotometrically analyzed as described earlier in adsorption experiments. Then, the percentage amount of desorbed dye (D) was determined as shown in the Equation 2.

$$D = 100 \times \frac{m_d}{m_a} \tag{2}$$

In which:

m<sub>d</sub> = the amount of desorbed congo red (g);

m<sub>2</sub> = the amount of adsorbed congo red (g) at equilibrium.

#### **RESULTS AND DISCUSSION**

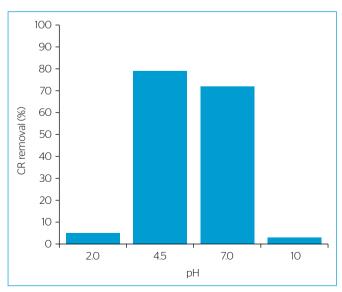
# Effect of pH

The percentages of adsorptive removal of CR using AMS from aqueous solution at pH 2.0, 4.5, 7.0 and 10 are shown in Figure 3. The higher CR percentage removal was observed in the pH range of 4.5 to 7.0. In an alkaline (pH 10) or too acidic (pH 2.0) environment,

the congo red removal was almost negligible. This result is consistent with previous publications about adsorption of anionic dyes (TOR & CENGELOGLU, 2006; MITTAL *et al.*, 2009; YIĞITOĞLU & TEMOÇIN, 2010).

In a strongly acidic solution, the hydroxyl groups and amino groups on the modified silica surface are extensively protonated, and consequently the adsorbent surface is positively charged. On the other hand, the amino functional groups are also protonated and the negative centers (sulfonate groups) are neutralized in the congo red molecule, making it a cationic species. So, the strong electrostatic repulsion between the dye and the adsorbent surface inhibits the adsorption process (COTORUELO et al., 2010). As the pH increases, the protonation of the dye is reduced and the sulfonate groups can interact electrostatically with the positive surface of grafted silica. In addition, hydrogen bonding and van der Waals forces can contribute significantly to increase the adsorption capacity in a neutral or slightly acid environment (DONIA et al., 2009; MITTAL et al., 2009). However, further increasing of the pH results in a system sufficiently alkaline that makes the adsorbent surface negatively charged (TOR & CENGELOGLU, 2006; MITTAL et al., 2009; COTORUELO et al., 2010), which causes a strong repulsion between modified silica surface and anionic dye, inhibiting again the adsorption process. Such behavior explains the results evidenced in Figure 3. Furthermore, it was observed that the influence of the buffering in the adsorption of congo red onto AMS and CGS is insignificant, since deviations in the percentage removal were lower than 5%.

Therefore, the dye solutions were buffered to pH 7.0 prior to adsorption experiments, considering also that this is generally the pH value targeted in domestic and industrial wastewaters.



**Figure 3** - Percentage removals of dye from 0.050 g L¹ CR aqueous solution (25°C) at different pH onto AMS.

## Adsorption experiments

#### Effect of contact time

The quantities of CR adsorbed per unit mass of adsorbent (q) at temperatures of 25 and 40°C as a function of time (t) are shown in Figure 4. It can be initially noted that the equilibrium was reached within about 24 hours. It can also be observed that, under the conditions studied, the CSG has a very low adsorption capacity for the congo red at equilibrium and the adsorption capacity of this adsorbent is considerably increased when it is grafted with APTES. This fact can be explained by the highly polar and hydrophilic surface of pure silica gel, inhibiting strong interactions with organic compounds (WU et al., 2006). Otherwise, aminopropyl groups grafted on the silica gel surface provide a higher hydrophobicity to the adsorbent, increasing the organophilic attraction and the electrostatic attraction between its surface and dye molecules (WU et al., 2006; ANDRZEJEWSKA; KRYSZTAFKIEWICZ; JESIONOWSKI, 2007), which are responsible for the improved adsorption capacity observed in this study.

The kinetic parameters are helpful for the prediction of adsorption rate, which gives important information for designing and modeling adsorption processes (ZHU *et al.*, 2011). Thus, the kinetic data were used to fit models of pseudo-first order, Equation 3, and pseudo-second order, Equation 4. Fitted pseudo-second order models are also shown in Figure 4. The fitting parameters of these models and the corresponding average relative deviations estimated by the experimental data are presented in Table 1.

$$\frac{dq}{dt} = k_t (m_1 - q) \tag{3}$$

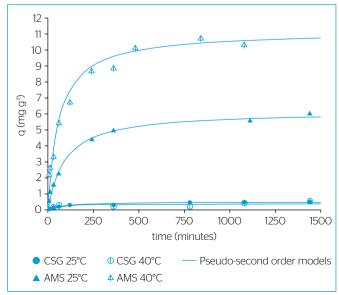


Figure 4 - Kinetic data and pseudo-second order models obtained.

In which:

 $q \text{ (mg g}^{-1})$  = the amount of dye adsorbed at time t (min), of dye adsorbed at saturation:

 $k_1$  (min<sup>-1</sup>) = the equilibrium rate constant of pseudo-first order equation.

$$\frac{dq}{dt} = k_t (m_1 - q)^2 \tag{4}$$

In which:

 $m_2$  (mg g  $^1$ ) = the amount of dye adsorbed at saturation;  $k_2$  (g mg  $^1$  min  $^1$ ) = the equilibrium rate constant of pseudo-second order equation.

From the analysis of the fitting results, it can be observed that the considered models are very inaccurate in representing the kinetic data of adsorption of the congo red onto CSG. However, these experimental data are in the same magnitude dimension of the dye quantification method sensibility, which may justify the high variation coefficient of the kinetic curves on CSG, and, consequently, the inadequacy of the evaluated methods. Concerning the adsorption of CR onto AMS, the model of pseudo-second order can be considered satisfactory in their representation, given that the average relative errors supplied were approximately 12%, suggesting the possible occurrence of chemisorption (XIA *et al.*, 2011) between the congo red and modified silica gel studied.

#### Equilibrium isotherms

Adsorption isotherms are fundamental to the understanding of how the adsorbate interacts with adsorbent surface, and they also provide important information on the amount of adsorbent required to adsorb a particular mass of congo red under the specified system conditions. Hence, the study of equilibrium data is essential for the adsorption interpretation and prediction of the extent of the phenomenon.

The well-known Langmuir and Freundlich models were tentatively adjusted to the equilibrium adsorption data obtained. The equations for these models are presented in Equations 5 and 6, respectively.

$$q_e = \frac{mK_L C_e}{1 + K_L C_e} \tag{5}$$

In which:

 $q_e$  = the equilibrium concentration of the adsorbate (mg g<sup>-1</sup>);

Ce = the adsorptive concentration at the equilibrium state of the system (mg  $L^{-1}$ );

m = the maximum adsorption capacity of the adsorbent (mg  $g^{-1}$ ) assuming a monolayer of adsorbate;

 $K_r$  = the Langmuir affinity constant (L mg<sup>-1</sup>).

$$q_e = K_F C_e^{1/n} \tag{6}$$

In which:

n = the Freundlich exponent (dimensionless);

 $K_{_F}$  = the Freundlich constant related with adsorption capacity (mg g<sup>-1</sup> (mg L<sup>-1</sup>)<sup>1/n</sup>).

The Langmuir and Freundlich coefficients were calculated by nonlinear regression, and the resultant average relative deviations are presented in Table 2.

Table 1 - Fitting parameters and deviation obtained in the kinetic modeling.

Adsorbent	Temperature	Model	Parameters	Deviation (%)
	25°C	pseudo-first order	<i>m</i> <sub>1</sub> =0.439±0.028 mg/g	142.05
			k <sub>1</sub> =(8.92±2.29) × 10³ min¹	142.65
CSG		$ m_1 = 0.439 \pm 0.028 \text{ mg/g} $ $ k_1 = (8.92 \pm 2.29) \times 10^3 \text{ min}^1 $ $ pseudo-second order $ $ pseudo-second order $ $ pseudo-first order $ $ pseudo-first order $ $ pseudo-second order $ $ pseudo-second order $ $ pseudo-first order $ $ pseudo-second order $ $ pseudo-second order $ $ pseudo-second order $ $ pseudo-first order $ $ pseudo-$	m <sub>2</sub> =0.497±0.031 mg/g	176.24
CCC			176.34	
CSG		proude first order	$m_{l}=0.439\pm0.028 \text{ mg/g}$ $k_{l}=(8.92\pm2.29)\times10^{3} \text{ min}^{-1}$ $m_{2}=0.497\pm0.031 \text{ mg/g}$ $k_{2}=(20.2\pm6.37)\times10^{3} \text{ g mg}^{-1} \text{ min}^{-1}$ $m_{l}=0.336\pm0.052 \text{ mg/g}$ $k_{l}=(2.19\pm14.3)\times10^{3} \text{ min}^{-1}$ $m_{2}=0.373\pm0.064 \text{ mg/g}$ $k_{2}=(60.6\pm57.2)\times10^{3} \text{ g mg}^{-1} \text{ min}^{-1}$ $m_{1}=5.545\pm0.252 \text{ mg/g}$ $k_{1}=(8.00\pm1.51)\times10^{3} \text{ min}^{-1}$ $m_{2}=6.163\pm0.200 \text{ mg/g}$ $k_{2}=(1.78\pm0.29)\times10^{3} \text{ g mg}^{-1} \text{ min}^{-1}$ $m_{1}=9.675\pm0.581 \text{ mg/g}$ $k_{1}=(15.8\pm3.5)\times10^{3} \text{ min}^{-1}$	279.75
	40°C	pseudo-iirst order	$k_1 = (21.9 \pm 14.3) \times 10^{-3} \text{min}^{-1}$	
		pseudo-second order	m <sub>2</sub> =0.373±0.064 mg/g	202.05
			$k_2 = (60.6 \pm 57.2) \times 10^3 \text{ g mg}^1 \text{ min}^1$	302.06
		pseudo-first order $k_1$ =(8.92±2.29) × 10³ min¹ $m_2$ =0.497±0.031 mg/g $m_2$ =0.497±0.031 mg/g $m_2$ =0.20.2±6.37) × 10³ g mg¹ min¹ $m_1$ =0.336±0.052 mg/g $m_1$ =0.336±0.052 mg/g $m_2$ =0.373±0.064 mg/g $m_2$ =0.373±0.064 mg/g $m_2$ =0.373±0.064 mg/g $m_2$ =0.373±0.064 mg/g $m_2$ =0.5545±0.252 mg/g $m_1$ =5.545±0.252 mg/g $m_1$ =6.163±0.200 mg/g $m_2$ =6.163±0.200 mg/g $m_2$ =6.163±0.200 mg/g $m_2$ =6.163±0.200 mg/g $m_1$ =9.675±0.581 mg/g $m_1$ =9.675±0.581 mg/g $m_2$ =11.121±0.451 mg/g	<i>m</i> <sub>i</sub> =5.545±0.252 mg/g	18.87
	2500		18.87	
	25°C		order $ m_1 = 0.439 \pm 0.028 \text{ mg/g} $ $ k_1 = (8.92 \pm 2.29) \times 10^3 \text{ min}^4 $ $ m_2 = 0.497 \pm 0.031 \text{ mg/g} $ $ k_2 = (20.2 \pm 6.37) \times 10^3 \text{ g mg}^4 \text{ min}^4 $ $ m_1 = 0.336 \pm 0.052 \text{ mg/g} $ $ k_1 = (21.9 \pm 14.3) \times 10^3 \text{ min}^4 $ $ m_2 = 0.373 \pm 0.064 \text{ mg/g} $ $ k_2 = (60.6 \pm 57.2) \times 10^3 \text{ g mg}^4 \text{ min}^4 $ $ m_1 = 5.545 \pm 0.252 \text{ mg/g} $ $ k_1 = (8.00 \pm 1.51) \times 10^3 \text{ min}^4 $ $ m_2 = 6163 \pm 0.200 \text{ mg/g} $ $ k_2 = (1.78 \pm 0.29) \times 10^3 \text{ g mg}^4 \text{ min}^4 $ $ m_1 = 9.675 \pm 0.581 \text{ mg/g} $ $ m_2 = 11.121 \pm 0.451 \text{ mg/g} $	11.75
AMC		25°C	11.75	
AMS			15.71	
	40°C		k₁=(15.8±3.5) × 10³ min¹	13./1
		pseudo-second order	m <sub>2</sub> =11.121±0.451 mg/g	12.01
			$k_2$ =(1.01±0.30) × 10 <sup>-3</sup> g mg <sup>-1</sup> min <sup>-1</sup>	12.01

It is observed that, in general, the adsorptive systems were better modeled by the Langmuir isotherm than by the Freundlich isotherm. Moreover, Langmuir isotherms had a good fit to data (average relative deviations varying from 7.39% to 12.84%). The equilibrium data obtained and the fitted Langmuir isotherms are plotted in Figure 5.

As also shown in Figure 5, the results reveal that the amount of congo red adsorbed by AMS increases with a rise in temperature

 $\label{eq:table 2 - Fitting parameters and deviation obtained in the equilibrium modeling. \\$ 

Temperature	Model	Parameters	Deviation (%)
	Langmuir	m=5.368±0.171 mg g <sup>-1</sup>	7.99
25°C		b=0.337±0.056 L mg <sup>-1</sup>	
25°C	Freundlich	k=2.258±0.228 mg g <sup>-1</sup> (mg L <sup>-1</sup> ) <sup>-0,215</sup>	12.16
		n=4.661±0.657	
	Langmuir	m=53.369±4.397 mg g <sup>-1</sup>	7.39
40°C	Langmuir	b=0.020±0.002 L mg <sup>-1</sup>	
40°C	Freundlich	k=1.510±0.108 mg g <sup>-1</sup> (mg L <sup>-1</sup> ) <sup>-0,757</sup>	9.62
		n=1.321±0.040	
	Langmuir	m=66.529±21.5171 mg g <sup>-1</sup>	12.84
50°C		b=0.028±0.0105 L mg <sup>-1</sup>	
J0°C	Freundlich	k=1.881±0.163 mg g <sup>-1</sup> (mg L <sup>-1</sup> ) <sup>-0,895</sup>	8.67
		n=1.117±0.060	
	Langmuir	m=19.103±3.148 mg g <sup>-1</sup>	12.18
60°C		b=0.031±0.009 L mg <sup>-1</sup>	
00-0	Freundlich	k=1.120±0.278 mg g <sup>-1</sup> (mg L <sup>-1</sup> ) <sup>-0,612</sup>	14.87
		n=1.634±0.207	

up to 50°C, and then a considerable decrease in the adsorption is observed. Similar behavior has been related by Moreira *et al.* (2001) and Acemioğlu (2004) for adsorption of dyes. It is probable that the temperature influences the orientation of large dye molecules on the surface of solids, as well as a swelling effect within the internal structure of the adsorbent, resulting in adsorption entropy variations, which explains the changes in the adsorption capacities observed in these studies. Anyway, the Langmuir and Freundlich coefficients indicate that adsorption is favorable under the conditions used (MITTAL *et al.*, 2009; ZHU *et al.*, 2011). The Langmuir adsorption capacity has reached a value of up to 66.5 mg g<sup>-1</sup> at 50°C for CR onto AMS.

## **Desorption experiments**

The values of percentage desorption at 25°C for the different desorbing agents and concentrations are presented in Figure 6. It can be observed that the percentage desorption increases with an increase in eluent concentration and respective increase in the pH of desorbing environment. This indicates that ion exchange was one of the main mechanisms involved in the adsorption and desorption processes.

In equal concentrations, the stronger bases were more efficient as desorbing agents. However, the aqueous solution of potassium hydroxide was the most effective desorbing agent, although the sodium hydroxide solution is slightly more basic than caustic potash. This fact can be explained by higher cation exchange capacity of potassium hydroxide, since it lost more easily its solvation water during the ion exchange process. A percentage desorption of 50% to 90% of CR could be recovered from the AMS using solutions of KOH.

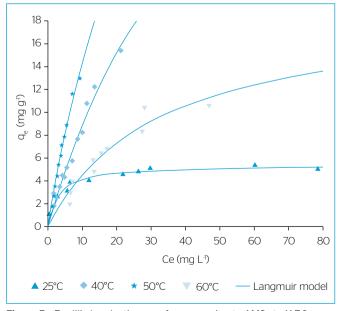
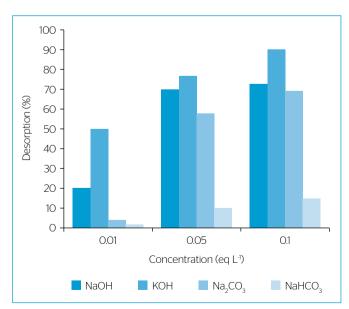


Figure 5 - Equilibrium isotherms of congo red onto AMS at pH 7.0.



**Figure 6** - Effect of different desorbing agents and their concentrations on percentage desorption of congo red from AMS at 25 °C.

#### CONCLUSION

The present study shows that the amino-functionalized silica is an effective adsorbent for the recovering of congo red from aqueous solution. Adsorption data at different pHs, contact times and temperatures were obtained. Equilibrium isotherms were also determined. The adsorption and desorption are strongly dependent of the environment pH. In slightly acidic and neutral environment, adsorption is enhanced. Conversely, desorption is enhanced when the environment is alkaline and strong bases are good desorbing agents. Therefore, desorption also depends on the kind and concentration of the desorbing agent, suggesting that the ion exchange

might be the major mode of adsorption. Equilibrium adsorption data followed preferably Langmuir isotherms. Kinetic data followed rather pseudo-second order than first-order model. Temperature also strongly influences the adsorption of congo red onto AMS.

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