Supplementary Information (SI) for CrystEngComm.
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Supplementary Information File

Chemically Grafting Ni(II)-dithiocarbamate complex onto graphene oxide nanosheets for selective and ultrafast removal of toxic anionic methyl orange dye from water

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1S. Kinetic study

Adsorption kinetics also controls the rate of adsorption, which determines the time required for reaching equilibrium for the adsorption process. Kinetic models can give information regarding adsorption pathways and probable mechanism involved. This is also an important data for the development of the process and the adsorption system design.[1S-4S]

In this study, removal percentage and adsorption capacity of MO with various contact times at same initial concentrations 200 mg $L^{-1}$and absorbent concentration 50 mg areanalyzed, respectively. As the reaction started, the concentrations of MO changed with time, and the corresponding equilibrium adsorption capacities were measured with the help of the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (1S)$$

where q_t(mg g^{-1}) - adsorption capacity and C_t (mg L^{-1}) - adsorption concentration at time t. To reach an understanding into the adsorption process, the kinetic data was investigated.

The Lagergren pseudo-first-order model is based on the assumption that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and the amount of solid uptake with time, which is generally applicable over the initial stage of an adsorption process. This model is expressed as the following equation:[5S]

$$\log\left(q_e - q_t\right) = \ln q_e - \frac{k_1}{2.303}t \qquad (2S)$$

where q_e and q_t are the amount of solute adsorbed per unit amount of adsorbent at equilibrium and any time, respectively (mg/g), k_1 is the pseudo-first-order rate constant (h^{-1}).The plot of log (q_e - q_t) against t gives a linear relationship from which k_1 and q_e are determined from the slope and intercept of plot, respectively

The pseudo-second-order kinetic model is based on the assumption that the rate-limiting step is chemical sorption or chemisorption and predicts the behavior over the whole range of adsorption. In this condition, the adsorption rate is dependent on adsorption capacity not on concentration of adsorbate. This model is expressed as the following equation:[6S-8S]

$$\frac{t}{q_t} = \left(\frac{t}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) \qquad (3S)$$

where k_2 is the pseudo second-order rate constant of adsorption (g/mg h). The values of q_e and k_2 are determined from the slope and intercept of the plot of t/q_t versus t.

The nonlinear pseudo-first-order kinetic model assumes that the rate of adsorption is proportional to the difference between the equilibrium adsorption capacity and the amount of adsorbate adsorbed at any given time. The nonlinear pseudo-first-order equation is expressed as:[9S]

$$q_t = q_e(1 - \exp\left(k_1 t\right)) \qquad (4S)$$

where:

- q_t is the amount of adsorbate adsorbed at time t (mg/g),
- q_e is the equilibrium adsorption capacity (mg/g),
- k_1 is the pseudo-first-order rate constant (1/min),
- t is the time (min).

The nonlinear pseudo-second-order kinetic model assumes that the adsorption rate is proportional to the square of the difference between the equilibrium adsorption capacity and the amount adsorbed. The nonlinear pseudo-second-order equation is expressed as: [10S]

$$q_t = \frac{(q_e^2 k_2 t)}{(1 + q_e k_2 t)} \qquad (5S)$$

where:

- q_t is the amount of adsorbate adsorbed at time t (mg/g),
- q_e is the equilibrium adsorption capacity (mg/g),
- k_2 is the pseudo-second-order rate constant (g/mg·min),
- t is the time (min).

2S. Isotherm study

Adsorption isotherms generally describe how different adsorbates interact with an adsorbent, with the relationship between the two parameters, q_e and C_e at constant temperature and pH. The information extracted from the isotherm is currently used to obtain information regarding capacities of adsorbents, the adsorption phenomenon, expression of the surface properties, the optimization of the adsorption mechanism pathways, and the design of effective and economically viable commercial treatment system.[11S]

The adsorption isotherms were carried out by varying the initial concentrations of MO dye from 10 to 100 ppm. Different isotherm models can be used to explore the distribution of adsorbed molecules on the solid–liquid interface at equilibrium by fitting the experimental data. The adsorption isotherm is then plotted with adsorbed amount q_e against the equilibrium concentration C_e.

In the monolayer adsorption and the Langmuir model, the adsorbent and the adsorbate are in dynamic Equilibrium. The mathematical development is then based on the physical simplicity of the mechanisms in relation with various assumptions: (1) the surface is homogeneous, which means that all sites are energetically equivalent; (2) adsorption is a monolayer process, and each site can adsorb only one adsorbate molecule; (3) there is no lateral interaction between adsorbed molecules, and (4) the adsorption is reversible.[12S,13S] It is expressed in linear form as:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \qquad (6S)$$

where Q_m (mg g^{-1} or mol g^{-1}) and C_e (mol L^{-1}) are maximum adsorption capacity and the concentration at equilibrium, respectively, and K_L is the Langmuir constant, which represents

the energy of adsorption or the equilibrium constant of adsorbate-absorbent equilibrium (L g^{-1} or L mol^{-1} depending on the unit of Q_m and C_e).Freundlich isotherm can describe nonideal, multilayer, reversible adsorption at a heterogeneous surface. The isotherm also assumed that all the adsorption sites have different binding energies. The energy distribution for adsorptive sites (in Freundlich isotherm) exhibits spectrum of different binding energies rather than one uniform energy and follows an exponential-type function, which is close to the real situation. The equation can be linearized by taking logarithms and is expressed as follows: [3S]

$$\log(q_e) = \log K_F + \left(\frac{1}{n}\right).\log C_e \qquad (7S)$$

where K_F and n are constants that measure the adsorption capacity and intensity, respectively.

The Langmuir isotherm model in its nonlinear form assumes monolayer adsorption on a homogeneous surface with a finite number of identical adsorption sites. The nonlinear Langmuir equation is expressed as:[14S]

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (8S)$$

where:
- q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),
- Q_{max} is the maximum adsorption capacity (mg/g),
- K_L is the Langmuir constant (L/mg),
- C_e is the equilibrium concentration of the adsorbate in solution (mg/L).

The Freundlich isotherm model in its nonlinear form describes multilayer adsorption on a heterogeneous surface. The nonlinear Freundlich equation is expressed as: [14S]

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (9S)$$

where:
- q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),
- K_F is the Freundlich constant indicating adsorption capacity (mg/g) $(L/mg)^{1/n}$),

- n is the adsorption intensity,
- C_e is the equilibrium concentration of the adsorbate in solution (mg/L).

3S. Thermodynamic study

Thermodynamic investigations are another important parameter of adsorption studies. For thermodynamic studies, the adsorption experiment was carried out at different temperature conditions and calculated parameters included enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG). Adsorption thermodynamic equations are expressed as the following:[15S,16S]

$$K_c = \frac{q_e}{C_e} \qquad (10S)$$

$$\Delta G^0 = -RT\ln K_c \qquad (11S)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (12S)$$

Where ΔG^0 is standard Gibbs free energy change (kJ mol^{-1}), ΔH^0 is standard enthalpy change (kJ mol^{-1}), ΔS^0 is standard entropy change (kJ mol^{-1} K^{-1}) and q_e, C_e, $K_c$and R are the amounts of antibiotic absorbed on the sorbent at equilibrium, the solution concentration at equilibrium, the distribution coefficient and the molar gas constant (8.314 J mol^{-1}K^{-1}), respectively. The adsorption capacity of MO onto $Ni(DTC)_2$-GO was performed at four different temperatures to evaluate adsorption thermodynamic process.

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