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SUPPLEMENTARY MATERIAL TO

# Copper ions biosorption onto bean shells: Kinetics, equilibrium and process optimization studies

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## MODELS

The pseudo-first order kinetic model is given by:[1]

$$\frac{dq_{(t)}}{dt} = k_1(q_e - q_{(t)}) \quad \text{(S-1)}$$

where: $q_{(t)}$ – is the adsorbent capacity defined as the mass of the adsorbed metal per unit mass of the adsorbent (mg $g^{-1}$) at time $t$; $q_e$ – is the adsorption capacity defined as mass of the adsorbed metal per unit mass of the adsorbent (mg $g^{-1}$) at equilibrium; $k_1$ – is the adsorption rate constant for the pseudo-first order kinetic model ($min^{-1}$).

Integrating the Eq. (S-1), it follows:

$$\log(q_e - q_{(t)}) = \log(q_e) - \frac{k_1}{2{,}303} \times \mathrm{t} \quad \text{(S-2)}$$

The pseudo-second order kinetic model can be expressed as:[2]

$$\frac{dq_{(t)}}{dt} = k_1(q_e - q_{(t)})^2 \quad \text{(S-3)}$$

where: $q_{(t)}$ - is the adsorbent capacity defined as the mass of the adsorbed metal per unit mass of the adsorbent (mg $g^{-1}$) at time $t$; $q_e$ - is the adsorption capacity defined as mass of the adsorbed metal per unit mass of the adsorbent (mg $g^{-1}$) at equilibrium; $k_2$ - is the adsorption rate constant for the pseudo-second order kinetic model (g $mg^{-1}$ $min^{-1}$).[3]

The linear form of Eq. (S-3) is:

$$\frac{1}{(q_e - q_{(t)})} = \frac{1}{q_e} + k_2 t \quad \text{(S-4)}$$

The intraparticle diffusion kinetic model is given as:[1]

$$q_{(t)} = k_i t^{1/2} + C_i \quad \text{(S-5)}$$

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where: $q_{(t)}$ - is the adsorption capacity defined as the mass of the adsorbed metal per unit mass of the adsorbent (mg $g^{-1}$) at time $t$; $k_i$ -is the internal particle diffusion rate constant (mg $g^{-1}$ $min^{-0.5}$); and $C_i$ – is a constant that provides insight into the thickness of the boundary layer. If the $C_i$ value is higher, the boundary layer effect is greater, so the effect of surface adsorption in controlling the process speed is greater (mg $g^{-1}$).

Elovich kinetic model is given in the following form:[1]

$$\frac{dq_{(t)}}{dt} = \alpha e^{-\beta q(t)} \quad \text{(S-6)}$$

where: $\alpha$ - is the starting adsorption rate (mg $g^{-1}$ $min^{-1}$); $\beta$ - is the parameter that expresses the degree of surface coverage and activation energy for chemisorption (g $mg^{-1}$); $q_{(t)}$ - is the adsorption capacity defined as the mass of the adsorbed metal per unit mass of the adsorbent (mg $g^{-1}$) at time $t$.

The Langmuir model can be expressed as:[1]

$$q_e = \frac{q_m K_L C_e}{1+K_l C_e} \quad \text{(S-7)}$$

where $C_e$ - is the equilibrium concentration of metal ions (mg $dm^{-3}$); $q_e$ - is the equilibrium adsorption capacity (mg $g^{-1}$); $q_m$ - is the maximum adsorption capacity (mg $g^{-1}$); and $K_L$ - is the Langmuir equilibrium constant ($dm^3$ $g^{-1}$).

Linearizing the Eq. (S-7) the following is obtained:

$$C_e/q_e = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \quad \text{(S-8)}$$

This model can be expressed as:[1]

$$q_e = K_f C_e^{1/n} \quad \text{(S-9)}$$

where $C_e$ - is the equilibrium concentration of copper ions in the solution (mg $dm^{-3}$); $q_e$ - is the adsorbent capacity defined as mass of the adsorbed metal per unit mass of the adsorbent (mg $g^{-1}$) at equilibrium; $K_F$ - is the Freundlich equilibrium constant ((mg $g^{-1}$) ($dm^3$ $mg^{-1}$)$^{1/n}$); and $1/n$ -is the coefficient of heterogeneity in the Freundlich adsorption isotherm equation.

Linear form of Eq. (S-9) is:

$$log q_w = log K_f + \frac{1}{n} log C_e \quad \text{(S-10)}$$

The Temkin isotherm model is given as:

$$q_e = B ln(K_T C_e) \quad \text{(S-11)}$$

where: $B = RT/b$ - is the Temkin constant, which refers to the adsorption heat (J $mol^{-1}$); $b$ - is the variation of adsorption energy (J $mol^{-1}$); $R$ - is the universal gas constant (J $mol^{-1}$ $K^{-1}$); $T$- is the temperature (K); $K_T$ - is the Temkin equilibrium constant ($dm^3$ $g^{-1}$); $q_e$ - is the adsorption capacity (mg $g^{-1}$) at equilibrium; and $C_e$ - is the equilibrium concentration of metal ions in the solution (mg $dm^{-3}$).[1]

Linear form of Eq. (S-11) is:

$$q_e = B ln K_T + B ln C_e \quad \text{(S-12)}$$



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The correlation between the following independent variables: linear ($\beta_1$, $\beta_2$, $\beta_3$), quadratic ($\beta_{11}$, $\beta_{22}$, $\beta_{33}$), interaction terms ($\beta_{12}$, $\beta_{13}$, $\beta_{23}$), and the response ($Y$), was described by fitting the following polynomial equation:[4]

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1 X_1 + \beta_{22} X_2 X_2 + \beta_{33} X_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad \text{(S-13)}$$

The obtained results are displayed in Table VI. The biosorption of copper ions onto bean shells was expressed using the following equation:

$$Y = 31{,}76 + 6{,}88X_1 - 28{,}56X_2 - 1{,}46X_3 - 3{,}71X_1 \cdot X_1 + 10{,}42X_2 \cdot X_2 + \\ +0{,}69X_3 \cdot X_3 - 16{,}06X_1 \cdot X_2 + 6{,}40X_1 \cdot X_3 + 4{,}57X_2 \cdot X_3 \quad \text{(S-14)}$$

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