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Adsorption kinetics and thermodynamics of azo-dye Orange II onto highly porous titania aerogel

Lara Abramian, Houssam El-Rassy*

Department of Chemistry, American University of Beirut, P.O. Box 11-0236, Riad El-Solh 1107 2020, Beirut, Lebanon

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ABSTRACT

We report herein a kinetic and thermodynamic study of the adsorption of azo-dye Orange II from aqueous solutions onto titania aerogels. Aerogels structure was confirmed by FTIR and N_2 adsorption revealed their specific surface area (500 m^2/g), pore volume (2.86 cm^3/g) and pore size (mean 13.9 nm). Adsorption tests were conducted in batch reactors under various conditions where the effect of pH, temperature, contact time, dye concentration, and adsorbent dose were studied. Experiments performed at pH 2 show the optimal adsorption due to the best surface charge interactions. The temperature shows a weak influence with a decrease in the adsorption uptake as the temperature increases. Adsorption kinetics is shown to be very fast and follows a pseudo second-order indicating the coexistence of chemisorption and physisorption with the intra-particle diffusion being the rate controlling step. The experimental data fit perfectly with Sips isotherms and reveal the ability of titania aerogel to adsorb 420 mg of Orange II per gram of adsorbent at the optimal conditions. The thermodynamic study reveals the activation energy (42.1 kJ mol^{-1}) and the changes in Gibbs free energy (1.2 kJ mol^{-1}), enthalpy (-16.4 kJ mol^{-1}), and entropy (-58 J mol^{-1} K^{-1}). The entire regeneration of the titania aerogel adsorption sites at pH 11 and 30 °C shows a total recovery of the dye and the efficient reusability and the economic interest of these adsorbing materials for environmental purposes.

1. Introduction

Dyes containing azo-aromatic groups are highly dispersible pollutants. They contribute to water toxicity and represent an increasing danger for the environment and human beings. These effluents discharged from various industries (e.g. textile, paper, leather, food, etc.) are known to be toxic [1], carcinogenic [2], mutagenic [3], teratogenic [4], and their release in the environment is a considerable source of non-aesthetic pollution since the existence of low concentrations of dyes is clearly visible. Thus, the removal of these colored compounds from wastewater is an important target from the environmental point of view. However, this process faces a major problem represented in the high stability of these azo-dyes in aqueous media and their resistance to light and oxidation agents [5]. Conventional treatment methods for the removal of dyes in wastewater include physical, chemical and biological processes such as adsorption [6], coagulation [7], oxidation [8], reduction [9], filtration [10], and biological treatment [11]. The physical adsorption process at solid-liquid interface is known to be a powerful method for decreasing the concentration of soluble dyes in effluents and has the advantage of being efficient and economic. A large number of adsorbing materials for soluble dyes have been studied such as activated carbon [12], alumina [13], clay [14], silica xerogel [15], titania [16], titania–silica mesoporous materials [17], waste materials [18–20] and many other materials. In this study we investigate for the first time the adsorption kinetics and thermodynamics of dyes from aqueous solutions onto highly porous titania aerogels. Well-known Orange II azo-dye whose molecular structure is shown in Fig. 1 was used as a model molecule for this purpose. This dye has been chosen as it is inexpensive and widely used in textile, pulp and paper industries. Table 1 regroups the results obtained in some recent research works where the adsorption of Orange II onto various adsorbents has been studied [21–28].

Aerogels obtained through the low-temperature sol–gel process [29] and dried under supercritical conditions [30] are exceptionally porous solids showing high specific surface areas (up to 1000 m^2/g), an extraordinarily large surface-to-volume ratio ($\sim 2 \times 10^9$ m^{-1}) and low densities (0.003–0.35 g cm^{-3}) [31–33]. These materials deserve particular interest due to their surface properties as well as the chemical reactivity of their surface groups.

The adsorption kinetics and thermodynamics were studied under various conditions and the adsorption equilibria were investigated to find out which isotherm model shows the best fitting to the experimental data. The effects of the adsorbate concentrations,

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* Corresponding author. Tel.: +961 1 350000x3970; fax: +961 1 365217.
E-mail address: Houssam.Rassy@aub.edu.lb (H. El-Rassy).

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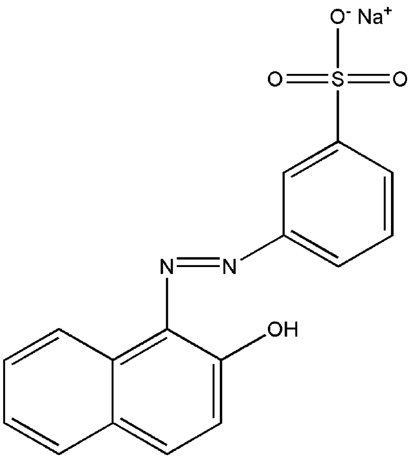

Fig. 1. Chemical structure of Orange II.

temperature, pH and adsorbent quantity were studied in order to determine the optimal adsorption conditions.

2. Experimental

2.1. Materials

The chemicals were used in this study as received and without further purification. Titanium isopropoxide ($Ti(OC_3H_7)_4$, TIP) was purchased from Sigma–Aldrich. Orange II ($C_{16}H_{11}N_2OSO_3Na$, C.I. 15510, C.I. Acid Orange 7, M.W. 350.32, certified pure) was provided from Acros Organics. Isopropanol and nitric acid (65%) were from Lab-Scan and Panreac, respectively. Double deionized water was prepared in our laboratory.

2.2. Synthesis of titania aerogels

Titania aerogels were prepared after the supercritical drying of wet alcogels synthesized through a one-pot sol–gel process. Titanium isopropoxide was mixed for 1 min in a polypropylene vial with isopropanol to which is added a nitric acid solution (65%). After stirring for another minute, deionized water is added and stirred together for 30 s before the stirring was stopped. The gelation of the sol was observed in the next few minutes and obtained gels were kept for aging for one day. The mixing steps as well as the gelation were performed at room temperature. The drying of the wet alcogels under supercritical carbon dioxide ($T_c = 31.1\,^\circ C$; $P_c = 73.7$ bar) led to the final titania aerogels. This terminal step was preceded by a 24 h-solvent exchange step, where the residual water and isopropanol in the alcogel were exchanged by acetone presenting a higher miscibility with liquid carbon dioxide. The final molar ratio TIP:Isopropanol:H_2O:HNO_3 for the synthesized titania aerogels was 1:20:4:8 × 10^{-2}.

2.3. Titania aerogels characterization

The textural properties were determined by using the nitrogen sorption technique. The nitrogen adsorption–desorption isotherms were measured using a Nova 2200e high-speed surface area and pore size analyzer (Quantachrome Instruments). Prior to the measurement, titania aerogels were degassed for 5 h at 70 °C. The specific surface area was calculated according to the BET theory [34] while the pore size and pore volume were calculated by the BJH method [35] based on the desorption branch of the isotherm. The structural characterization of the titania aerogels was carried out using a Thermo Nicolet 4700 Fourier Transform Infrared Spectrometer equipped with a Class 1 Laser. The experiment was done in the range between 4000 and 400 cm^{-1} using the transmission KBr pellet technique where 1% in weight aerogel powder-containing potassium bromide pellets were used.

2.4. Adsorption studies

Several adsorption experiments were carried out in different experimental conditions. All experiments were performed in glass vials placed in a controlled-temperature shaking water bath operating at 200 rpm. In typical adsorption experiments, 30 mg of titania aerogel were added to 15 mL of 50 mg/L dye solution at 30, 40, and 50 °C. Aliquots were carefully withdrawn from the solution at predetermined time intervals over 24 h and the solution absorbance was measured in the UV–visible range at the maximum absorption ($\lambda = 483$ nm) using a JASCO V-570 UV/VIS/NIR spectrophotometer. Centrifugations performed on several samples showed that the aliquots were particle free and therefore there is no need to carry out centrifugations for taken aliquots. The amount of adsorbed dye on titania aerogels was calculated according to the following equation:

$$q_e = \frac{C_i - C_e}{m} V \qquad (1)$$

where q_e is the amount of dye adsorbed (mg/g), C_i and C_e are the initial and equilibrium liquid-phase concentrations of dye (mg/L), respectively, V is the volume of solution (L) and m is the amount of adsorbent (g).

The effect of pH was studied after the adjustment of the dye solutions pH between 1 and 12 using dilute HCl and NaOH solutions; A Corning Pinnacle 542 pH conductivity meter with a combined pH

Table 1
Comparison of the maximum monolayer adsorption capacities of Orange II onto various adsorbents.

Adsorbents	Maximum monolayer adsorption capacities (mg/g)	References
Chitosan bead	1940 (30 °C)	[21]
Commercial activated carbon fibers—generated from pitch	1260 (30 °C)	[22]
Commercial activated carbon fibers—made with polyacrylonitrile	230 (30 °C)	[22]
Sludge adsorbent	350 (30 °C)	[22]
Activated carbon	404 (25 °C)	[23]
$CuFe_2O_4$/activated carbon composite	392 (25 °C)	[23]
Activated carbon cloths	90 (30 °C)	[24]
Chitosan	116 (20 °C); 113 (60 °C)	[25]
Spent brewery grains	28.54 (20 °C); 30.47 (30 °C)	[26]
Unmodified zeolite	0.63 (25 °C)	[27]
Surfactant-modified zeolite	3.62 (35 °C)	[27]
Bottom ash	13.24 (50 °C); 12.68 (40 °C); 12.50 (30 °C)	[28]
De-oiled soya	9.58 (50 °C); 9.18 (40 °C); 8.87 (30 °C)	[28]