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Nature Environment & Pollution Technology

This is a peer-reviewed prepublished version of the paper to be published in Vol. 25, No. 2, June 2026 issue

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

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Key Words	*Eichhornia crassipes*, Heavy metals, Phytoremediation, Kinetic and thermodynamics modeling, Adsorption isotherms
DOI	https://doi.org/10.46488/NEPT.2026.v25i02.D1864 (DOI will be active only after the final publication of the paper)
Citation for the Paper	Nongbe, M.C., Kone, M., Diarra, M., Zamble, B.K.V., Naki, G.J., 2026. Experimental assessment and modeling of heavy metal bioaccumulation by *Eichhornia crassipes* in mining-polluted waters of Côte d'Ivoire. *Nature Environment and Pollution Technology*, 25(2), D1864. https://doi.org/10.46488/NEPT.2026.v25i02.D1864

Abstract

Illegal gold mining in Côte d'Ivoire has led to severe contamination of 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, 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 plant's phytoremediation potential. Temporal analysis showed rapid adsorption during the first four weeks, followed by saturation, with pseudo-second-order kinetic models providing the best fit ($R^2 > 0.98$). Adsorption isotherms fitted the Langmuir model for Pb, Zn, and Cu, indicating monolayer chemisorption with maximum capacities of 384.6 mg/kg (Pb), 529.3 mg/kg (Zn), and 185.9 mg/kg (Cu). Thermodynamic parameters ($\Delta G° < 0$; $\Delta H° > 0$; $\Delta S° > 0$) demonstrated that metal adsorption was spontaneous, endothermic, and favored at higher temperatures. Principal Component Analysis explained 92% of total variance, grouping Pb, Cd, Zn, and Cu together, while As and Hg exhibited distinct behavior. Overall, *Eichhornia crassipes* represents a low-cost, eco-friendly solution for remediating mining-polluted waters in developing countries.

1. Introduction

Heavy metal pollution of 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) or copper (Cu) are known for their high persistence in ecosystems, their ability to bioaccumulate in living organisms, and their deleterious effects on biodiversity and human health (Osei et al., 2024). In West Africa, and more particularly in Côte d'Ivoire, illegal artisanal gold panning has intensified considerably over the past decade. This activity, carried out on 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. It 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, stands out for its ability to accumulate various heavy metals in a variety of environments (Singh & Kumar, 2022; Zhang et al., 2024). Its phytodepolluting potential is influenced by a number of 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 synthesis shows that aquatic macrophytes—including *Eichhornia*, *Pistia*, *Lemna* and *Typha*—achieve substantial pollutant removal across diverse wastewaters through complementary mechanisms (rhizofiltration, phytoextraction, phytostabilization) and root-associated microbial interactions. However, the review also underscores key gaps: limited integration of mechanistic kinetic, isotherm, thermodynamic modelling 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 modelling.

This study therefore aims 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, while offering a sustainable alternative to conventional depollution methods and improving water quality in areas affected by illegal gold panning.

2. Materials and methods

2.1. 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, uncontaminated, and an illegal gold-panning site in Kokumbo, heavily polluted by mining activities.

2.1.1. *Eichhornia crassipes* sampling site

The first site is located in Songon, a peri-urban area south of Abidjan. The sampling point is 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, guaranteeing a natural aquatic environment. The presence of *E. crassipes* is stable, confirmed throughout the field campaigns.

GPS coordinates: 5°21'48.2 "N; 5°0'0 "W.

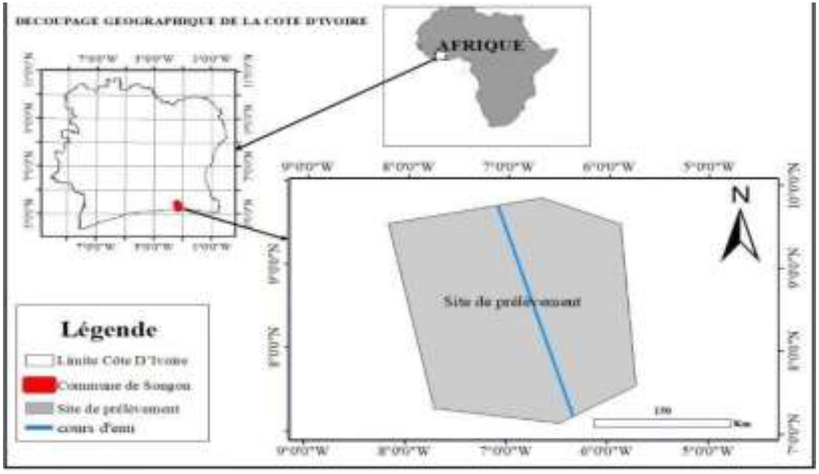


Figure 1. Map of *Eichhornia crassipes* sampling site

2.1.2. Illegal gold-panning site

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

GPS coordinates: 6°32'30 "N; 5°16'30 "W.

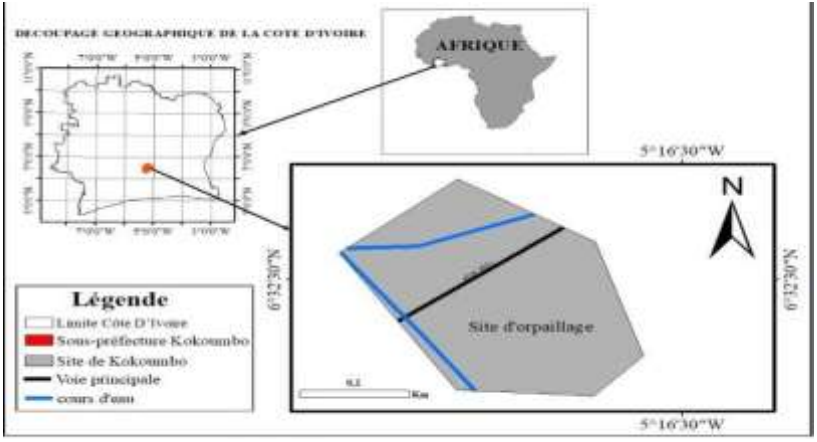


Figure 2. Map of the illegal gold panning site at Kokumbo

2.2 Experimentation: Cultivation

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

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

Culture conditions were rigorously controlled throughout the experiment. This protocol not only standardized their culture conditions, but also ensured the reliability and reproducibility of results relating to the bioaccumulation of heavy metals.

2.3 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 BOD_5.

2.4 Sample preparation for SAA analysis

Soil and plant samples were prepared according to protocols suitable for heavy metal analysis. 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, then dried in an oven at 60-70°C until a constant mass was obtained. The dried samples were then ground to 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 (H_2O_2) and 10 mL concentrated nitric acid (HNO_3). The resulting digestate was made up 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 standard EPA method 3050B, using concentrated nitric acid (HNO_3) and Hydrogen peroxide. The digested samples were filtered, then the digestates were transferred to 50 mL volumetric flasks with distilled water, for metal analyses.

2.5 Determination of heavy metals by SAA

Concentrations of Pb, Cd, Zn Cu, As and Hg were quantified in digested samples using Atomic Absorption Spectrometry (AAS). Results were expressed in mg/kg dry matter (mg/kg DM). Concentration calculations are based on the following relationship:

$$\mathrm{C_{measured}} = \frac{\mathrm{V_{final}} \times \mathrm{C_{solution}}}{\mathrm{m_{sample}}} \qquad (1)$$

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

Each measurement was performed in triplicate ($n = 3$) for every sampling period. Mean ± standard deviation (SD) values were reported, and error bars corresponding to SD were included in all quantitative figures. Quality assurance and quality control (QA/QC) procedures included calibration with five-point standard curves ($R^2 > 0.999$), analysis of reagent blanks, spiked recoveries (90–110 %), and duplicate samples analyzed every 10 runs to ensure analytical precision. Instrumental detection limits ranged from 0.01 to 0.05 mg L^{-1} depending on the element.

2.6. Calculation of bioconcentration factors

Bioconcentration factors (BCF) were calculated for each metal according to the formula:

$$\mathrm{BCF} = \frac{\mathrm{C_{MP}}}{\mathrm{C_{MS}}} \qquad (2)$$

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

2.7. Kinetic modeling

- First-order model fitting

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

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

- Pseudo-second-order model fitting

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

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

2.8. Isothermal adsorption modeling

- Langmuir model

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

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

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

- Freundlich model

This empirical model assumes multilayer adsorption on a heterogeneous surface:

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

Where K_F is the adsorption capacity constant (L/mg) 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: $q_e = B\ln A + B\ln C_e$ with $B = \frac{RT}{b}$ (7)

Where A is the Temkin constant for capacity, b is the constant for heat of adsorption, R is the perfect gas constant (8.314 J/mol.K) and T is the absolute temperature (K).

2.9. Thermodynamic modeling

Thermodynamic parameters were calculated from the equilibrium constant Kc, determined for different temperatures (298, 308 and 318 K), according to the following relationships:

- Equilibrium constant

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

Where q_e is the quantity adsorbed at equilibrium (mg/g), and C_e the residual concentration in solution (mg/L).

- Van't Hoff equation:

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

Linear equation of type $y = ax + b$

Where R is the perfect gas constant (8.314 J/mol.K) and T the absolute temperature (K).

- Gibbs free energy :

$$\Delta G = \Delta H\square - T\Delta S\square = - RT\ln Kc \qquad (10)$$

2.10. 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 the XLSTAT software.

3. Results and discussion

3.1. Physico-chemical and organic parameters of water at the illegal gold panning site

Table 1 shows the values of physico-chemical 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 µS/Cm	3.68 KΩ-Cm	6.7 mV	22,6 °C	4.799 mg/L
Standards (WHO)	6,5-8,5	<500 µS/Cm	>2 KΩ-Cm	+200 to +400mV	25-30°C	<0.1 mg/L

Analysis shows a slightly acid 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 for aquatic fauna and local populations (Nyame et al., 2012). The temperature of 22.6°C is typical of shallow tropical waters and influences the solubility of dissolved gases. The conductivity of 272 µS/cm 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.

The relatively low redox potential (6.7 mV) indicates a weakly oxidizing environment, favoring the mobility of metals such as mercury (Hg^{2+}) and arsenic (As^{3}-), often involved in artisanal extraction processes (Basu et al., 2015). The high phosphate concentration (4.799 mg/L) far exceeds the WHO standard (<0.1 mg/L), indicating organic pollution, probably linked to waste and chemicals from gold panning. These parameters show a disturbed environment, characterized by organic and mineral pollution, with risks for public health and aquatic ecosystems (Hilson & van der Vorst, 2002). Table 2 shows the measured values of COD, BOD_5 and the BOD_5/COD ratio, enabling interpretation of effluent biodegradability.

Table 2. COD, BOD_5 values and the COD/BOD_5 ratio.

Parameters	DCO	DBO_5	DBO_5/DCO
Values	1297 mg O_2/L	300 mg O_2/L	0,231
Standards	≤ 25 mg O_2/L	≤ 6 mg O_2/L	-

The COD value (1297 mg O_2/L) indicates a high load of oxidizable matter, typical of water heavily contaminated by uncontrolled activities, far exceeding regulatory thresholds (AFNOR, 1997). BOD_5 at 300 mg O_2/L remains high, confirming significant pollution by organic matter. 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 (GuittonnyPhilippe et al., 2015). These data underline the dangerousness of illegal gold panning discharges, introducing non-biodegradable pollutants that compromise the local ecological balance and water potability.

3.2 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 analyses measured heavy metal levels in three environmental compartments: water, soil and *Eichhornia crassipes*, collected at a control site in Songon.

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

Heavy metals	Pb	Cd	Hg	As	Zn	Cu

Concentration in water (mg/L)	0,86	0,12	0,03	0,08	1,40	0,56
Soil concentration (mg/kg)	320	41	2,7	12	150	98
Plant concentration (mg/kg)	5,2	0,8	0,05	0,9	12,4	3,6

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

Concentrations measured in the soil show severe contamination, notably in lead (320 mg/kg), cadmium (41 mg/kg), copper (98 mg/kg) and zinc (150 mg/kg), 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 plant *Eichhornia crassipes* showed a notable capacity for bioaccumulation, particularly for zinc (12.4 mg/kg), lead (5.2 mg/kg) and copper (3.6 mg/kg). These results underline its potential as a bioindicator of metal pollution and support its use in 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, 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 measures.

3.3. 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 for plants. A controlled experiment evaluated the effect of pH on the bioaccumulation of six heavy metals (*Pb*, *Cd*, *Zn*, *Cu*, *As*, *Hg*) by *Eichhornia crassipes*. Results of metal concentrations after two weeks' exposure at different pH levels are shown in Table 4 and Figure 6.

Table 4. Metal concentrations in plants (mg/kg 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

The results show that pH influences 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), Cd (26.8 mg/kg), Zn (297.3 mg/kg), Cu (104.3 mg/kg), As (14.4 mg/kg) and Hg (1.5 mg/kg). This can be explained by the increased mobilization of metal cations at slightly acidic pH, where metals are more soluble and less adsorbed onto soil particles (Ali et al., 2013). At pH $\leq$ 5.08, acid toxicity or reduced root uptake can occur (Gao et al., 2018). Above pH 7, a decrease in accumulated concentrations is observed, indicating 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 show 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 pH in phytoremediation systems could optimize the extraction of heavy metals from contaminated areas.

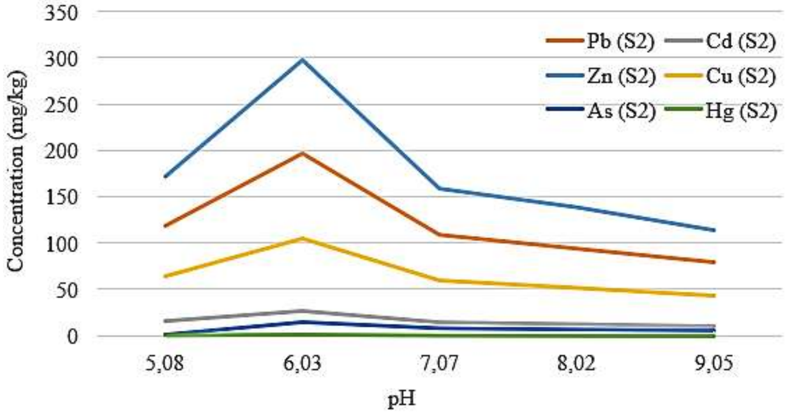


Figure 3: Effect of pH on heavy metal bioaccumulation by *Eichhornia crassipes*

Beyond metal-rich matrices, studies on detergent effluents show that *Pistia stratiotes* and *Eichhornia crassipes* effectively remove MBAS (anionic surfactants; 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 base our interpretation on metal-specific kinetic, isotherm, and thermodynamic models calibrated under near-field conditions.

3.4. 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: $\mathrm{BCR} = \frac{C_{\mathrm{Plant}}}{C_{\mathrm{Medium}}}$ (11)

In this study, BCR values were calculated for each metal as a function of pH, based on concentrations measured in contaminated water and in the plant after 2 weeks. Table 5 shows the BCR values obtained for pH 6.03, the value identified as optimal.

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 under slightly acidic conditions. The combination of an extensive root surface, rapid growth and high tolerance to heavy metals explains this remarkable capacity (Rai, 2008).

3.5. Principal Component Analysis (PCA)

A 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, while 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 around pH 6.03. In contrast, the vectors for As and Hg were slightly offset, suggesting absorption less dependent on pH or 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).

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

3.6. Predictive modeling of heavy metal bioaccumulation by *E. crassipes*

Predictive modeling enables us to anticipate 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. The aim is to propose a model for predicting bioaccumulation, estimating kinetic parameters and optimizing treatment time and conditions of use.

3.6.1. Multiple regression model based on pH

Bioaccumulation efficiency depends on pH, which influences metal bioavailability. A quadratic regression was performed for each metal based on experimental data (Tables 7 and Figure 4):

$q = a\,pH^2 + b.\,pH + c$ (12)

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

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 results show a bioaccumulation optimum around pH 6.03, confirming experimental observations. At this slightly acidic pH, the bioavailability of metal cations is maximized, enabling optimal metal adsorption. This model makes it possible to predict bioaccumulation as a function of pH without prior biological testing.

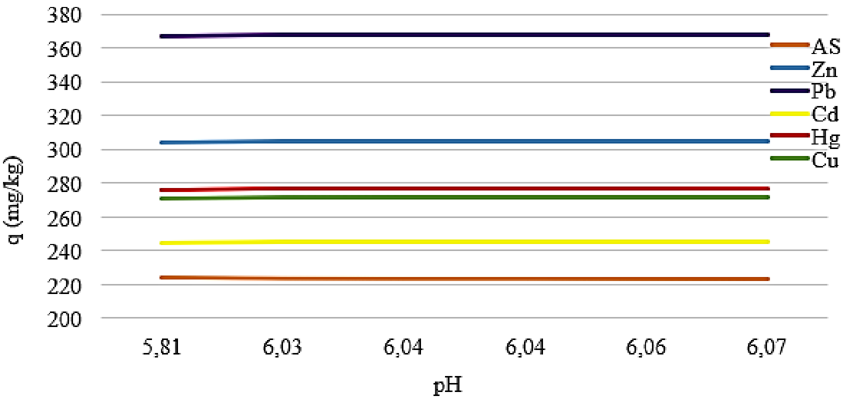


Figure 4. Bioaccumulation curve as a function of pH variation

The curve of bioaccumulation of metals (*As*, *Zn*, *Pb*, *Cd*, *Hg*, *Cu*) as a function of pH shows a parabolic trend typical of a quadratic model, with a maximum of 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, -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 Cu^{2+}, Pb^{2+} or Zn^{2+} precipitate as metal hydroxides (e.g. $Cu(OH)_2$, $Pb(OH)_2$), reducing their availability to plant 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 to a loss of affinity in plant tissues. The optimum pH varies slightly depending on the metal: Pb, Cd, and Zn reach their maximum between 6.03 and 6.04, suggesting a similar affinity for the same functional sites; Hg peaks at pH 6.06, while As shows 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.

3.6.2. Analysis of the temporal bioaccumulation predictive model

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

This trend reflects classic asymptotic kinetics in biosorption: initially, active sites are numerous, facilitating rapid adsorption. Then, as these sites become saturated, accumulation decreases, illustrated by the concave shape of the curves (Ho & McKay, 1999). Zinc has the highest accumulation capacity (529.3 mg/kg DM at 42 days), followed by lead (348.5 mg/kg) and copper (185.9 mg/kg), due to their strong affinity for carboxyl and hydroxyl groups in aquatic plant cell walls (Behera et al., 2022). Their progressive accumulation indicates a significant biochemical capacity of *E. crassipes* to capture metal cations.

Cadmium, although accumulated at lower levels, follows similar kinetics, suggesting a slow but efficient chemisorption process. Mercury (Hg) and arsenic (As) show lower accumulation levels, with curves reaching a plateau more quickly, indicating rapid adsorption but in small quantities, either due to their low affinity or to unfavorable conditions (Wang et al., 2020; Tang et al., 2023). Quadratic models identify a saturation time of between 28 and 35 days, beyond which accumulation becomes 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. Finally, the shape of the curves anticipates desorption or cell toxicity trends beyond 42 days, a phenomenon observed when excessive accumulation alters plant structures (Zhou et al., 2022). It is therefore advisable to optimize the exposure time according to the target pollutant and environmental conditions (figure 5).

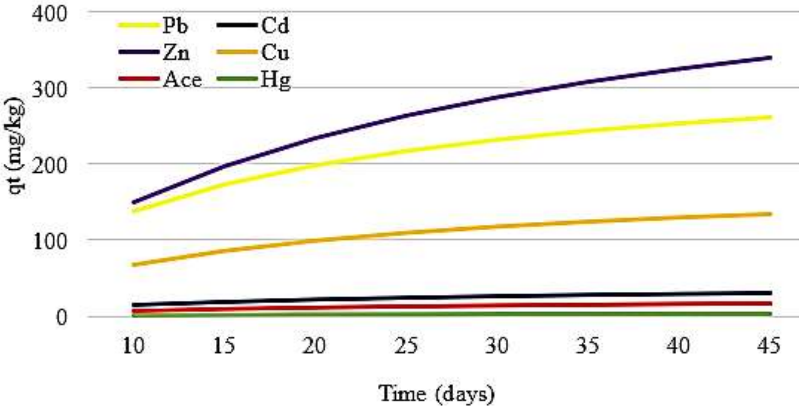


Figure 5. Prediction curves for metal accumulation as a function of time

3.7. 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 to identify key periods of maximum accumulation. This knowledge is essential for optimizing 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 in the total biomass after 2, 4, and 6 weeks (Table 8 and figure 6).

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

Week/ heavy metals (mg/kg 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

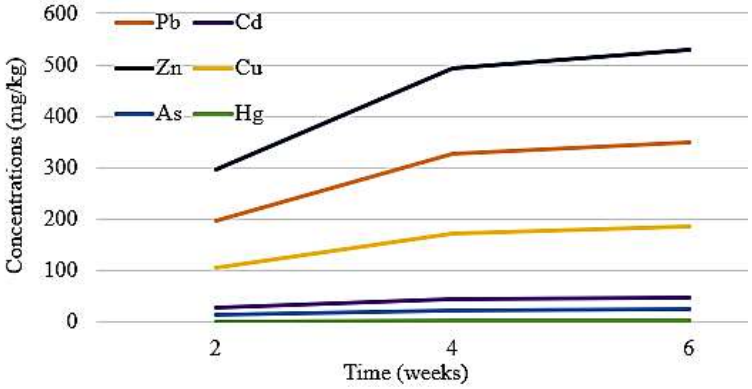


Figure 6. Contact time between heavy metals and *Eichhornia crassipes*

The results show a two-phase accumulation pattern. From the 2^e to the 4^e week, metals display 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 binding sites.

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

Table 9. Kinetic regression parameters for heavy metals in *Eichhornia crassipes*

Metal	**Model**	**k**	**q_e(th) (mg/kg)**	**q_e(exp) (mg/kg)**	**R^2 ajusted**
Pb	1er	$k_1 = 0{,}057\ j^{-1}$	344,2	348,5	0,985
	2e	$k_2 = 0{,}00019$ g/mg·j	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·j	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·j	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·j	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·j	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·j	2,76		0,989

The pseudo-second-order model describes the adsorption kinetics more accurately, suggesting a chemisorption mechanism involving electron exchange between metal ions and functional groups (Ho & McKay, 1999). These findings align with 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 mg/kg for Zn, 348.5 mg/kg for Pb, and 185.9 mg/kg for Cu—indicate these metals are the most strongly accumulated due to their divalent cationic nature and affinity for oxygenated ligands. In contrast, As and Hg show lower but faster kinetics (higher k_2), reflecting rapid adsorption limited by site availability. Mercury displays the highest k_2 (0.080 g/mg·d), indicating fast but low-capacity uptake, consistent with Wang et al. (2019), who noted rapid Hg–S interactions but limited accumulation. Pb shows slower yet stable adsorption (Zhou et al., 2021).

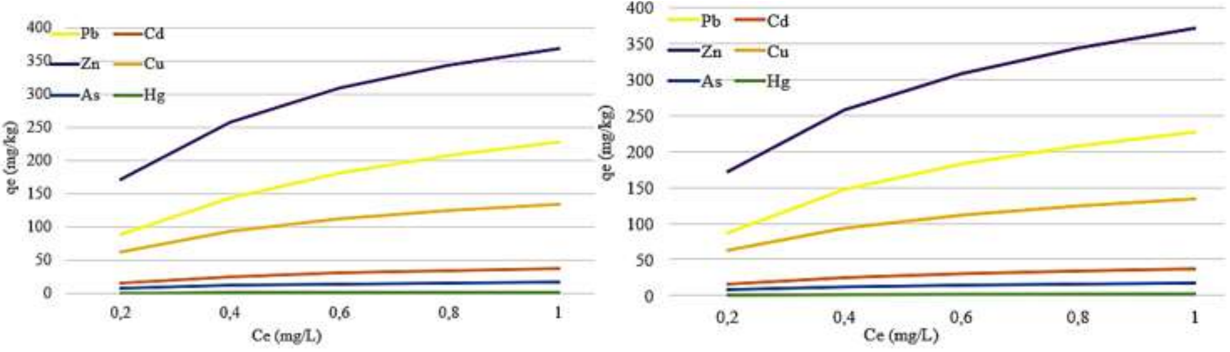
Comparison of kinetic constants reveals the order of adsorption rate (k_2): Hg > As > Cd > Cu > Pb > Zn, while adsorption capacity follows Zn > Pb > Cu > Cd > As > Hg. Thus, adsorption rate is not directly proportional to capacity but to ion reactivity and accessibility to active sites. These results,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

3.8. Modeling heavy metal adsorption isotherms by *E. crassipes*

The study of adsorption isotherms provides insight into the interactions between heavy metals and the biomass of *Eichhornia crassipes*. Three classical models—Langmuir, Freundlich, and

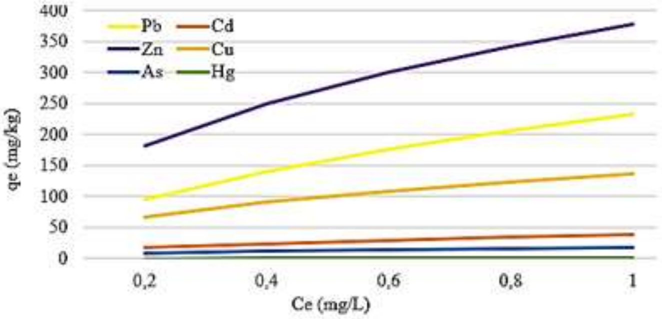
Temkin—were used to describe the distribution of metals between the solution and the plant surface, and to estimate the thermodynamic and structural parameters of the process (Foo & Hameed, 2010).

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



a) Langmuir adsorption isotherms for heavy metals

b) Temkin adsorption isotherms for heavy metals



c) Freundlich adsorption isotherms for heavy metals

Figure 7. Isotherm modeling for heavy metals

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, 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 parameters.

Table 10. Calculated adsorption isotherm parameters for each metal

Isotherm	**Parameter**	**Pb**	**Cd**	**Zn**	**Cu**	**As**	**Hg**
Langmuir	qmax (mg/kg)	372,89	56,42	518,54	187,38	23,38	2,23
	K_L (L/mg)	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)	86,41	13,53	123,65	44,31	5,58	0,51

	AT (L/mg)	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

The results confirm that *E. crassipes* is an effective biosorbent with notable affinity for Pb, Zn, and Cu, which exhibit the highest qmax values. Arsenic and especially mercury show lower qmax values, reflecting more limited but still effective adsorption. The Freundlich model better describes these metals, 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 mg/kg), consistent with its weak interaction and volatile behavior.

These findings agree with previous studies by Ho & McKay (2000), Foo & 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 Freundlich and Temkin for heterogeneous or energetically variable systems. Overall, these results confirm the potential of *Eichhornia crassipes* for targeted phytoremediation of metal-contaminated environments.

3.9. Thermodynamic analysis of heavy metal adsorption

The thermodynamic study evaluates the nature, spontaneity, and mechanisms of heavy metal adsorption by *Eichhornia crassipes* through three key parameters: Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), calculated from equilibrium constants at different temperatures (298, 308, and 318 K). The equilibrium constants (Kc) were derived from qe and Ce 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 Figure 8).

Table 11. Thermodynamic parameters and equilibrium constants for each metal

Metal	**K$_C$ 298 K**	**Kc 308 K**	**Kc 318 K**	**ΔG° 298 K (kJ/mol)**	**ΔG° 308 K (kJ/mol)**	**ΔG° 318 K (kJ/mol)**	**ΔH° (kJ/mol)**	**ΔS° (J/mol·K)**
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

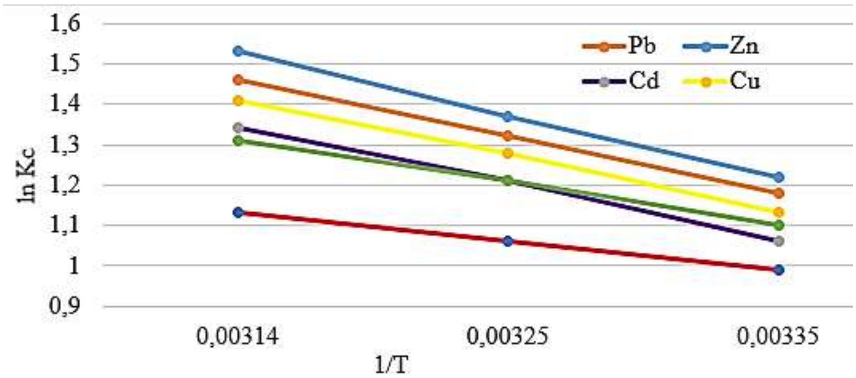


Figure 8. Van't Hoff plot for each metal

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

ΔH° values ranging from 21.5 to 28.1 kJ/mol indicate endothermic adsorption favored by increasing temperature, suggesting specific chemical interactions such as metal–ligand bonding rather than simple physisorption. As noted by Ho & McKay (1999), ΔH° values above 20 kJ/mol 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 metal ions and the rearrangement of surface functional groups. This agrees with Kumari & 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 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 ($\Delta G° < 0$), endothermic ($\Delta H° > 0$), and entropic ($\Delta S° > 0$) nature of the process confirms that *E. crassipes* is an efficient and versatile biosorbent for heavy-metal remediation. These thermodynamic findings support its application under tropical conditions, where higher ambient temperatures enhance adsorption efficiency, and highlight the involvement of functional groups (–OH, –COOH, –Ph–OH) in metal binding.

Conclusion

The expansion of illegal gold mining in Côte d'Ivoire is causing concerning metal pollution in aquatic environments, 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 DM), followed by zinc (318.7 mg/kg DM) and copper (205.4 mg/kg DM). The bioaccumulation factor (BAF) exceeded 1 for all metals at pH 6.03, indicating a clear capacity for concentration from the medium.

pH emerged as a key parameter, with a highly significant influence ($p < 0.001$) according to the one-way ANOVA. Maximum bioaccumulation was recorded at pH 6.03, while 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). Adsorption kinetics followed a two-phase pattern: rapid uptake during the first 28 days, 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.

Adsorption isotherms were fitted to the Langmuir, Freundlich, and Temkin models. The Langmuir model gave the best results for Pb, with a maximum adsorption capacity (qmax) estimated at 384.6 mg/g. Thermodynamic analysis confirmed spontaneous ($\Delta G° < 0$) and endothermic ($\Delta H° > 0$) adsorption for all metals, indicating 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, 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 the involvement of 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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