SUPPLEMENTARY DOCUMENT

Synthesis and Characterization of Versatile Polymer Particles for the Adsorption of Bromophenol Blue and Phenol

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Characterisation of GD polymer particles

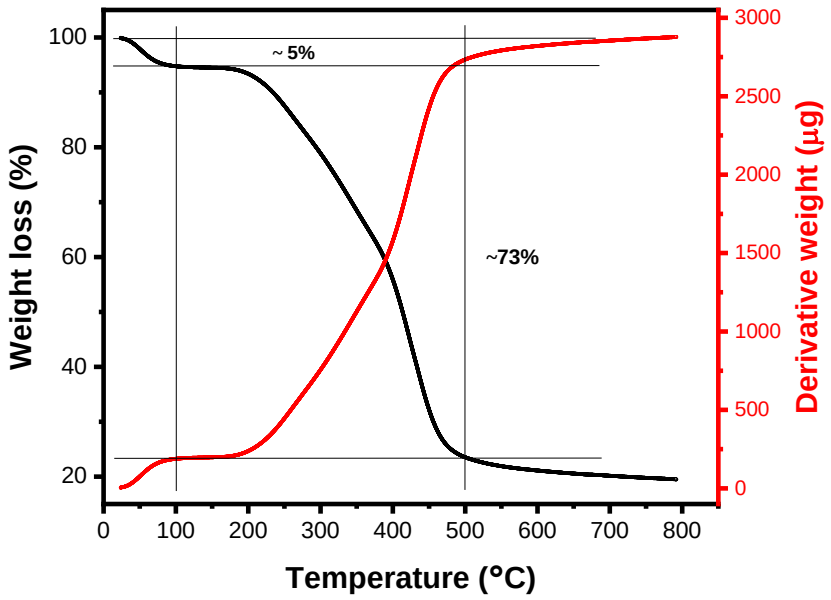

Figure S1. Thermogravimetric analysis of GD particles

Adsorption kinetics

Pseudo first order (PFO) kinetic model (Lagergren, 1898), pseudo second order (PSO) kinetic model (Ho ve McKay, 1999), Weber-Morris intraparticle diffusion (Weber ve Morris, 1980) and Elovich (Chien ve Clayton, 1980) kinetic models were used to understand the mechanism of adsorption between bromophenol blue, phenol and GD particles. The models were calculated with the equations I, II, III and IV given below, respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2{,}303} \quad \textbf{(I)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \textbf{(II)}$$

$$q_t = k_i t^{1/2} + C \quad \textbf{(III)}$$

$$q_t = \frac{1}{\alpha}\ln(\alpha * \beta) + \frac{1}{\alpha} lnt \quad \textbf{(IV)}$$

where q_e and q_t are the amount of dye adsorbed by the adsorbent at equilibrium time and adsorption time (mg/g), respectively. t is the adsorption time (min). k_1 (min-1), k_2 (g.mg-1.min-1) and k_i ($mg.g^{-1}min^{-1/2}$) are constants of pseudo-first, pseudo-second-order and Weber-Morris intraparticle diffusion models, respectively. C is a constant that gives information about the thickness of the layer formed between the adsorbate and the adsorbent. α is the initial adsorption rate (mg/g.min) and β is a constant (g/mg) associated with the size of the surface area and the activation energy of chemical adsorption.

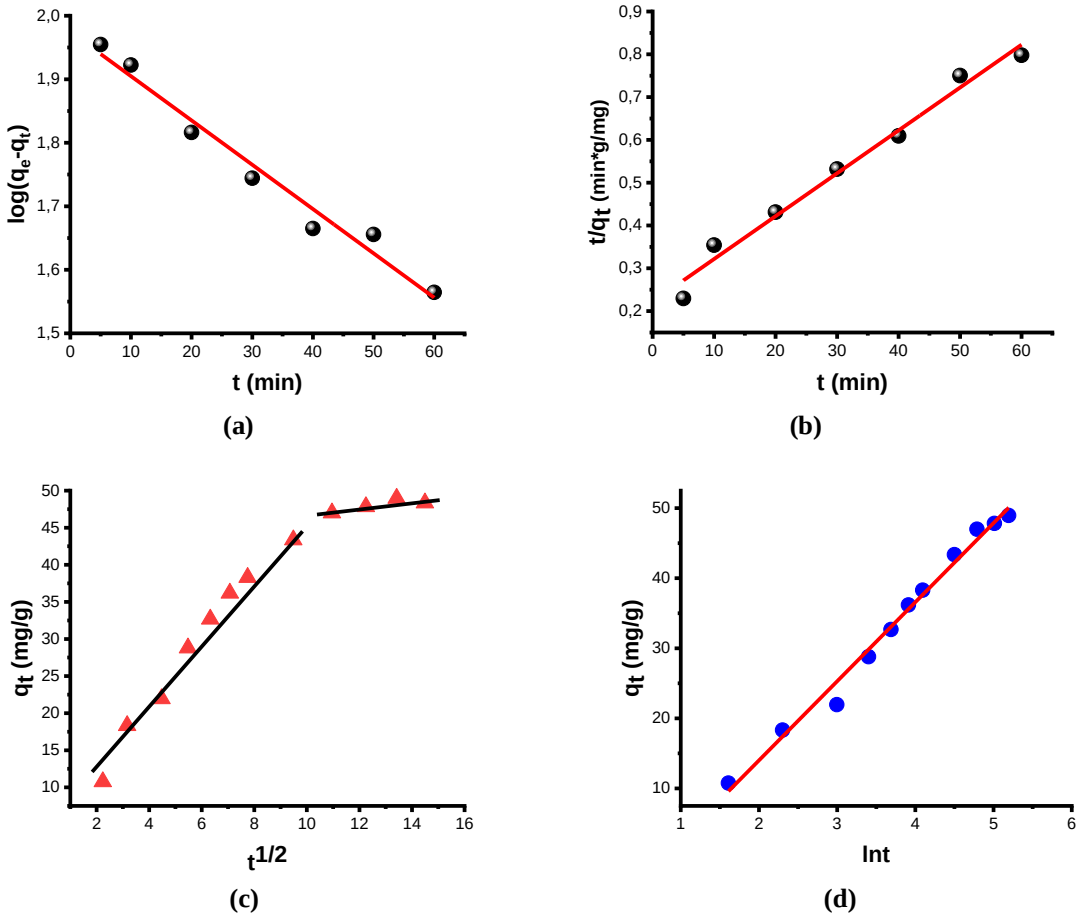

Figure S2. (a) Pseudo first order, (b) pseudo second order, (c) interparticle diffusion model and (d) Elovich kinetic models for the adsorption of BPB dye on GD polymer particles **linear fit model** (t: 0-180 min; initial conc.: 100 mg/L; T: 25ºC; adsorbent: 50 mg; V: 25 mL)

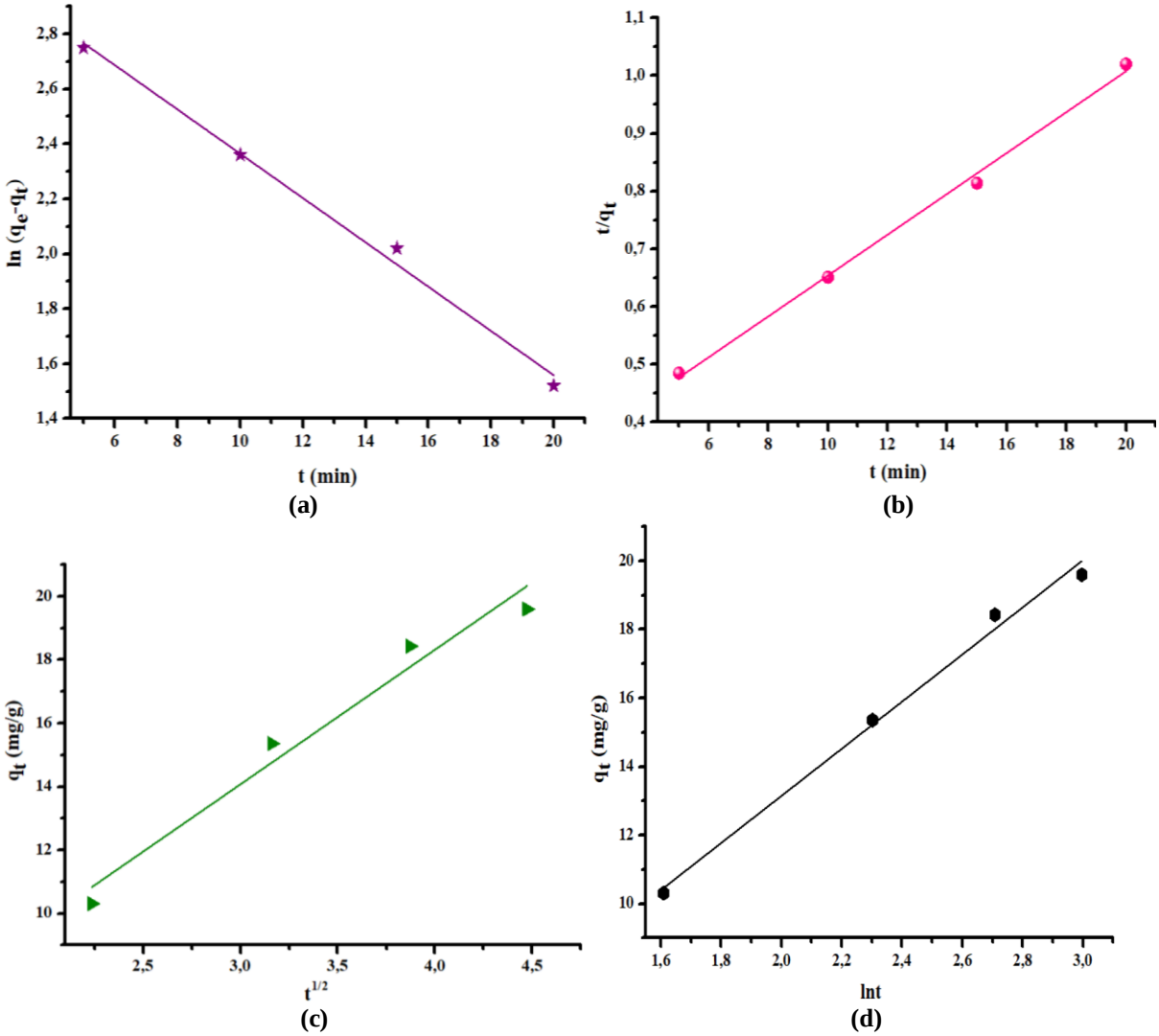

Figure S3. (a) Pseudo first order, (b) pseudo second order, (c) interparticle diffusion model and (d) Elovich kinetic models for the adsorption of phenol on GD polymer particles **linear fit model** (pH:5.5; initial conc. 50 mg/L; adsorbent 15 mg, V:10 mL, T:25°C, 400 rpm)

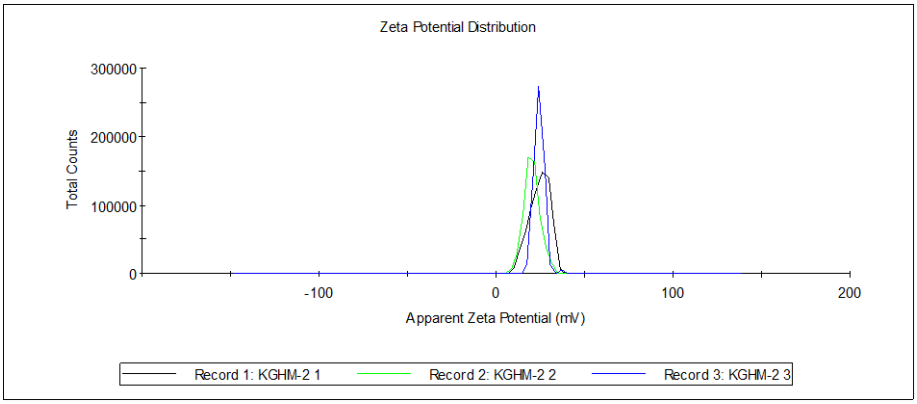

Figure S4. Zeta potential of GD polymer particles

Adsorption isotherms

- Langmuir isotherm

In the Langmuir isotherm; i) there is no interaction between pollutants, ii) each region of the adsorbent has the same (homogeneous) adsorption efficiency, and iii) it is assumed that the pollutants are adsorbed on the adsorbent

surface as a single layer (Jiang et al., 2017; You et al., 2018; Kloster et al., 2019; Dai et al., 2020) and the following equation was calculated with V.

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

where C_e is the concentration of the dye solution at equilibrium (mg/L), q_e is the amount of dye adsorbed per unit weight of the adsorbent at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g) of the GD particles adsorbate corresponding to the monolayer, and K_L is the Langmuir adsorption constant (L/mg) related to the affinity between the adsorbate and binding sites of the adsorbate. Also, the feasibility of adsorption can be demonstrated by the dimensionless separation factor R_L given by the following equation:

$$R_L = \frac{1}{(1 + K_L C_0)} \qquad (VI)$$

C_0 (mg/L) is the initial dye concentration. The value of the separation factor indicates the suitability of the adsorption process as follows: If $R_L > 1$, adsorption is unfavorable; linear if $R_L = 1$; If $0 < R_L < 1$, the adsorption is appropriate and if $R_L = 0$, the adsorption is irreversible.

- Freundlich isotherm

It is accepted that the adsorbent surface is heterogeneous in the Freundlich isotherm and therefore the adsorption takes place in a multilayered manner (Guo et al., 2019; Kloster et al., 2019; Kumar et al., 2019). The following equation was calculated with VII.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (VII)$$

Here K_F is the Freundlich isotherm constant for the amount of dye adsorbed for an equilibrium concentration. n is a number revealing the property of the energy distribution function and the value of 1/n is estimated from the slope of the same graph. The graph of $\log q_e$ as a function of $\log C_e$ allows the determination of the constant K_F and n.

- Temkin isotherm

Unlike the Langmuir and Freundlich equations, the Temkin isotherm takes into account the interaction between adsorbate and adsorbent. According to the Temkin isotherm, the decrease in the heat of adsorption of all molecules occurs in a linear order. This indicates that the binding energy is homogeneous (Adeogun and Balakrishnan, 2015; Ahmed and Abou-Gamra, 2016; Chauhan et al., 2021). The linear equation of the Temkin constant is shown below in equations VIII and IX:

$$q_e = \beta_t \ln K_T + \beta_t \ln C_e \qquad (VIII)$$

$$\beta_t = {RT}/{b} \qquad (IX)$$

K_T is the equilibrium constant corresponding to the maximum binding energy (L/g). β_t is the constant with respect to the heat of adsorption. b is the Temkin constant for heat absorption (J/mg). R is the gas constant (J/mol K) and T is the temperature (K). K_T and β_t are calculated from the slope and intersection of the plot of $\ln C_e$ versus q_e.

- Dubinin- Radushkevich (D-R) isotherm

This isotherm is used to estimate the heterogeneity of surface energies and the nature of the adsorption process physically or chemically by calculating the adsorption energy (Altaher et al., 2014; Adeogun and Balakrishnan

2015; Ahmed and Abou-Gamra 2016; Mazaheri et al. 2016). The isotherm was calculated with the following equation X.

$$\boldsymbol{lnq_e = lnq_m - B\varepsilon^2} \qquad (\boldsymbol{X})$$

Here, q_e is the amount of adsorbate (mg/g) adsorbed on the adsorbent surface at equilibrium. q_m, is the D-R monolayer capacity (mg/g). B is a constant related to the average free adsorption energy per mole of adsorbate as it is transferred from infinite distance to the surface of the solid. $\mathcal{E}$ is the Polonyi potential associated with the equilibrium concentration.

$$\boldsymbol{\varepsilon = RTln(1 + 1/C_e)} \qquad (\boldsymbol{XI})$$

Here R is the ideal gas constant (kJ/mol K) and T is the temperature (K). The coefficients q_m and B can be calculated from the graph of $\mathcal{E}^2$ versus lnq$e$. The constant B (mg^2/J^2) allows us to find the adsorption energy (E).

$$\boldsymbol{E = \frac{1}{\sqrt{2B}}} \qquad (\boldsymbol{XII})$$

If E < 8 kJ/mol, the adsorption process is physical, if 8 < E < 16 kJ/mol, the adsorption process is ion exchange, and if E > 16 kJ/mol, the adsorption process is chemical.

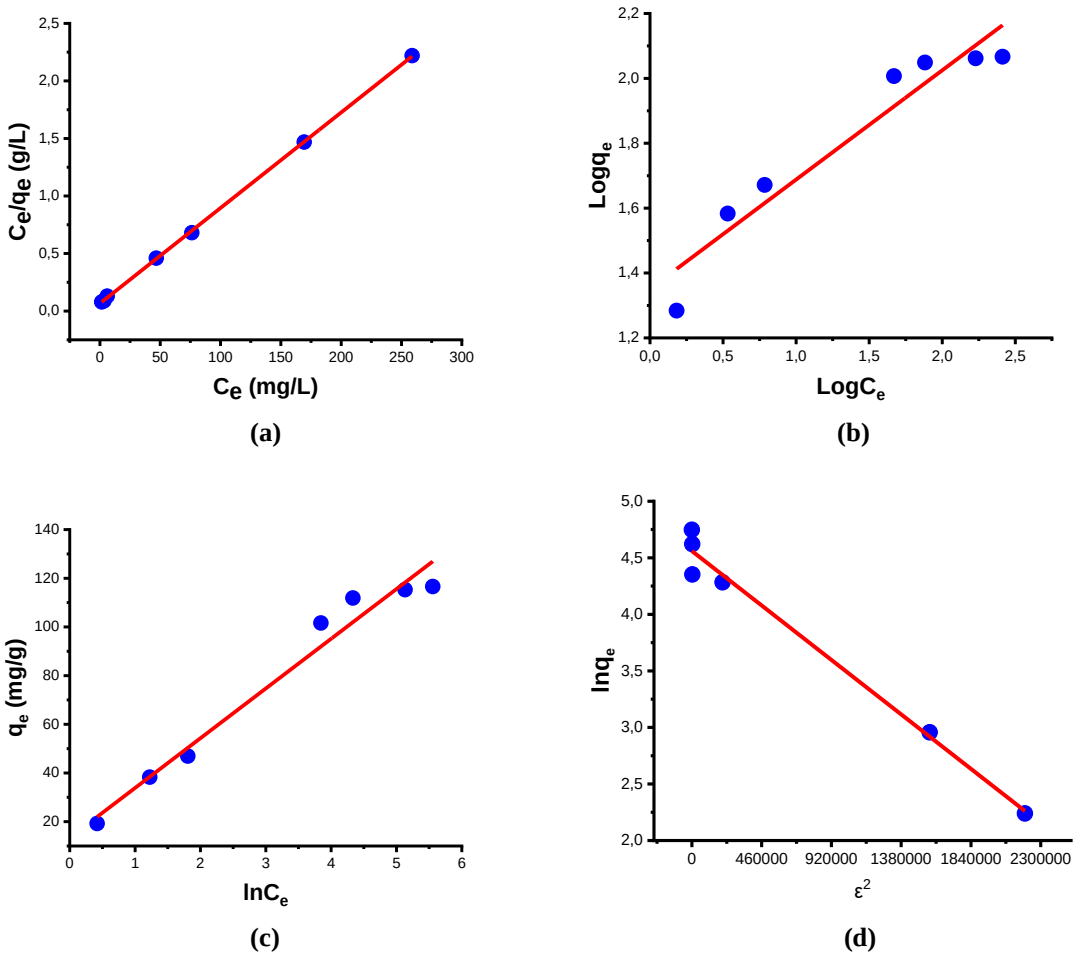

Figure S5. (a) Langmuir, (b) Freundlich, (c) Temkin and (d) D-R adsorption isotherm for the adsorption of BPB dye on GD polymer particles **linear fit model** (t: 180 min; pH: 4.0; T: 25ºC; adsorbent: 50 mg; V: 25 mL)

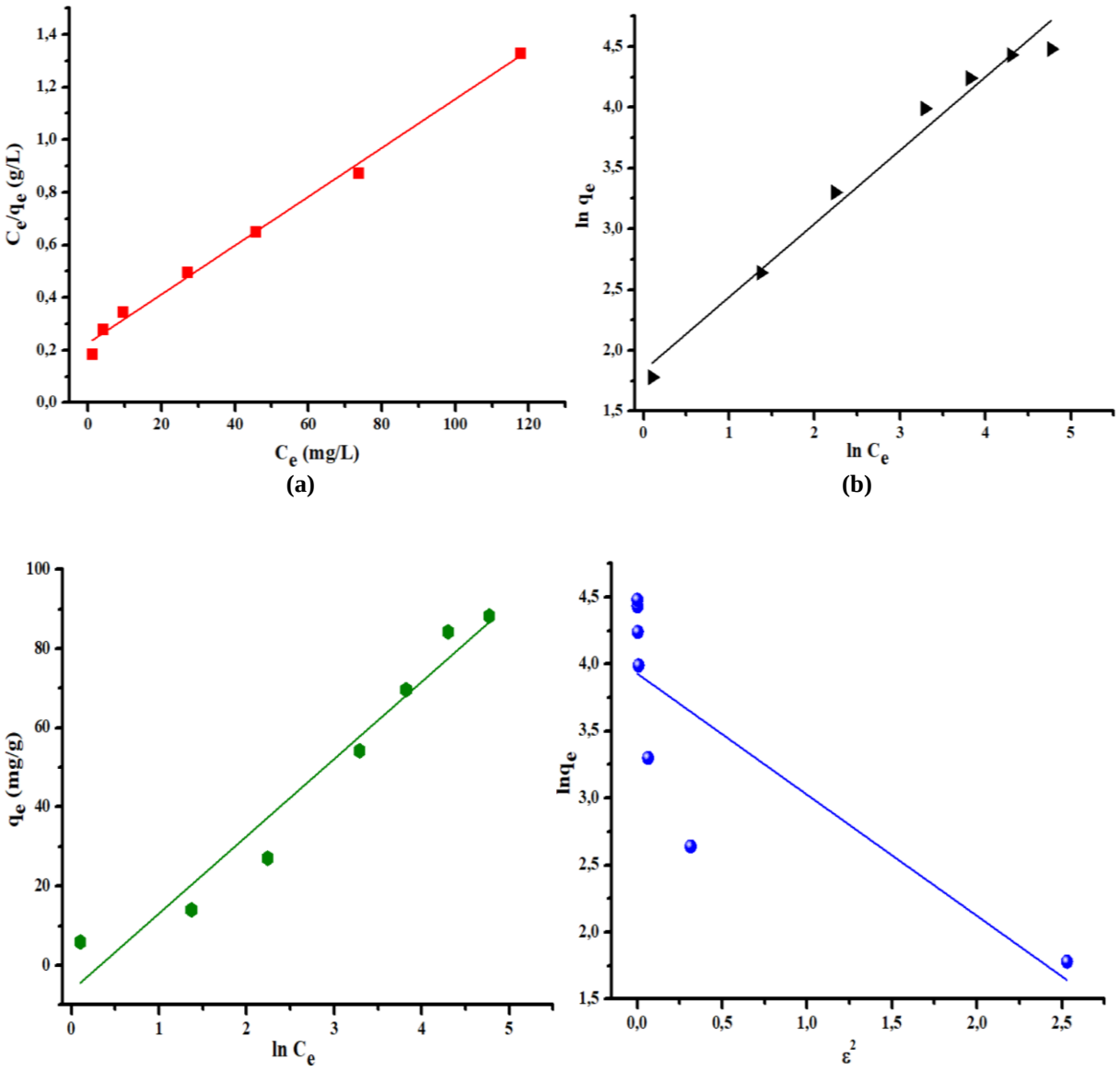

Figure S6. (a) Langmuir, (b) Freundlich, (c) Temkin and (d) D-R adsorption isotherm for the adsorption of phenol on GD polymer particles **linear fit model** (t: 30 min; pH: 5.0; adsorbent 15 mg, V:10 mL, 400 rpm)

Adsorption thermodynamics

In this study, the thermodynamics of adsorption was evaluated with parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes. Gibbs free energy, ΔH° and ΔS° were calculated with the following equations XIII, VIV and XV, respectively.

$$K_d = \frac{C_e}{q_e} \qquad (XIII)$$

$$\ln K_d = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (XIV)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (XV)$$

The plot of lnKd versus 1/T yields ΔH° and ΔS° from slope and intersection, respectively (Fig. S7). R is the universal gas constant (8.314 J/molK). ΔG° is calculated from the third equation at different temperatures.

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