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Investigation of methylene blue dye adsorption on nanographite oxide prepared by electrochemical exfoliation

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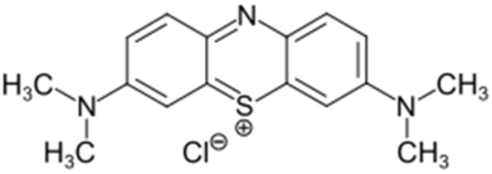
For this study, nanographite oxide (NGO) was synthesized by electrochemical exfoliation of graphite foil of the ‘Graflex’ brand according to the reported method.[S1]

We chose a solution of a cationic dye, methylene blue (*N*,*N*,*N′*,*N′*-tetramethylthionine chloride trihydrate, 3,7-bisdimethylaminophenothiocyanite chloride, MB), as a model solution for studying the adsorption capacity of NGO obtained by the electrochemical method. MB has the form of green crystals that dissolve in water to give dark blue solutions. The chemical formula of methylene blue is $C_{16}H_{18}ClN_3S$, its molecular weight is 319.86 g/mol.



The adsorption properties of NGO were studied using the standard photometric analysis technique based on a calibration graph at a predetermined analytical wavelength of 660 nm.

Adsorption of the dye at a certain point in time (a_t) and at the equilibrium point (a_e) at an initial concentration of 0.25 to 20 mg dm^{-3} was calculated using equations (S1) and (S2):

$$a_{\mathrm{t}} = \frac{(C_0 - C_{\mathrm{t}})}{m} V, \tag{S1}$$

$$a_{\mathrm{e}} = \frac{(C_0 - C_{\mathrm{e}})}{m} V, \tag{S2}$$

where a_e is the adsorption value at the equilibrium point (mg g^{-1}), a_t is the adsorption value at time *t* (mg g^{-1}), C_0 is the concentration of the starting solution (mg dm^{-3}), C_e is the concentration of the equilibrium solution (mg dm^{-3}), V is the volume of solution (dm^3), and m is the mass of the adsorbent (4.5×10^{-3} g).

Adsorption isotherms were modeled using basic equilibrium equations, namely, the Langmuir equation,

$$\frac{C_\mathrm{e}}{a_\mathrm{e}} = \frac{1}{K_\mathrm{L} a_\mathrm{max}} + \frac{C_\mathrm{e}}{a_\mathrm{max}} \quad , \tag{S3}$$

the Freundlich equation,

$$\ln a_\mathrm{e} = \ln K_\mathrm{F} + \frac{1}{n}\ln C_\mathrm{e}, \tag{S4}$$

and the Dubinin–Radushkevich equation,

$$\ln a_\mathrm{e} = \ln a_\mathrm{max} + K_\mathrm{DR}\varepsilon, \tag{S5}$$

$$\varepsilon = RT\ln(1 + 1/C_\mathrm{e}),$$

$$E = (-2K_\mathrm{DR})^{-0.5},$$

where a_max is the adsorption capacity of the sorbent at saturation (mg g^{-1}), K_L, K_F and K_DR are the constants of the Langmuir, Freundlich and Dubinin–Radushkevich equations (dm^3 mg^{-1}), respectively, R is the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T is the absolute temperature (K), and E is the activation energy (kJ mol^{-1}).

For all equations, their parameters were calculated using linear regression analysis, modeling curves were plotted and correlation coefficients R^2 were determined.

The thermodynamic characteristics of the adsorption process were determined according to the reported procedure.[S2] The standard Gibbs free energy (ΔG) was calculated using the equation

$$\Delta G = RT\ln K_\mathrm{d}, \tag{S6}$$

where K_d is the distribution coefficient and T is the absolute temperature (K).

The equilibrium constant was determined as the limit:

$$K_\mathrm{d} = \lim_{C_\mathrm{e}\to 0} \frac{a_\mathrm{e}}{C_\mathrm{e}}, \tag{S7}$$

where a_e and C_e are the dye concentrations (mg cm^{-3}) in the adsorbed phase and in the volume of the solution at equilibrium, respectively. This was accomplished by plotting the dependence of $\ln\left(\frac{a_e}{C_e}\right)$ on C_e, approximating it with a linear function and determining its value at $C_e = 0$.

Changes in standard enthalpy (ΔH) and entropy (ΔS) were determined graphically from the dependence of ΔG on T.

Kinetic studies were performed at an initial MB concentration of 4 mg dm^{-3}, an adsorbent mass of 4.5×10^{-3} g and a temperature from 298 to 343 K.

Processing of adsorption kinetic curves was carried out within the framework of the Lagergren pseudo-first-order model,

$$\ln(a_e - a_t) = \ln a_e - k_1 t, \tag{S8}$$

where k_1 is the pseudo-first-order rate constant (min^{-1}), and the pseudo-second-order model,[S3]

$$\frac{t}{a_t} = \frac{1}{k_2 a_e^2} + \frac{t}{a_e}, \tag{S9}$$

where k_2 is the sorption rate constant in the pseudo-second-order model (g mg^{-1} min^{-1}), and $k_2 a_e^2$ can be considered as the initial adsorption rate at $t \rightarrow 0$.

Based on the parameters of the pseudo-second-order equation, the initial adsorption rate (mg g^{-1} min^{-1}) was calculated according to the equation

$$h = a_e^2 \cdot k_2. \tag{S10}$$

To estimate the contribution of internal and external diffusion to the overall rate of the sorption process, experimental kinetic data were processed within the framework of the Boyd–Adamson[S4] model [equation (S11)] and the Weber–Morris[S5] model [equation (S12)].

Table S1 Kinetic parameters in the pseudo-first order and pseudo-second order coordinates.

	Kinetic parameters	
Pseudo-first order		
	k_1 min^{-1}	0.5173
	R^2	0.8684
Pseudo-second order		
	k_2 (g mg^{-1} min^{-1})	$0.1 \cdot 10^{-4}$
	R^2	0.9992

To calculate external diffusion (transport in solution at the interface with the sorbent), a simplified form of the Boyd–Adamson film diffusion equation was used:

$$\ln(1-F) = -\beta t, \tag{S11}$$

where $F = \frac{a_\mathrm{t}}{a_\mathrm{e}}$ is the degree of completeness of the process, and β is the rate constant of external diffusion.

With an increase in the degree of surface coverage, the adsorption curve according to the Morris–Weber model [equation (S12)] becomes linear in coordinates a *vs.* $t^{1/2}$, which indicates the appearance of intra-diffusion constraints:

$$a = K_\mathrm{id} t^{1/2} + C, \tag{S12}$$

where K_id is the diffusion rate constant (mg g^{-1} min$^{-1/2}$), and C is a parameter related to the thickness of the boundary layer (mg g^{-1}).

To estimate the effect of temperature on the adsorption of MB on the NGO surface, we calculated the value of the Gibbs energy (Table 2) using the Van 't Hoff equation and equations (6) and (7) and determined the entropy and enthalpy of the reaction graphically (Figure S1).

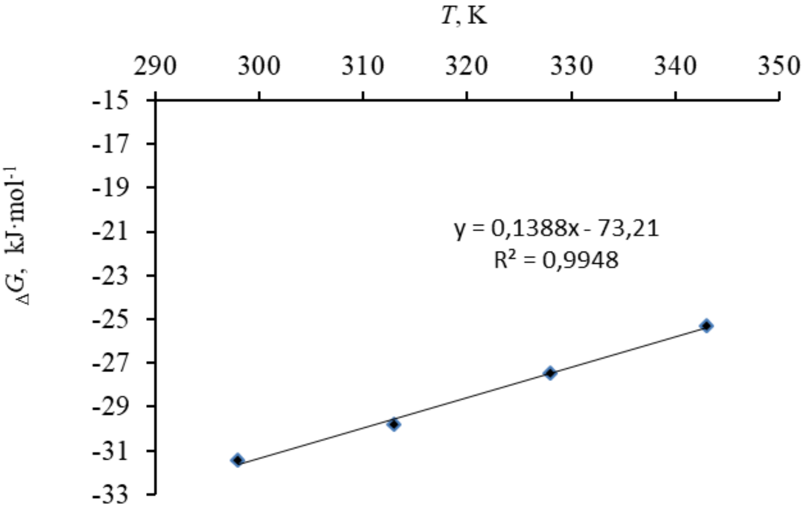


Figure S1 Plot of the Gibbs energy *versus* temperature.

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