ADSORPTION OF CONGO RED ON TITANIUM DIOXIDE DOPED WITH S

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Titanium dioxide (TiO_2) is a versatile material with exceptional adsorption properties. Its utility extends to various environmental and industrial applications, including wastewater treatment, air purification, and photovoltaics. Adsorption capabilities of TiO_2 can be enhanced by the incorporation of dopants. In this work we studied effect of doping with sulfur (S).

Titanium dioxide was synthesized using the sol-gel method, employing a precursor solution that featured the titanium aqua complex [1]. In the preparation of TiO_2 doped with 2%, 4%, and 8% sulfur (S), corresponding quantities of sodium sulfate (Na_2SO_4) in a 10% (w/w) solution were added. In the case of mesoporous TiO_2, this process was executed without the inclusion of any salt.

The adsorption properties of S-TiO_2 samples were assessed at neutral pH values. Conical flasks containing 10 mg of the samples and 25 mL of Congo red (CR) dye solution were sealed with silicone stoppers. The mixtures were stirred for 1.5 hours. The equilibrium concentration of CR in solution was determined by measuring optical density at 500 nm using a ULAB 102-UV spectrophotometer after removal of S-TiO_2 samples by centrifugation.

The adsorption was analyzed using the Langmuir and Freundlich isotherms, two the most commonly used adsorption models in chemistry. These models are particularly useful for understanding how molecules are adsorbed at equilibrium between the solid and liquid phases. Eq. (1) and (2) represent the linearized forms of the Langmuir and Freundlich isotherms, respectively

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (1)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (2)$$

where C_e is the equilibrium solution concentration, mg/L; q_e is the adsorption capacity at equilibrium, mg/g; q_{max} is the maximum adsorption capacity, mg/g; K_F is the Freundlich constant, mg/g.

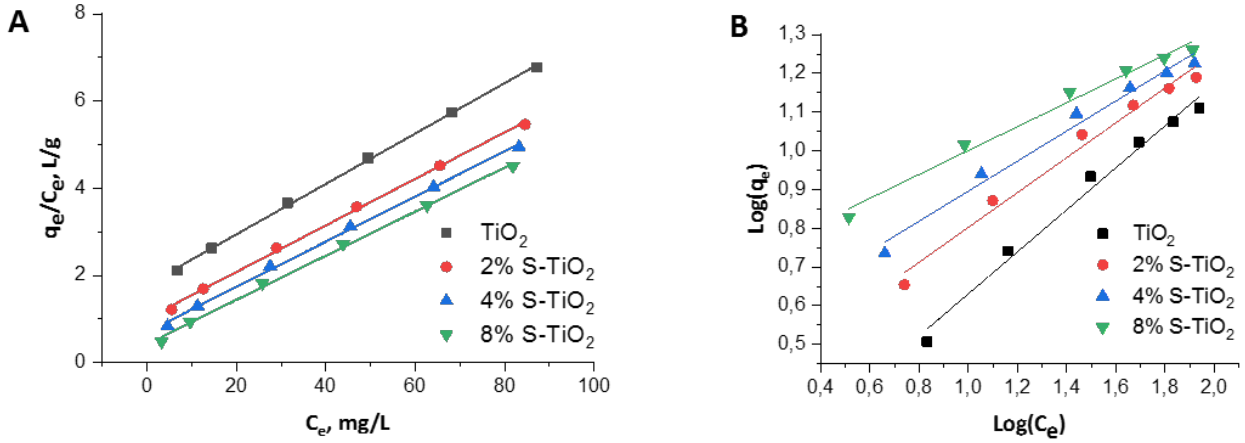

Fig. 2. Langmuir (a) and Freundlich (b) isotherms in linearized form for adsorption of Congo red (4 to 100 mg/mL) on TiO_2 doped with 0 to 8% S

The Langmuir adsorption model describes the monolayer coverage of adsorbate molecules on adsorbent sites without any interactions between adsorbate molecules on adjacent sites. In this isotherm all sites are equivalent and the surface is homogeneous. Fig. 2a shows the applicability of the Langmuir isotherm for a monolayer coating of dye on TiO_2 photocatalysts. C_e/q_e linearly increases with C_e, as shown in Fig. 2a, allowing to estimate the constants q_{max} and K_L. The Freundlich isotherm is an adsorption isotherm for rough and heterogeneous surfaces with interaction between adsorbed molecules. Figure 2b illustrates a linear plot of $\log(q_e)$ versus $\log(C_e)$, representing the Freundlich isotherm for the adsorption of Congo red on the TiO_2 surface. In this isotherm 1/n is the heterogeneity factor and indicates deviation from linear adsorption. If the value of n = 1, the adsorption is linear; if n < 1, the adsorption is chemical; and if n > 1, the adsorption is a favorable physical process. In our current study, the reciprocal of 'n', denoted as 1/n, is less than one (Table 1). The value of 3.24 for n indicates that adsorption of CR on TiO_2 is a favorable physical process [2].

Table 1. Langmuir and Freundlich isotherm constants for the adsorption of Congo red on TiO_2 photocatalysts

Photocatalyst	Constants of Langmuir isotherms			Constants of Freundlich isotherms			
	q_{max}, mg/g	K_L, g/L	R^2	K_f, L/g	n	1/n	R^2
TiO_2	17.29±0.25	32.4±0.8	0.9989	1.2±0.7	1.84±0.11	0.54±0.03	0.9818
2S-TiO_2	18.73±0.37	52.7±2.6	0.9981	2.3±0.3	2.22±0.15	0.45±0.03	0.9783
4S-TiO_2	19.29±0.42	73.8±5.8	0.9976	3.2±0.2	2.57±0.17	0.39±0.03	0.9779
8S-TiO_2	19.75±0.49	117±16	0.9976	4.9±0.2	3.24±0.20	0.31±0.02	0.9812

The Langmuir and Freundlich models were used to describe the mechanism of adsorption of the Congo red dye on the surface of S-TiO_2 samples. Based on the results of the study on the adsorption of Congo red on the S-doped TiO_2 surface, it was found that all samples best fit the Langmuir model.

The correlation coefficients of Langmuir isotherms fall within the range of 0.9976 to 0.9989, while the R^2 values for Freundlich isotherms range from 0.9779 to 0.9818. The weak correlation of the experimental data with the Freundlich model suggests that these samples do not exhibit characteristics of multilayer adsorption and a heterogeneous adsorbent surface.

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