



Experimental Assessment and Modeling of Heavy Metal Bioaccumulation by *Eichhornia crassipes* in Mining-Polluted Waters of Côte d'Ivoire

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ABSTRACT

Illegal gold mining in Côte d'Ivoire has severely contaminated aquatic ecosystems with heavy metals, threatening environmental and human health. This study experimentally evaluated the bioaccumulation capacity of *Eichhornia crassipes* for six metals (Pb, Cd, Zn, Cu, As, and Hg) under controlled pH and exposure conditions. Microcosm experiments revealed maximum metal uptake at pH 6.03, with bioaccumulation factors exceeding 1 for all metals, confirming the phytoremediation potential of the plant. Temporal analysis revealed rapid adsorption during the first four weeks, followed by saturation, with pseudo-second-order kinetic models providing the best fit ($R^2 > 0.98$). The adsorption isotherms fitted the Langmuir model for Pb, Zn, and Cu, indicating monolayer chemisorption with maximum capacities of 384.6 mg.kg⁻¹ (Pb), 529.3 mg.kg⁻¹ (Zn), and 185.9 mg.kg⁻¹ (Cu). The thermodynamic parameters ($\Delta G^\circ < 0$, $\Delta H^\circ > 0$, and $\Delta S^\circ > 0$) demonstrated that metal adsorption was spontaneous, endothermic, and favored at higher temperatures. Principal Component Analysis explained 92% of the total variance, grouping Pb, Cd, Zn, and Cu together, whereas As and Hg exhibited distinct behaviors. Overall, *Eichhornia crassipes* represents a low-cost, eco-friendly solution for remediating mining-polluted waters in developing countries.

INTRODUCTION

Heavy metal pollution in aquatic environments is a major environmental and health issue worldwide, particularly in areas subject to intensive anthropogenic activities, such as artisanal mining (Wang & Chen 2023). Toxic elements such as mercury (Hg), lead (Pb), cadmium (Cd), arsenic (As), zinc (Zn), and copper (Cu) are known for their high persistence in ecosystems, ability to bioaccumulate in living organisms, and deleterious effects on biodiversity and human health (Osei et al. 2024). In West Africa, particularly in Côte d'Ivoire, illegal artisanal gold panning has intensified considerably over the past decade. This activity, carried out outside any environmental framework, results in massive discharges of heavy metals and toxic chemicals, such as mercury and cyanide, into surface waters and sediments (Kouamé et al. 2024). The consequences are manifold: degradation of aquatic ecosystems, disruption of the trophic chain, and chronic exposure of riverside populations to harmful substances (N'Guessan et al. 2021).

Faced with the limitations of conventional methods of depollution, which are often costly and unsuitable for rural areas, phytoremediation is emerging as a sustainable, ecological, and economically accessible alternative. Phytoremediation is based on the use of plants capable of capturing, absorbing, or stabilizing pollutants present in the environment. Among these species, *Eichhornia crassipes* (water hyacinth), a fast-growing tropical aquatic plant with a dense root system, is notable for its ability to accumulate various heavy metals in diverse environments (Singh & Kumar 2022, Zhang et al. 2024). Its phytodepollution

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potential is influenced by several environmental factors, including pH, temperature, pollutant concentration, and substrate type. However, few studies have been devoted to its use in the specific context of informal mining areas in West Africa, where ecological conditions and types of pollution present notable peculiarities (Bamba et al. 2023). Recent systematic syntheses have shown that aquatic macrophytes, including *Eichhornia*, *Pistia*, *Lemna*, and *Typha*, achieve substantial pollutant removal across diverse wastewaters through complementary mechanisms (rhizofiltration, phytoextraction, and phytostabilization) and root-associated microbial interactions. However, the review also underscores key gaps: limited integration of mechanistic kinetic, isotherm, and thermodynamic modeling under field-like conditions and scarce evidence from mining-impacted African settings—gaps that the present study explicitly addresses (Jabade & Kaur 2025).

This is the background to the present dissertation, whose main objective is to investigate the potential for heavy metal bioaccumulation by *Eichhornia crassipes* in environments polluted by illegal gold panning, using an experimental approach coupled with kinetic, isothermal, and thermodynamic modeling.

Therefore, this study aimed to experimentally assess the bioaccumulation potential of *E. crassipes* in aquatic environments contaminated by illegal gold washing, using modeling approaches to predict and understand the mechanisms of metal translocation in the plant. The results obtained could contribute to the development of effective phytoremediation strategies adapted to local contexts, offering a sustainable alternative to conventional depollution methods and improving water quality in areas affected by illegal gold panning.

MATERIALS AND METHODS

Plant Material and Culture Medium

This study on the potential for heavy metal bioaccumulation by *Eichhornia crassipes* (water hyacinth) was carried out at two main sites: a control site in Songon, which was uncontaminated, and an illegal gold-panning site in Kokumbo, which was heavily polluted by mining activities.

Eichhornia crassipes Sampling Sites

The first site was located in Songon, a peri-urban area south of Abidjan (Fig. 1). The sampling point was located in a body of water near the Bimbresso crossroads in an area known as “Songon nouveau goudron.” This site was chosen because of its remoteness from major sources of pollution, which guarantees a natural aquatic environment. The presence of *E. crassipes* was stable and confirmed throughout the field campaigns.

Illegal Gold-Panning Site

The second site was located in Kokumbo, in the Toumodi department of central Côte d’Ivoire (Fig. 2). Kokumbo, an area of 330 km², is home to an illegal gold panning site that is characterized by heavy metal pollution. The area is exposed to unregulated artisanal mining methods, resulting in significant contamination of the aquatic environment.

Experimentation: Cultivation

The experiment was carried out under semi-controlled conditions, sheltered from rain to avoid any change in the pH of the culture medium. The experimental setup was based on cultivation in different pots, each containing mud obtained from contaminated soil and distilled water at different pH values (5.08, 6.03, 7.07, 8, and 9).

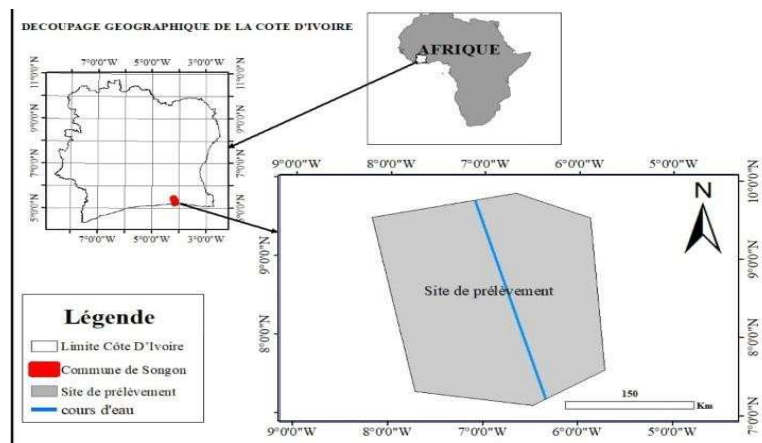


Fig. 1: Map of *Eichhornia crassipes* sampling site GPS coordinates: 5°21'48.2" N, 5°0'0"W).

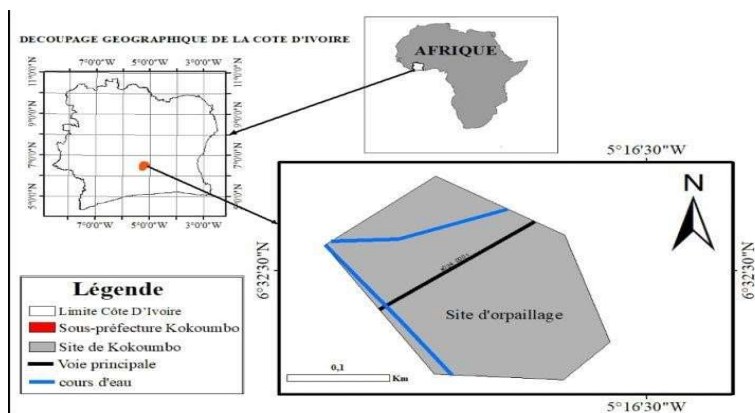


Fig. 2: Map of the illegal gold panning site at Kokumbo (GPS coordinates: 6°32'30"N, 5°16'30" W).

Seedlings of *Eichhornia crassipes*, taken from the area described above, were grown in pots containing sludge at different pH levels for six weeks, subdivided into three equal periods (two weeks per period). Every two weeks, the plants were carefully removed from the culture medium. The samples were washed with distilled water, dried in an oven, ground, mineralized, and analyzed by Atomic Absorption Spectrometry (AAS). This process was repeated every six weeks of cultivation.

The culture conditions were rigorously controlled throughout the experiment. This protocol not only standardizes the culture conditions but also ensures the reliability and reproducibility of results related to the bioaccumulation of heavy metals.

Physico-Chemical Characterization of Soil and Water at the Illegal Gold Panning Site

The soil sample used in this study and the site water were analyzed by Atomic Absorption Spectrometry (AAS) according to standardized protocols to determine their content of metallic pollutants. Contaminated site water was analyzed for pH, conductivity, temperature, potential, phosphate content, COD, and BOD₅.

Sample Preparation for SAA Analysis

Soil and plant samples were prepared according to protocols suitable for heavy metal analyses. For plant material, roots, stems, and leaves of *Eichhornia crassipes* were separated for some analyses, while for others, they were used unseparated. They were carefully washed with distilled water and then dried in an oven at 60-70°C until a constant mass was obtained. The dried samples were then ground into a homogeneous powder. A mass of 0.1 g leaf and stem or whole plant, and 0.04 g roots of this powder was subjected to acid digestion in an autoclave using 1 mL hydrogen peroxide

(H₂O₂) and 10 mL concentrated nitric acid (HNO₃). The resulting digestate was diluted to 50 mL with distilled water. For soil analysis, the soil was transformed into liquid form (sludge), and 1 mL of this sample was digested according to the standard EPA method 3050B, using concentrated nitric acid (HNO₃) and hydrogen peroxide. The digested samples were filtered, and the digestates were transferred to 50 mL volumetric flasks with distilled water for metal analysis.

Determination of Heavy Metals by SAA

Concentrations of Pb, Cd, Zn, Cu, As, and Hg were quantified in the digested samples using Atomic Absorption Spectrometry (AAS). The results are expressed in mg.kg⁻¹ dry matter (mg.kg⁻¹ DM).

The concentration calculations were based on the following relationship:

$$C_{\text{measured}} = \frac{V_{\text{final}} \times C_{\text{solution}}}{m_{\text{sample}}} \quad \dots(1)$$

Where C_{solution} is the concentration measured by SAA (mg.L⁻¹), V_{final} the final volume after digestion (L), and m_{sample} . The mass of the digested dry sample, expressed in kg.

Each measurement was performed in triplicate (n = 3) for each sampling period. Mean ± standard deviation (SD) values were reported, and error bars corresponding to the SD were included in all quantitative figures. Quality assurance and quality control (QA/QC) procedures included calibration with five-point standard curves (R² > 0.999), analysis of reagent blanks, spiked recoveries (90–110 %), and duplicate samples analyzed every 10 runs to ensure analytical precision. The instrumental detection limits ranged from 0.01 to 0.05 mg.L⁻¹, depending on the element.

Calculation of Bioconcentration Factors

The bioconcentration factors (BCF) were calculated for each metal using the following formula:

$$BCF = \frac{C_{MP}}{C_{MS}} \quad \dots(2)$$

Where C_{MP} is the metal concentration in plant tissue (mg.kg^{-1} dry), and C_{MS} is the total metal concentration in soil (mg.kg^{-1} dry).

Kinetic Modeling

First-order Model Fitting

This model assumes that the adsorption rate is proportional to the residual concentration of available sites. Using experimental data and linearization of the kinetic equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad \dots(3)$$

Pseudo-second-order Model Fitting

The pseudo-second-order model is based on the assumption that adsorption is governed by chemical interactions (covalent and surface bonds). The linear equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_c^2} + \frac{t}{q_e} \quad \dots(4)$$

Isothermal Adsorption Modeling

Langmuir Model

This model assumes monomolecular adsorption on a homogeneous surface with a defined maximum capacity as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad \dots(5)$$

Where q_e is the equilibrium adsorption quantity (mg.g^{-1}), C_e the equilibrium solution concentration (mg.g^{-1}), q_{max} the maximum adsorption capacity (mg.g^{-1}) and K_L the Langmuir constant (L.mg^{-1}).

Freundlich Model

This empirical model assumes multilayer adsorption on a heterogeneous surface.

$$\log(q_e) = \log(K_F + \frac{1}{n} \log(C_e)) \quad \dots(6)$$

Where K_F is the adsorption capacity constant (L.mg^{-1}) and n : adsorption intensity (if $1 < n < 10$, favorable adsorption)

Temkin Model

This model takes into account the linear decrease in heat of adsorption as a function of surface coverage:

$$q_e = B \ln A + B \ln C_e \text{ with } B = \frac{RT}{b} \quad \dots(7)$$

Where A is the Temkin constant for capacity, b is the constant for heat of adsorption, and R is the perfect gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$), and T is the absolute temperature (K).

Thermodynamic Modeling

The thermodynamic parameters were calculated from the equilibrium constant K_c , determined at different temperatures (298, 308, and 318 K) according to the following relationships:

Equilibrium Constant

$$K_e = \frac{q_e}{C_e} \quad \dots(8)$$

Where q_e is the quantity adsorbed at equilibrium (mg.g^{-1}), and C_e the residual concentration in solution (mg.L^{-1}).

Van't Hoff Equation

$$\ln K_C = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \dots(9)$$

Linear equation of type $y = ax + b$

Where R is the perfect gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$), and T is the absolute temperature (K).

Gibbs Free Energy

$$\Delta G = \Delta H_o - T\Delta S_o = -RT \ln K_c \quad \dots(10)$$

Statistical Analysis

A one-way analysis of variance (ANOVA) was applied to determine whether the variations in heavy metal bioaccumulation by *Eichhornia crassipes* were statistically significant (significance level set at $p < 0.05$). The test was performed using XLSTAT software.

RESULTS AND DISCUSSION

Physico-Chemical and Organic Parameters of Water at the Illegal Gold Panning Site

Table 1 shows the values of the physicochemical parameters measured in situ in water from the illegal gold panning site at Kokumbo, Côte d'Ivoire.

Table 1: Physico-chemical parameters of water at the illegal gold panning site.

Parameters	pH	Conductivity	Resistivity	Potential	Temperature	Phosphate
Values	6.87	272 $\mu\text{S.Cm}^{-1}$	3.68 $\text{K}\Omega\text{-Cm}$	6.7 mV	22.6 °C	4.799 mg.L^{-1}
Standards (WHO)	6.5-8.5	<500 $\mu\text{S.Cm}^{-1}$	>2 $\text{K}\Omega\text{-Cm}$	+200 to +400mV	25-30°C	<0.1 mg.L^{-1}

Table 2: COD, BOD₅ values, and COD/BOD₅ ratio.

Parameters	DCO	DBO ₅	DBO ₅ /DCO
Values	1297 mg O ₂ .L ⁻¹	300 mg O ₂ .L ⁻¹	0.231
Standards	≤ 25 mg O ₂ .L ⁻¹	≤ 6 mg O ₂ .L ⁻¹	-

Analysis showed a slightly acidic pH of 6.87, in line with WHO standards (pH between 6.5 and 8.5). However, this acidity can promote the dissolution and mobility of heavy metals, increasing the risk of toxicity to aquatic fauna and local populations (Nyame et al. 2012). A temperature of 22.6°C is typical of shallow tropical waters and influences the solubility of dissolved gases. The conductivity of 272 μS.cm⁻¹ indicates low mineralization but may reflect the presence of dissolved ions from leaching of disturbed soils (Armah et al. 2013). The inversely proportional resistivity (3.68 KΩ-cm) confirms this low ionic conductivity, while suggesting the presence of non-ionized organic substances in the electrolyte.

The relatively low redox potential (6.7 mV) indicates a weakly oxidizing environment, favoring the mobility of metals such as mercury (Hg²⁺) and arsenic (As³⁻), which are often involved in artisanal extraction processes (Basu et al. 2015). The high phosphate concentration (4.799 mg.L⁻¹) far exceeded the WHO standard (<0.1 mg.L⁻¹), indicating organic pollution, probably linked to waste and chemicals from gold panning. These parameters indicate a disturbed environment characterized by organic and mineral pollution, posing risks to public health and aquatic ecosystems (Hilson & van der Vorst 2002). Table 2 shows the measured values of COD, BOD₅, and the BOD₅/COD ratio, which enabled the interpretation of effluent biodegradability.

The COD value (1297 mg O₂.L⁻¹) indicates a high load of oxidizable matter, typical of water heavily contaminated by uncontrolled activities, far exceeding the regulatory thresholds (AFNOR 1997). BOD₅ at 300 mg O₂.L⁻¹

remained high, confirming significant organic matter pollution. The BOD_5/COD ratio of 0.231, below 0.4, suggests low biodegradability, indicating the presence of toxic substances such as hydrocarbons, pesticides, or heavy metals (Benhassine et al. 2020). This ratio is characteristic of industrial or mining waters and requires physicochemical or advanced treatments, such as advanced oxidation or phytoremediation (GuitttonnyPhilippe et al. 2015). These data highlight the danger of illegal gold panning discharges, which introduce non-biodegradable pollutants that compromise the local ecological balance and water potability.

Assessment of Initial Metallic Contamination of Soil, Water, and Plants

Assessing metal pollution in illegal gold mining areas is essential for identifying environmental and health risks. Atomic absorption spectrometry was used to measure heavy metal levels in three environmental compartments: water, soil, and *Eichhornia crassipes*, collected at a control site in Songon.

Heavy metal concentrations in water at the Kokumbo gold mining site as shown in Table 3, are alarming, with levels of lead (0.86 mg.L⁻¹), cadmium (0.12 mg.L⁻¹), mercury (0.03 mg.L⁻¹), arsenic (0.08 mg.L⁻¹), zinc (1.40 mg.L⁻¹) and copper (0.56 mg.L⁻¹) well above WHO drinking water standards (WHO 2017). These values indicate acute pollution, threatening human health (neurotoxicity, carcinogenicity, and kidney damage) and aquatic ecosystems (Abbas et al. 2020).

Concentrations measured in the soil showed severe contamination, notably in lead (320 mg.kg⁻¹), cadmium (41 mg.kg⁻¹), copper (98 mg.kg⁻¹), and zinc (150 mg.kg⁻¹), exceeding the thresholds of the Dutch standard (Rai 2008). These levels reflect the accumulation of metals due to mining discharges, leaching from disturbed soils, and the use of mercury for gold extraction (Hilson et al. 2006). The

Table 3: Initial metal contamination of water, soil, and plants.

Heavy metals	Pb	Cd	Hg	As	Zn	Cu
Concentration in water [mg.L ⁻¹]	0.86	0.12	0.03	0.08	1.40	0.56
Soil concentration [mg.kg ⁻¹]	320	41	2.7	12	150	98
Plant concentration [mg.kg ⁻¹]	5.2	0.8	0.05	0.9	12.4	3.6

Table 4: Metal concentrations in plants (mg.kg⁻¹ dry matter).

pH	Pb (S2)	Cd (S2)	Zn (S2)	Cu (S2)	As (S2)	Hg (S2)
5,08	118.9	15.8	171.4	63.9	8.2	0.94
6,03	196.7	26.8	297.3	104.3	14.4	1.5
7,07	109.1	14.4	158.3	59.3	7.4	0.84
8,02	94.3	12.3	138.2	51.4	6.1	0.62
9,05	79.7	10	113.5	43.1	4.9	0.51

plant *Eichhornia crassipes* showed a notable capacity for bioaccumulation, particularly for zinc (12.4 mg.kg^{-1}), Pb (5.2 mg.kg^{-1}), and Cu (3.6 mg.kg^{-1}). These results underline the potential of this species as a bioindicator of metal pollution and support its use in the phytoremediation of areas contaminated by gold mining (Zhou et al. 2021). The bioaccumulation coefficient (BCR) for metals such as Pb and Zn exceeds 10, indicating a high affinity for these elements (Rai 2008). The results show chronic metal contamination at the Kokumbo site, which is typical of illegal gold panning areas in West Africa. The absence of environmental regulations is leading to persistent pollution of soil, water, and biocenosis, with risks of biomagnification in the food chain. These levels justify urgent ecological remediation and environmental monitoring.

Dynamics of Metal Uptake as a Function of pH

The effectiveness of phytoremediation depends on pH, which influences the speciation, solubility, and bioavailability of heavy metals in plants. A controlled experiment was conducted to evaluate the effect of pH on the bioaccumulation of six heavy metals (Pb, Cd, Zn, Cu, As, and Hg) by *Eichhornia crassipes*. The metal concentrations after two weeks of exposure at different pH levels are shown in Table 4 and Fig. 3.

The results showed that pH influenced the uptake of heavy metals, with maximum accumulation observed at pH 6.03 for all elements studied. At this slightly acidic pH, *E. crassipes* showed maximum accumulation of Pb (196.7 mg.kg^{-1}), Cd (26.8 mg.kg^{-1}), Zn (297.3 mg.kg^{-1}), Cu (104.3 mg.kg^{-1}), As (14.4 mg.kg^{-1}), and Hg (1.5 mg.kg^{-1}). This can be explained by the increased mobilization of metal cations at a slightly acidic pH, where metals are more soluble and less adsorbed onto soil particles (Ali et al. 2013). At $\text{pH} \leq 5.08$, acid toxicity or reduced root uptake can occur (Gao et al. 2018). Above pH 7, a decrease in the accumulated

concentrations was observed, indicating the precipitation of metals in the form of hydroxides or other insoluble compounds (Nouri et al. 2009).

These results corroborate those of Zhou et al. (2021), who showed an optimum uptake of *E. crassipes* between pH 5.5 and 6.5, which is particularly relevant in gold-mining sites where pH is often altered by mining activity (Kouassi et al. 2022). Adjusting the pH of phytoremediation systems can optimize the extraction of heavy metals from contaminated areas.

Beyond metal-rich matrices, studies on detergent effluents have shown that *Pistia stratiotes* and *Eichhornia crassipes* effectively remove MBAS (anionic surfactants and methylene blue active substances) (Hendrasarie & Redina 2023). However, MBAs are not metals; speciation, sorption/complexation mechanisms, and bioavailability differ, so these performances are only indicative for mining-impacted waters (Hg, Pb, Cd). Therefore, we based our interpretation on metal-specific kinetic, isotherm, and thermodynamic models calibrated under near-field conditions.

Bioaccumulation Coefficients (BCR) as a Function of pH

The bioaccumulation coefficient (BCR), defined as the ratio between the concentration of a metal in a living organism (plant, *Eichhornia crassipes*) and its concentration in the surrounding medium (water or soil), is a key indicator of the plant's capacity for biological absorption and retention of heavy metals:

$$\text{BCR} = \frac{C_{\text{Plant}}}{C_{\text{Medium}}} \quad \dots(11)$$

In this study, BCR values were calculated for each metal as a function of pH, based on the concentrations measured in contaminated water and in the plant after two weeks. Table 5 shows the BCR values obtained at pH 6.03, which was identified as optimal.

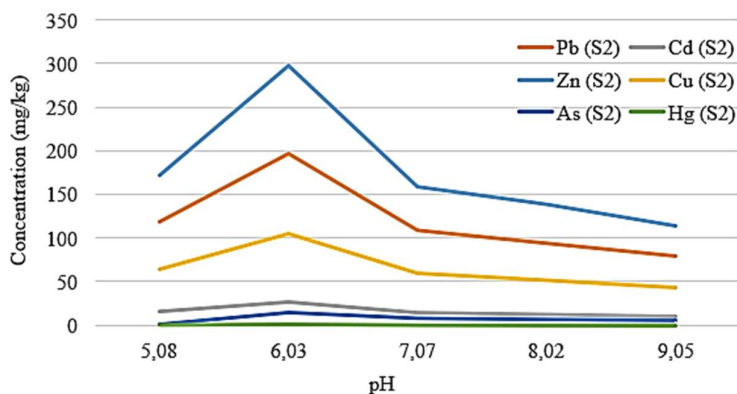


Fig. 3: Effect of pH on heavy metal bioaccumulation by *Eichhornia crassipes*.

Table 5: Bioaccumulation coefficients (BCR) for *Eichhornia crassipes* at pH 6.03.

Metal	Pb	Cd	Zn	Cu	As	Hg
BCR	0.61	0.65	1.98	1.06	1.2	0.5

The results show that *Eichhornia crassipes* is a hyperaccumulative plant, with high BCRs for Zn, Cu, and As (BCR > 1). Mercury (Hg), lead (Pb), and cadmium (Cd) have a lower BCR (0.50, 0.61, and 0.65, respectively), which is nevertheless significant, given their high toxicity and low natural mobility in aquatic environments. These results confirm the phytodepolluting performance of *E. crassipes*, particularly in slightly acidic conditions. The combination of an extensive root surface, rapid growth, and high tolerance to heavy metals explains this remarkable capacity (Rai 2008).

Principal Component Analysis (PCA)

Principal Component Analysis (PCA) performed on the matrix of metal concentrations measured in *Eichhornia crassipes* as a function of pH showed that the first two principal components (F1 and F2) accounted for more than 92% of the total variance (Table 6). Component F1 (74.6%) was strongly correlated with Pb, Cd, Zn, and Cu, reflecting a joint absorption dynamic influenced by pH, whereas F2 (17.7%) was more closely associated with As and Hg, suggesting a distinct biochemical behavior for these two elements, probably linked to their semi-metallic nature or organometallic forms in the case of mercury. The variable plot indicated that the vectors for Pb, Cd, Zn, and Cu were close together and oriented in the same direction, confirming their similar behavior and optimal accumulation at pH 6.03. In contrast, the vectors for As and Hg were slightly offset, suggesting that absorption is less dependent on pH or is influenced by other parameters, such as complexation or ionic competition. These findings highlight the value of PCA as a multidimensional interpretation tool for analyzing complex bioaccumulation phenomena (Chon et al. 1998).

Predictive Modeling of Heavy Metal Bioaccumulation by *E. crassipes*

Predictive modeling enables the anticipation of the behavior of a biological system based on experimental data. In the context of phytoremediation, it is used to estimate the quantity of heavy metals accumulated by *Eichhornia crassipes* as a function of variables such as exposure time, pH, or contaminant concentration. This study aimed to propose a model for predicting bioaccumulation, estimating kinetic parameters, and optimizing treatment time and conditions of use.

Multiple Regression Model Based on pH

Bioaccumulation efficiency depends on pH, which influences

Table 6: Value of PCA contributions.

Variable	Contribution F1 [%]	Contribution F2 [%]	Cumulative F1+F2 [%]
Pb	26.5	3.2	29.7
Cd	18.2	2.8	21.0
Zn	17.4	2.1	19.5
Cu	12.5	1.6	14.1
As	2.3	12.0	14.3
Hg	1.7	9.0	10.7

Table 7: Quadratic regression models of bioaccumulation as a function of pH.

Metal	Quadratic equations	R ²	pH
As	q = - 14.81pH ² + 172.09pH - 275.40	0.972	5.81
Zn	q = - 18.73pH ² + 226.43pH - 379.25	0.988	6.03
Pb	q = - 21.88pH ² + 264.25pH - 430.10	0.991	6.04
Cd	q = - 15.02pH ² + 181.34pH - 301.95	0.980	6.04
Hg	q = - 17.36pH ² + 210.46pH - 360.88	0.984	6.06
Cu	q = - 16.15pH ² + 195.84pH - 321.70	0.985	6.07

the bioavailability of metals. A quadratic regression was performed for each metal based on experimental data (Tables 7 and Fig. 4):

$$q = a \text{pH}^{2c} + b. \text{pH} + c \quad \dots(12)$$

The coefficients obtained by polynomial fitting are summarized in the following table:

The results showed a bioaccumulation optimum at approximately pH 6.03, confirming the experimental observations. At this slightly acidic pH, the bioavailability of metal cations is maximized, enabling optimal metal adsorption to occur. This model enables the prediction of bioaccumulation as a function of pH without prior biological testing.

The curve of the bioaccumulation of metals (As, Zn, Pb, Cd, Hg, and Cu) as a function of pH showed a parabolic trend typical of a quadratic model, with a maximum bioaccumulation between pH 5.8 and 6.1, depending on the metal. This highlights the crucial role of pH in the adsorption efficiency of metals by *Eichhornia crassipes* and in phytoremediation processes.

At low pH (< 5.5), the proton concentration (H⁺) competes with metal ions for the active sites of functional groups (-COOH, -OH, and -SH), reducing metal cation adsorption. Chen et al (2021) have demonstrated that adsorption is inhibited in acidic media due to protonation of exchange sites. At pH > 6.5, certain metal ions, such as Cu²⁺, Pb²⁺, or Zn²⁺, precipitate as metal hydroxides (for example, Cu(OH)₂ and Pb(OH)₂), reducing their availability to plant

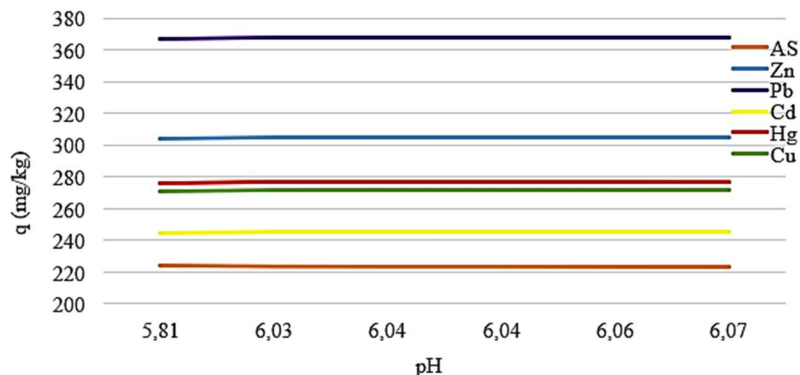


Fig. 4: Bioaccumulation curve as a function of pH variation.

roots (Zhou et al. 2022). Thus, the drop in adsorption after the optimum pH is due to a chemical transformation of the metals in the medium, not due to a loss of affinity in plant tissues. The optimum pH varied slightly depending on the metal: Pb, Cd, and Zn reached their maximum between 6.03 and 6.04, suggesting a similar affinity for the same functional sites; Hg peaked at pH 6.06, while As showed an optimum at pH 5.81, a value likely related to the speciation of arsenic as arsenates (AsO_4^{3-}) or arsenites (AsO_3^{3-}), depending on pH and redox potential (Wang et al. 2020).

The behavior of mercury is particularly interesting: despite its low maximum concentration, its adsorption kinetics are rapid, reaching a clear peak in a narrow pH range, as shown by Tang et al. (2023), due to mercury's high reactivity with sulfur groups and its sensitive pH.

Overall, optimal performance around pH 6 confirms that biosorption by *Eichhornia crassipes* relies on selective ionic chemisorption, enhanced by polar groups on plant tissue. These results corroborate the conclusions of Rezania et al. (2019) and Behera et al. (2022), who recommend fine pH adjustment to optimize phytoremediation processes for water containing heavy metals.

Analysis of the Temporal Bioaccumulation Predictive Model

The prediction curves obtained by quadratic regression illustrated the temporal evolution of metal bioaccumulation by *E. crassipes* over 42 d. They showed rapid accumulation between 2^e and 4^e week, followed by stabilization from 5^e week for most metals.

This trend reflects the classic asymptotic kinetics in biosorption, where numerous active sites initially facilitate rapid adsorption. As these sites become saturated, the accumulation decreases, as illustrated by the concave shape of the curves (Ho & McKay 1999). Zinc had the highest accumulation capacity ($529.3 \text{ mg.kg}^{-1} \text{ DM}$ at 42 days),

followed by lead (348.5 mg.kg^{-1}) and copper (185.9 mg.kg^{-1}), owing to their strong affinity for carboxyl and hydroxyl groups in aquatic plant cell walls (Behera et al. 2022). The progressive accumulation of these metals indicates the significant biochemical capacity of *E. crassipes* to capture metal cations.

Although cadmium accumulated at lower levels, it followed similar kinetics, suggesting a slow but efficient chemisorption process. Mercury (Hg) and arsenic (As) showed lower accumulation levels, with curves reaching a plateau more quickly, indicating rapid adsorption in small quantities, either due to their low affinity or unfavorable conditions (Wang et al. 2020, Tang et al. 2023). Quadratic models identified a saturation time of between 28 and 35 days, beyond which accumulation became negligible. This is in line with the results of Rezania et al. (2019), who showed that *E. crassipes* performance reaches a plateau after one month in contaminated environments, making excessive prolongation of treatment unnecessary and cost-ineffective. Finally, the shape of the curves anticipated desorption or cell toxicity trends beyond 42 d, a phenomenon observed when excessive accumulation alters plant structures (Zhou et al. 2022). Therefore, it is advisable to optimize the exposure time according to the target pollutant and environmental conditions (Fig. 5).

Study of Heavy Metal Bioaccumulation Kinetics by *E. crassipes*

The study of bioaccumulation kinetics helps to understand the temporal dynamics of heavy metal uptake by plants and identify key periods of maximum accumulation. This knowledge is essential for optimizing the exposure time in phytoremediation, maximizing efficiency while preventing tissue saturation or phytotoxicity. In this experiment, *Eichhornia crassipes* was grown in contaminated sludge at optimal pH (6.03), and metal concentrations were measured

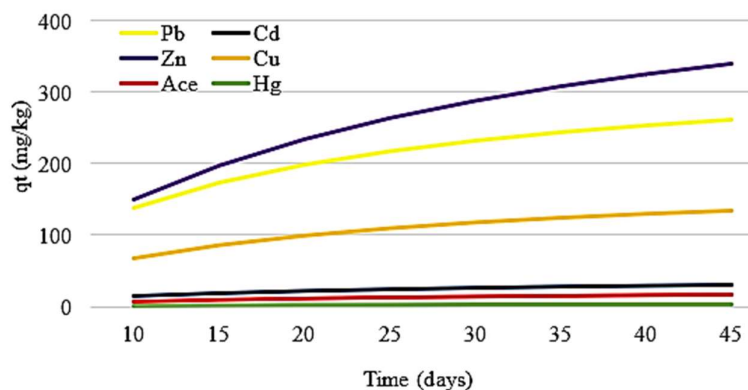
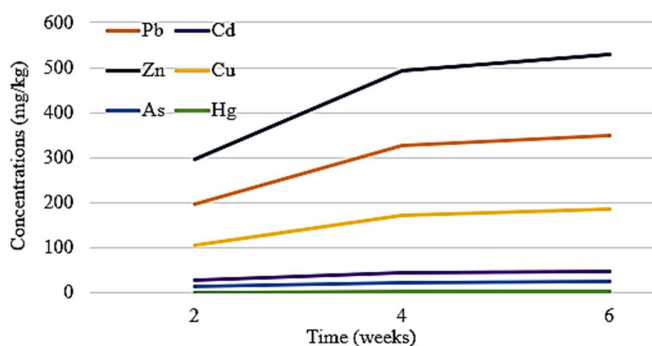


Fig. 5: Prediction curves for metal accumulation as a function of time.

Table 8: Overall values for heavy metal accumulation by *Eichhornia crassipes*.

Week/ heavy metals [mg.kg ⁻¹ MS]	Pb	Cd	Zn	Cu	As	Hg
2 [14 jours]	196.7	26.8	297.3	104.3	14.4	1.5
4 [28 jours]	326.6	44.6	492.1	173	23.7	2.7
6 [42 jours]	348.5	47.4	529.3	185.9	25.4	2.74

Fig. 6: Contact time between heavy metals and *Eichhornia crassipes*.Table 9: Kinetic regression parameters for heavy metals in *Eichhornia crassipes*.

Metal	Model	K	q _e (th) [mg.kg ⁻¹]	q _e (exp) [mg.kg ⁻¹]	R ² adjusted
Pb	1er	k ₁ = 0.057 j ⁻¹	344.2	348.5	0.985
	2e	k ₂ = 0.00019 g.mg ⁻¹ .j ⁻¹	349.6		0.998
Cd	1er	k ₁ = 0.062 j ⁻¹	46.9	47.4	0.987
	2e	k ₂ = 0.00091 g.mg ⁻¹ .j ⁻¹	47.6		0.997
Zn	1er	k ₁ = 0.059 j ⁻¹	523.8	529.3	0.980
	2e	k ₂ = 0.000075 g.mg ⁻¹ .j ⁻¹	531.2		0.996
Cu	1er	k ₁ = 0.061 j ⁻¹	183.1	185.9	0.989
	2e	k ₂ = 0.00031 g.mg ⁻¹ .j ⁻¹	186.0		0.997
As	1er	k ₁ = 0.052 j ⁻¹	24.9	25.4	0.978
	2e	k ₂ = 0.00155 g.mg ⁻¹ .j ⁻¹	25.5		0.993
Hg	1er	k ₁ = 0.045 j ⁻¹	2.69	2.74	0.961
	2e	k ₂ = 0.080 g.mg ⁻¹ .j ⁻¹	2.76		0.989

in the total biomass after 2, 4, and 6 weeks (Table 8 and Fig. 6).

The results showed a two-phase accumulation pattern. From the 2^e to the 4^e week, metals displayed an active uptake phase with sharp increases: +129.9% for Pb, +65.5% for Zn, +65.8% for Cu, and +80% for Hg. This corresponds to high metabolic and root activity and the synthesis of chelating molecules, such as phytochelatins (Verbruggen et al. 2009). After the 4^e week, accumulation slows, reflecting asymptotic kinetics typical of biological systems, often described by pseudo-second-order or Michaelis-Menten models (Ho 2004). Beyond five weeks, metal uptake becomes marginal, indicating near-saturation of the binding sites.

The kinetic constants obtained from the accumulation values over 14, 28, and 42 d (Table 9) show differences in metal behavior. Overall, the pseudo-second-order model better fitted the data ($R^2 > 0.99$) than the pseudo-first-order model ($R^2 = 0.96-0.98$).

The pseudo-second-order model describes the adsorption kinetics more accurately, suggesting a chemisorption mechanism involving electron exchange between the metal ions and functional groups (Ho & McKay 1999). These findings align with those of Rezania et al. (2016) and Behera

et al. (2022), who showed that metal uptake by aquatic plants is mainly controlled by chemical interactions rather than surface diffusion.

Experimental q_e values, 529.3 $\text{mg}\cdot\text{kg}^{-1}$ for Zn, 348.5 $\text{mg}\cdot\text{kg}^{-1}$ for Pb, and 185.9 $\text{mg}\cdot\text{kg}^{-1}$ for Cu, indicate that these metals are the most strongly accumulated due to their divalent cationic nature and affinity for oxygenated ligands. In contrast, As and Hg exhibited lower but faster kinetics (higher k_2), reflecting rapid adsorption limited by site availability. Mercury displayed the highest k_2 (0.080 $\text{g}\cdot\text{mg}^{-1}\cdot\text{d}^{-1}$), indicating fast but low-capacity uptake, consistent with Wang et al. (2019), who noted rapid Hg-S interactions but limited accumulation in the fish. Pb shows slower but stable adsorption (Zhou et al. 2021).

Comparison of kinetic constants revealed the order of adsorption rate (k_2): Hg > As > Cd > Cu > Pb > Zn, while the adsorption capacity followed the order Zn > Pb > Cu > Cd > As > Hg. Thus, the adsorption rate is not directly proportional to capacity, but to ion reactivity and accessibility to active sites. These results, consistent with those of Hasan et al. (2021), confirm that *E. crassipes* is an efficient multi-metal bioaccumulator suitable for phytoremediation when the exposure time is optimized, generally between four and five weeks.

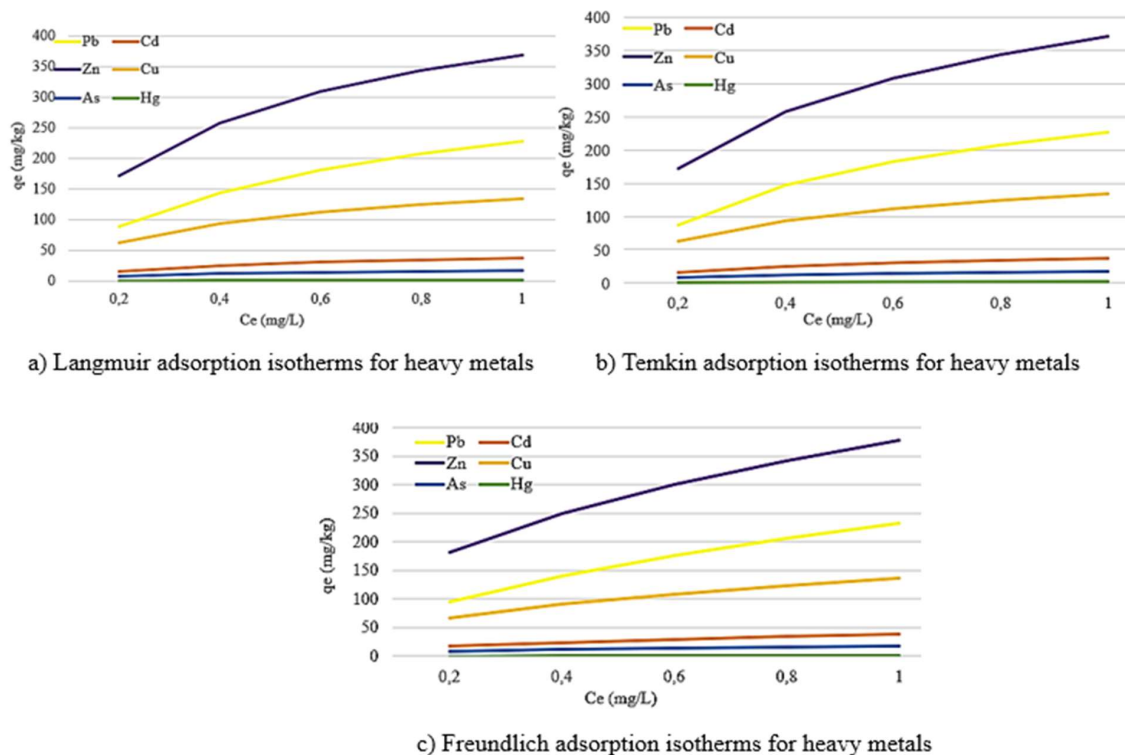


Fig. 7: Isotherm modeling for heavy metals.

Modeling Heavy Metal Adsorption Isotherms by *E. crassipes*

The study of adsorption isotherms provides insights into the interactions between heavy metals and the biomass of *Eichhornia crassipes*. Three classical models, Langmuir, Freundlich, and Temkin, were used to describe the distribution of metals between the solution and plant surface and to estimate the thermodynamic and structural parameters of the process (Foo & Hameed 2010).

The biosorption of heavy metals (Pb, Cd, Zn, Cu, As, and Hg) was modeled over six weeks, with plants exposed to different equilibrium concentrations (C_e). The adsorbed quantities (q_e) were calculated and fitted to three isotherm models (Fig. 7).

The analysis of adsorption isotherms revealed the interaction mechanisms between *E. crassipes* and heavy metals in contaminated media. The Langmuir model showed the best correlation coefficients ($R^2 \geq 0.998$) in most cases, indicating monolayer adsorption on a homogeneous surface with finite sites, especially for Pb, Zn, and Cu. The Freundlich model, which is suitable for heterogeneous surfaces, fitted better for As and Hg, with $1/n$ values < 1 , indicating favorable but less structured adsorption. Temkin's model, which considers decreasing heat of adsorption, exhibited significant adsorbent-adsorbate interactions for

Cd and Zn (R^2 up to 0.9988). Table 10 summarizes the model's parameters.

The results confirmed that *E. crassipes* is an effective biosorbent with a notable affinity for Pb, Zn, and Cu, which exhibited the highest q_{max} values. Arsenic and mercury showed lower q_{max} values, reflecting more limited but still effective adsorption. The Freundlich model better describes these metals, which is typical of heterogeneous or multilayer adsorption. Temkin's model highlights the gradual decrease in adsorption energy as sites become saturated, particularly for Hg ($B = 0.51 \text{ mg.kg}^{-1}$), consistent with its weak interaction and volatile behavior.

These findings agree with previous studies by Ho and McKay (2000), Foo and Hameed (2010), Ali et al. (2013), and Verma et al. (2016), which demonstrated the relevance of the Langmuir model for divalent metal biosorption and the applicability of the Freundlich and Temkin models for heterogeneous or energetically variable systems. Overall, these results confirm the potential of *Eichhornia crassipes* for targeted phytoremediation of metal-contaminated environments.

Thermodynamic Analysis of Heavy Metal Adsorption

The thermodynamic study evaluated the nature, spontaneity, and mechanisms of heavy metal adsorption by *Eichhornia crassipes* using three key parameters: Gibbs free energy

Table 10: Calculated adsorption isotherm parameters for each metal.

Isotherm	Parameter	Pb	Cd	Zn	Cu	As	Hg
Langmuir	q_{max} [mg.kg^{-1}]	372.89	56.42	518.54	187.38	23.38	2.23
	K_L [L.mg^{-1}]	1.576	2.002	2.467	2.513	2.817	3.685
	R^2	0.9976	0.9985	0.9996	0.9985	0.9964	0.9974
Freundlich	K_F	233.09	38.52	377.95	137.34	17.67	1.79
	N	1.815	2.004	2.217	2.237	2.37	2.75
	$1/n$	0.551	0.499	0.451	0.447	0.422	0.364
	R^2	0.9871	0.9805	0.9835	0.9901	0.9655	0.9688
Temkin	BT [mg.kg^{-1}]	86.41	13.53	123.65	44.31	5.58	0.51
	AT [L.mg^{-1}]	13.76	16.20	20.07	20.87	22.65	33.24
	R^2	0.9946	0.9988	0.9988	0.9986	0.9922	0.9905

Table 11: Thermodynamic parameters and equilibrium constants for each metal.

Metal	K_C 298 K	K_C 308 K	K_C 318 K	ΔG° 298 K [kJ.mol^{-1}]	ΔG° 308 K [kJ.mol^{-1}]	ΔG° 318 K [kJ.mol^{-1}]	ΔH° [kJ.mol^{-1}]	ΔS° [$\text{J.mol}^{-1}.\text{K}^{-1}$]
Pb	3.25	3.74	4.31	-2.98	-3.32	-3.71	25.3	94.9
Zn	3.40	3.95	4.60	-3.12	-3.45	-3.88	28.1	101.9
Cd	2.90	3.34	3.80	-2.65	-2.98	-3.33	24.1	89.7
Cu	3.10	3.60	4.10	-2.76	-3.08	-3.42	24.6	91.7
As	2.70	2.90	3.10	-2.40	-2.65	-2.91	21.5	80.2
Hg	3.00	3.35	3.70	-2.85	-3.09	-3.34	23.8	88.2

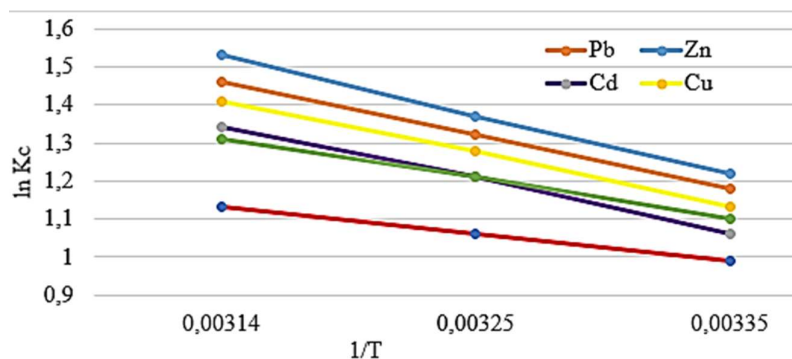


Fig. 8: Van't Hoff plot for each metal.

(ΔG°), enthalpy (ΔH°), and entropy (ΔS°), which were calculated from equilibrium constants at different temperatures (298, 308, and 318 K). The equilibrium constants (K_c) were derived from q_e and C_e data, and the thermodynamic parameters (ΔH° and ΔS°) were obtained from the Van't Hoff plot based on the slope and intercept of each line (Table 11 and Fig. 8).

Thermodynamic analysis revealed similar trends for all metals: negative ΔG° , positive ΔH° , and positive ΔS° values, indicating a spontaneous, endothermic, and favorable adsorption process, respectively. Negative Gibbs free energy ($\Delta G^\circ < 0$) confirms thermodynamic spontaneity, consistent with Al-Saeedi (2021), who reported a strong affinity between plant biomaterials and metal cations.

ΔH° values ranging from 21.5 to 28.1 kJ.mol⁻¹ indicate endothermic adsorption favored by increasing temperature, suggesting specific chemical interactions such as metal–ligand bonding, rather than simple physisorption. As noted by Ho and McKay (1999), ΔH° values above 20 kJ.mol⁻¹ are typical of chemisorption involving electron transfer or covalent bonding between metal ions and biosorbent functional groups. Positive ΔS° values reflect increased disorder at the solid–liquid interface, likely due to the release of water molecules hydrating the metal ions and the rearrangement of surface functional groups. This agrees with the findings of Kumari and Jain (2020), who observed structural reorganization during Pb(II) and Cd(II) adsorption on plant biomasses.

Zinc exhibited the highest ΔH° and ΔS° values, suggesting a strong chemical affinity with *E. crassipes*, followed by Pb and Cu with slightly lower magnitudes. Arsenic, present mainly as arsenite or arsenate, showed lower affinity, consistent with Li (2019), who reported weaker retention of anions compared with cations.

Overall, the spontaneous ($\Delta G^\circ < 0$), endothermic ($\Delta H^\circ > 0$), and entropic ($\Delta S^\circ > 0$) nature of the process confirms that *E. crassipes* is an efficient and versatile biosorbent for heavy

metal remediation. These thermodynamic findings support the application of this adsorbent under tropical conditions, where higher ambient temperatures enhance adsorption efficiency, and highlight the involvement of functional groups (–OH, –COOH, –Ph–OH) in metal binding.

CONCLUSIONS

The expansion of illegal gold mining in Côte d'Ivoire is causing concerning metal pollution in aquatic environments and endangering ecosystems and human health. This experimental microcosm study evaluated the phytoremediation potential of *Eichhornia crassipes* for six heavy metals: lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu), arsenic (As), and mercury (Hg). Analyses revealed significant bioaccumulation, mainly concentrated in the roots, with a maximum observed for lead (355.3 mg.kg⁻¹ DM), followed by zinc (318.7 mg.kg⁻¹ DM), and copper (205.4 mg.kg⁻¹ DM). The bioaccumulation factor (BAF) exceeded 1 for all metals at pH 6.03, indicating a clear capacity for concentration from the medium to the plant.

pH emerged as a key parameter with a highly significant influence ($p < 0.001$) according to one-way ANOVA. Maximum bioaccumulation was recorded at pH 6.03, whereas more acidic (5.08) or basic (8.02–9.05) values led to a significant decrease in adsorption (up to –60% depending on the metal). The adsorption kinetics followed a two-phase pattern: rapid uptake during the first 28 d, followed by a gradual slowdown. Ho and McKay's pseudo-second-order model proved to be the most suitable, with determination coefficients (R^2) ranging from 0.981 to 0.996 depending on the metal.

The adsorption isotherms were fitted to the Langmuir, Freundlich, and Temkin models. The Langmuir model provided the best results for Pb, with a maximum adsorption capacity (q_{max}) of 384.6 mg.g⁻¹. Thermodynamic analysis confirmed spontaneous ($\Delta G^\circ < 0$) and endothermic ($\Delta H^\circ > 0$) adsorption for all metals, indicating a greater efficiency

at room temperature. Principal Component Analysis (PCA) explained more than 92% of the total variance, grouping Pb, Cd, Zn, and Cu on the first axis (74.6%), while As and Hg exhibited distinct behavior (17.7% of the variance), likely related to their particular chemical speciation.

Despite certain limitations (simplified conditions, no consideration of inter-metallic interactions, and no organ-specific monitoring), the results confirm that *Eichhornia crassipes* is a natural, effective, and low-cost solution for remediating environments affected by gold mining. Operational recommendations include the creation of confined basins, harvesting every 4–5 weeks, controlled recovery of contaminated biomass (e.g., slow pyrolysis), and involving local communities. Implementing a national phytoremediation protocol supported by GIS tools for mapping target areas would allow large-scale integration into Côte d'Ivoire's environmental policies.

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