

**Supporting Information for:**  
**Amine-Grafted Pomegranate Peels for the Simultaneous Removal**  
**of Nitrate and Phosphate Anions from Wastewater**

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## **Experimental**

### **Materials and instrumentation**

All chemicals were reagent grade (Aldrich Chemical Co.) and were used as purchased without further purification. Uv-Vis spectra were recorded on a Varian Cary-4000 spectrophotometer, using 0.1 or 1 cm quartz cuvettes. Infrared spectra were recorded in a KBr disk on a Perkin Elmer-Spectrum BX FTIR system. Absorbances are shown in wavenumbers ( $\text{cm}^{-1}$ ). X-ray powder diffraction (XRD) was performed with Philips diffractometer with single-chromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The zeta potentials of the samples were measured by Zetacad equipment at  $25^\circ\text{C}$ .

### **Adsorption and Desorption Study**

The adsorption capacities of  $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$  anions using PP/AEAPTES were investigated as a function of the controllable parameters, including solution pH, contact time, amount of adsorbent, and anion concentration at different temperatures.  $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$  adsorption experiments were performed by adding the adsorbent (20 to 200 mg) to 50 mL of nitrate or phosphate solution (20 to 300 mg/L), under stirring (250 rpm) at different temperatures ( $25^\circ\text{C}$  to  $50^\circ\text{C}$ ), and different pH (2 to 11), for different periods of time (0 to 300 min). The initial pH values were adjusted by 0.1 M NaOH or HCl solutions. Before and after the adsorption experiments, the nitrate concentration was calculated by ultraviolet spectrophotometry and the phosphate concentration by ammonium molybdate spectrophotometry [1]. The adsorption capacity  $q_e$  ( $\text{mg g}^{-1}$ ) and removal rate (R) of PP/AEAPTES to adsorb  $\text{PO}_4^{3-}$  and  $\text{NO}_3^-$  anions were calculated as follows:

$$q_e = \frac{C_0 - C_e}{m} * V \quad (S1)$$

$$R = \frac{C_0 - C_e}{C_0} * 100 \quad (S2)$$

Where V (l) is the solution volume, m (g) is the weight of PP/AEAPTES; C<sub>0</sub> (mg/L) is the initial concentration of the anions; C<sub>e</sub> (mg/L) is the aqueous-phase anion concentration at equilibrium.

All adsorption experiments were repeated three times and expressed as the mean ± standard deviation (SD).

### Adsorption isotherms

To study the equilibrium relation between PO<sub>4</sub><sup>3-</sup> and NO<sub>3</sub><sup>-</sup> anions and PP/AEAPTES, the Langmuir isotherm [2] was used to formulate the adsorption equilibrium according to equation (S3) :

$$C_e/q_e = 1/q_{\max}b + C_e/q_{\max} \quad (S3)$$

Where q<sub>e</sub> is adsorbing capacity (mg g<sup>-1</sup>), C<sub>e</sub> is the equilibrium anions concentration (mg/l), q<sub>max</sub> is the anion maximum adsorption capacity per unit mass of PP/AEAPTES (mg/g), and b is the adsorption coefficient (L/mg) calculated from the linear plot of C<sub>e</sub> versus C<sub>e</sub>/q<sub>e</sub>. The equilibrium parameter R<sub>L</sub> of the Langmuir isotherm is calculated following equation (S4) [3].

$$R_L = 1 / (1 + bC_0) \quad (S4)$$

The R<sub>L</sub> value suggests if the isotherm type is unfavourable (R<sub>L</sub>>1), linear (R<sub>L</sub> = 1), favourable (0<R<sub>L</sub><1), or irreversible (R<sub>L</sub> = 0).

The Freundlich isotherm describes the adsorption on a heterogeneous surface [4]. It is expressed by the following equation (S5):

$$\ln(q_e) = \ln K_F + (1/n) \ln C_e \quad (S5)$$

where K<sub>F</sub>((mg/g)(L/mg)<sup>1/n</sup>) and n are the Freundlich constants of the system, which indicate the adsorption capacity and adsorption intensity respectively.

By plotting ln q<sub>e</sub> versus ln C<sub>e</sub>, 1/n and K<sub>F</sub> are generated.

The shape of the isotherm depends on the value of 1/n, which represents the adsorption intensity and gives important information on the mechanisms governing the adsorption of the compound on the adsorbent. According to the value of 1/n, the following cases are distinguished:

- 1/n = 1 : the isotherm is linear of type C;
- 1/n > 1 : the isotherm is convex of type S;
- 1/n < 1 : the isotherm is concave type L;

- $1/n \ll 1$  : the isotherm is of type H.

A value of  $1/n$  between 0 and 1 indicates that the adsorption process is favorable. The value of the parameter  $1/n$  is 0.6821 indicating that the isotherm is of type L and the biosorption process is favorable.

Temkin [5,6] (Eq. S6,S7) and Dubinin-Radushkevich [7-10] (Eq. S8-S10) models are expressed as follows:

$$q_e = B \cdot \ln K_T + b \ln C_e \quad (S6)$$

$$B = RT/b_T \quad (S7)$$

$$\ln q_e = \ln q_s - K_{DR} \cdot \varepsilon^2 \quad (S8)$$

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (S9)$$

$$E = 1/\sqrt{2K_{DR}} \quad (S10)$$

Where  $q_e$  (mg/g) is the amount of adsorbate in the adsorbent at equilibrium;  $K_T$  (L/mg) is Temkin isotherm equilibrium binding constant;  $b_T$  is Temkin isotherm constant;  $B$  (J/mol) is Constant related to heat of sorption;  $q_s$  (mg/g) is theoretical isotherm saturation capacity;  $K_{DR}$  ( $\text{mol}^2/\text{kJ}^2$ ) is Dubinin–Radushkevich isotherm constant and  $\varepsilon$  (J/mol) is the Polanyi potential.  $R$  (8.314 J/mol K),  $T$  (K), and  $C_e$  (mg/L) represent the gas constant, absolute temperature, and adsorbate equilibrium concentration respectively.  $E$  ( $\text{kJ} \cdot \text{mol}^{-1}$ ) is the sorption energy.

The Sips isotherm [11] is expressed following the equation (S11):

$$q_e = (q_m K_s C_e^{1/n}) / (1 + K_s C_e^{1/n}) \quad (S11)$$

where  $q_m$  ( $\text{mg} \cdot \text{g}^{-1}$ ) is the Sips maximum adsorption capacity;  $K_s$  ( $\text{L} \cdot \text{mg}^{-1}$ ) is the Sips equilibrium constant and  $1/n$  is the Sips model exponent.

### Adsorption thermodynamic

The Gibbs free energy change ( $\Delta G^\circ$ ), the enthalpy change ( $\Delta H^\circ$ ), and the entropy change ( $\Delta S^\circ$ ) were calculated according to the equations (S12-S14).

$$\Delta G^\circ = -RTK_d \quad \text{and} \quad K_d = q_e/C_e \quad (S12)$$

$$\ln K_d = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \quad (S13)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (S14)$$

where  $K_d$  is the constant of thermodynamic equilibrium,  $R$  is the universal gas constant ( $8.314 \text{ J} (\text{mol} \cdot \text{K})^{-1}$ ), and  $T$  is the temperature (K).

### Adsorption kinetics

The pseudo-first-order and pseudo-second-order kinetic models were used to investigate the adsorption kinetic of nitrate and phosphate anions onto PP/AEAPTES by applying the pseudo-first-order (Eq. S15), pseudo-second-order (Eq. S16), Elovich (Eq. S17), and intra-particle diffusion (Eq. S18) equations.

$$\text{Log } (q_e - q_t) = \text{Log } q_e - K_1 t / 2.303 \quad (\text{S15})$$

$$t/q_t = 1/(K_2 q_e^2) + t/q_e \quad (\text{S16})$$

$$q_t = 1/\beta \text{Ln}(\alpha\beta) + 1/\beta \text{Ln}(t) \quad (\text{S17})$$

$$q_t = K_{id} t^{1/2} + C_i \quad (\text{S18})$$

Where  $q_e$  and  $q_t$  ( $\text{mg.g}^{-1}$ ) are the quantities of the anions adsorbed per unit weight of  $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{Cs-NH}_2$  at equilibrium time; time  $t$  (min); the constants  $K_1$  ( $\text{min}^{-1}$ ),  $K_2$  ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ), and  $K_{id}$  ( $\text{g.mg}^{-1}.\text{min}^{-0.5}$ ) are the pseudo-first-order rate, pseudo-second-order equilibrium rate, and intra-particle diffusion rate constant, respectively; For the Elovich coefficients,  $\alpha$  ( $\text{mg g}^{-1}.\text{min}^{-1}$ ) is the initial adsorption rate and  $\beta$  ( $\text{g.mg}^{-1}$ ) is the desorption constant;  $C_i$  is the intercept related to the thickness of the boundary layer.

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