Supplementary Information

Removal and recovery of dissolved oil from high-salinity wastewater using graphene-iron oxide nanocomposites

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1. Adsorption Isotherms

The batch experiment results were analyzed to reveal the adsorption mechanism using Langmuir isotherm, the Freundlich isotherm, Temkin isotherm, and Dubinin-Radushkevich (D-R) and the results were consistent with the Freundlich isotherm.

1.1. The Langmuir Isotherm

The Langmuir model is expressed by:

$$q_e = \frac{q_m * b C_e}{(1 + b C_e)} \quad (1)$$

The linearized form of the Langmuir model is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

where Ce is the equilibrium adsorbate concentration (mg/L), qe is the equilibrium adsorption capacity (mg/g), qm is the maximum amount of dissolved oil per adsorbent unit mass (mg/g), and b is constant related to the affinity of the adsorbate to the binding sites (L/mg). A linear fit of the Ce/qe versus Ce data is used to test the model applicability to the adsorption results [1].

Figure S1 shows the fitting the experimental results to the Langmuir model by plotting Ce/qe vs Ce. The experimental data do not follow the Langmuir isotherm is indicated by the very poor fit (R2 = 0.126)

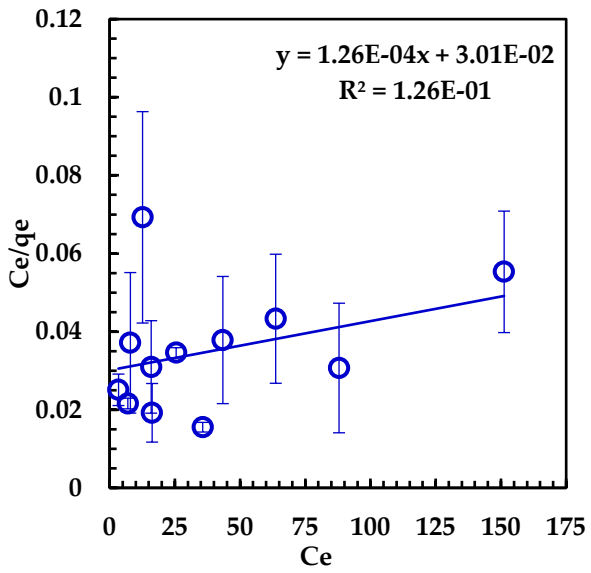

Figure S1. Langumir Isotherm fitting of the adsorption data

1.2. The Freundlich Isotherm

The Freundlich isotherm is an empirical equation that describes heterogeneous adsorption. The Freundlich isotherm model is given by:

$$q_e = k_f C_e^{\frac{1}{n}} \quad (3)$$

where n and kf are the constants related to the sorption intensity and capacity of the adsorbent [2]. The linearized form of the Freundlich model is:

$$lnq_e = lnk_f + \frac{1}{n} lnC_e \quad (4)$$

Figure S2 shows the fitting the experimental results to the Freundlich model by plotting ln qe vs ln Ce. The experimental data follow the Freundlich isotherm is indicated by the very good fit (R2 = 0.922). It is worth noting that the experimental data are collected under different initial concentrations and different adsorbent dose. The results were consistent with the Freundlich isotherm assumes a saturated monolayer of adsorbate molecules on a defined set of homogeneous sites on the adsorbent surface [2].

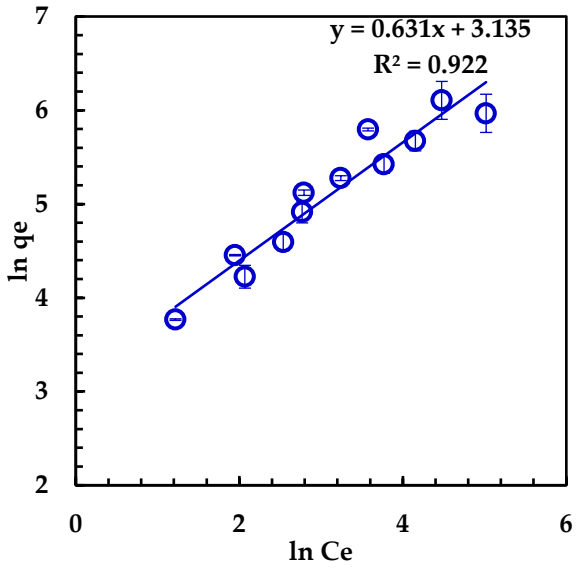

Figure S2 Freundlich Isotherm fitting of the adsorption data

The parameters of the Freundlich isotherm obtained from the slop and intercept of the fitting are n = 1.6 and kf = 23, indica ting the adsorption process is physical.

1.3. Temkin Isotherm

The Temkin isotherm assumes the heat of adsorption decreases linearly with the adsorbent saturation. The Temkin isotherm model in the general and linearized forms is presented by equations 8 and 9 [3]:

$$q_e = \frac{RT}{b} \ln (AC_e) \quad (5)$$

$$q_e = BlnA + BlnC_e \quad (6)$$

where b is the Temkin constant associated with the sorption energy, A is the equilibrium binding constant (L/mg), and $B = \frac{RT}{b}$ is a constant related to the heat of adsorption. These coefficients are obtained by plotting q_e versus C_e.

The Temkin model did not provide good fit to the experimental data as shown in Figure S3.

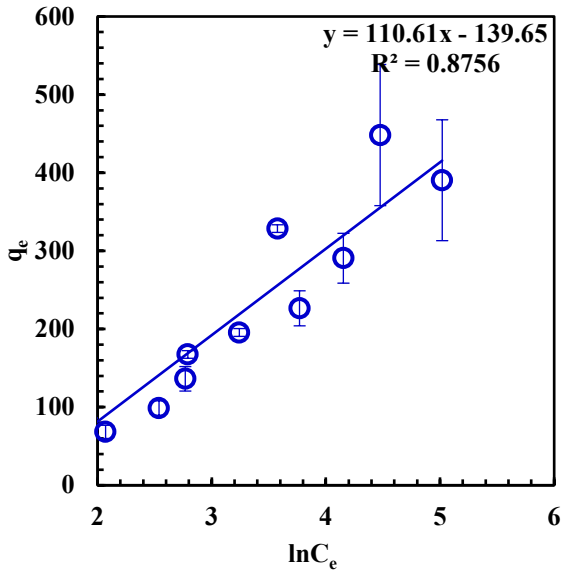

Figure S3. Temkinr Isotherm fitting of the adsorption data

The parameters of the Temin isotherm obtained from the slop and intercept of the fitting are A = 0.28, B = 110.6, and b = 22.6.

1.4. Dubinin-Radushkevich (D-R) Isotherm

The Dubinin-Radushkevich (D-R) isotherm model differentiate between the chemisorption and physisorption adsorption based on the adsorption energy. The mathematical expression of the D-R model is given by:

$$lnq_e = lnq_m - B_d\varepsilon^2 \quad (7)$$

where ε is the Polanyi potential (J/mol) that is given by equation 11, B_d is the D-R constant (mol^2/kJ^2), and qm and q_e are the maximum and equilibrium adsorption capacity (mol/g).

$$\varepsilon = RTln\left[1 + \left(\frac{1}{C_e}\right)\right] \quad (8)$$

where T is the temperature (K), and R is the universal gas constant. E is the free energy per molecule of adsorbate that is related to Bd via:

$$E = \frac{1}{\sqrt{2Bd}} \quad (9)$$

E describes the mechanism of the adsorption process, where a chemisorption process has $8 < E < 16$ kJ/mol and a physisorption process has $E < 8$ [4].

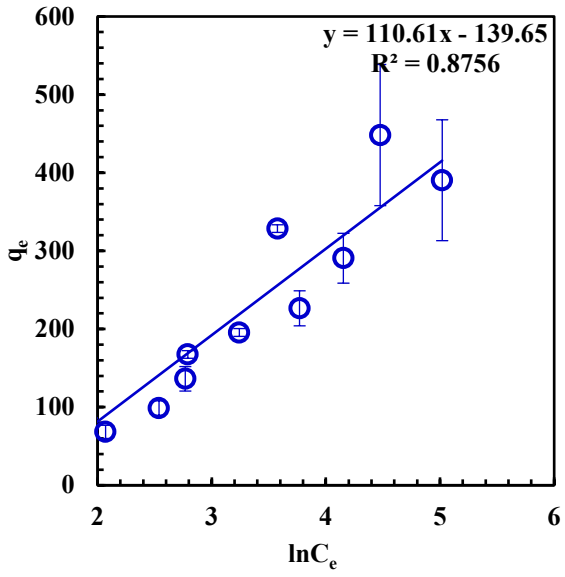

Figure S4. Dubinin-Radushkevich (D-R) Isotherm fitting of the adsorption data

The D-R model did not provide good fit to the experimental data as shown in Figure S4. The parameters of the D-R isotherm obtained from the slop and intercept of the fitting are Bd = 0.015 (1/kJ2), qm = 238 mol/g, and E = 5.8 kJ.

References:

1. Dada, A., et al., *Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk.* IOSR Journal of Applied Chemistry, 2012. **3**(1): p. 38-45.
2. Gulistan, A.S., *Oil removal from produced water using natural materials*. 2014.
3. Yang, M., *Measurement of oil in produced water*, in *Produced water*. 2011, Springer. p. 57-88.
4. Yuh-Shan, H., *Citation review of Lagergren kinetic rate equation on adsorption reactions.* Scientometrics, 2004. **59**(1): p. 171-177.