Supporting Information

Kinetics, Thermodynamics and Mechanism of Cu(II) Ion Sorption by Biogenic Iron Precipitate: Using the Lens of Wastewater Treatment to Diagnose a Typical Biohydrometallurgical Problem

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### Table S1. Elemental composition of iron precipitate residue before and after Cu(II) adsorption

| Element | Before adsorption (%) | After adsorption (%) |
|---------|-----------------------|----------------------|
| C       | 9.17                  | 24.80                |
| O       | 54.36                 | 40.20                |
| Mg      | 8.69                  | 5.17                 |
| Al      | 0.81                  | 0.57                 |
| Si      | 13.72                 | 9.08                 |
| S       | 4.83                  | 7.15                 |
| Cl      | 0.42                  | -                    |
| K       | 0.03                  | -                    |
| Ca      | 5.23                  | -                    |
| Fe      | 2.74                  | 7.68                 |
| Cu      | -                     | 5.35                 |
Table S2. Langmuir isotherm model correlations and separation factor ($R_L$) values for Cu(II) adsorption onto iron precipitate powder at the studied temperatures

| T (K) | $q_m$ (mg/g) | $b$ | $R^2$ | 150 mg/L | 300 mg/L | 400 mg/L | 500 mg/L |
|-------|--------------|-----|-------|----------|----------|----------|----------|
| 303   | 7.541        | 0.0082 | 0.996 | 0.450    | 0.290    | 0.234    | 0.197    |
| 313   | 9.091        | 0.0083 | 0.993 | 0.446    | 0.287    | 0.232    | 0.191    |
| 318   | 10.593       | 0.0074 | 0.967 | 0.474    | 0.310    | 0.252    | 0.213    |
| 323   | 11.086       | 0.0083 | 0.974 | 0.445    | 0.286    | 0.231    | 0.194    |
| 328   | 12.937       | 0.0079 | 0.965 | 0.457    | 0.296    | 0.240    | 0.202    |
Table S3. Freundlich isotherm model correlations for Cu(II) adsorption onto iron precipitate powder at the studied temperatures

| T (K) | Freundlich model |     |     |     |
|-------|------------------|-----|-----|-----|
|       | $K_f$            | $1/n_f$ | $n_f$ | $R^2$ |
| 303   | 0.549            | 0.397    | 2.518  | 0.999 |
| 313   | 0.570            | 0.426    | 2.346  | 0.985 |
| 318   | 0.632            | 0.428    | 2.336  | 0.991 |
| 323   | 0.701            | 0.425    | 2.351  | 0.990 |
| 328   | 0.730            | 0.444    | 2.254  | 0.991 |
**Figures**

![Graph showing pH\textsubscript{pzc} of iron precipitate powder.](image)

**Figure S1.** pH\textsubscript{pzc} of iron precipitate powder
Figure S2. Elovich model kinetic plots of Cu(II) adsorption onto iron precipitate powder at the studied initial Cu(II) concentrations
Texts

Text S1. Separation Factor ($R_L$) of Langmuir Isotherm

An important feature of the Langmuir isotherm which indicates the type of adsorption is expressed through a dimensionless constant termed separation factor ($R_L$), as shown in eq S1:

$$R_L = \frac{1}{1 + bC_0}$$  \hspace{1cm} (S1)

where $b$ is Langmuir constant and $C_0$ is initial Cu(II) concentration (mg/L).

Adsorption is unfavourable, linear, irreversible or favourable when $R_L > 1$, $R_L = 1$, $R_L = 0$ or $0 < R_L < 1$, respectively. The calculated $R_L$ values in this study ranged between 0 and 1 (Table S2), indicating that the adsorption system of Cu(II) ions onto iron precipitate powder is favourable.
Text S2. Heterogeneity Factor ($n_f$) of Freundlich Isotherm

The values of $n_f$ indicate the feasibility of the adsorption process. Adsorption is deemed easier when $2 < n_f < 10$, mildly difficult when $1 < n_f < 2$ and unfavourable when $n_f < 1$ \(^4\). Since $n_f > 2$ for all conditions covered in this study, it suggests that utilising iron precipitate powder as a sorbent of Cu(II) recovery is a technically favourable process. Also, the values of $1/n_f < 1$ signifies a more heterogeneous adsorption site and a feasible chemisorption process \(^5,6\).
Text S3. Arrhenius Expression

The relationship between $k$ and $T$ can be expressed in an Arrhenius form as follows:

$$k = 417.05 \exp(-23.57/8.314T)$$  \hspace{1cm} (S2)

The positive value obtained for the activation energy also implies that an increase in temperature favours the adsorption process. This further supported that the adsorption of Cu(II) ions onto iron precipitate powder is endothermic in nature.
Text S4. pH at Point of Zero Charge (pH\textsubscript{pzc}) Determination

The pH\textsubscript{pzc} experiments were carried out using the salt addition method. In different 250-mL Erlenmeyer flasks, 50 mL of 0.1 M NaNO\textsubscript{3} solutions were prepared, with initial pH (pH\textsubscript{i}) readings adjusted to an initial pH range between 2–11 (±0.1 pH unit), using either 0.1 N NaOH or 0.1 N HCl. Adsorbent samples of 0.2 g were then added to the flasks and were mixed at 150 rpm and 298 K for 48 h. On completion, the suspensions were centrifuged, and the final pH (pH\textsubscript{f}) measurement of the supernatants were determined. The pH\textsubscript{pzc} was determined from the plot of ΔpH (=pH\textsubscript{f} – pH\textsubscript{i}) versus pH\textsubscript{i} values. The pH\textsubscript{i} at which ΔpH is zero was taken to be the PZC.
Text S5. Adsorption Kinetics, Isotherms and Thermodynamics

Adsorption kinetics investigation was performed to evaluate the contact time needed to reach equilibrium. For the adsorption kinetic study, 1 g adsorbent was added to 50 mL working solutions of initial Cu(II) concentrations (150, 300, 400 and 500 mg/L) and subjected to 30 °C temperature, 150 rpm stirring speed and pH 5. Pseudo-first-order, pseudo-second-order and Elovich models were appraised for the process kinetic studies.

The adsorption isotherms were examined with the Langmuir and Freundlich models for initial Cu(II) concentrations (150, 300, 400 and 500 mg/L) and temperatures (30, 40, 45, 50 and 55 °C) using 1 g iron precipitate powder in a 50 mL working solutions of Cu(II) at 60 min contact time, 150 rpm shaking speed and pH 5.

Adsorption thermodynamic experiments were conducted under the same process conditions for the adsorption isotherms study. Thermodynamic parameters namely; standard enthalpy change (ΔH°), standard entropy change (ΔS°) and free energy change (ΔG°) were all studied.
SUPPORTING REFERENCES

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