

Removal of Copper Ions by Non-living Aquatic Macrophytes *Egeria Densa*

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Abstract: In this work, the removal potential of Cu^{2+} ions by non-living macrophytes *Egeria densa* has been studied. Adsorption kinetic and equilibrium tests were carried out in flasks under batch operations and controlled pH and temperature. The biosorption kinetic results have shown that Cu^{2+} ions removal rate was at its maximum at the beginning of the process. The equilibrium state was achieved after 60 min, and the Cu^{2+} ions removal was higher than 70% for the given experimental conditions. The kinetic biosorption data were better fitted by using a pseudo second order model. The equilibrium data at pH 5 were better described by the Langmuir isotherm than the Freundlich one, with a maximum metal content value of $1.47 \text{ mequiv}\cdot\text{g}^{-1}$ and an adsorption rate value of $3.73 \text{ l}\cdot\text{mequiv}^{-1}$. The kinetic parameters values were in agreement with other biosorbents data published in the literature, indicating that the macrophytes *E. densa* have a good potential to be used as biosorbent material in industrial effluent treatment system.

Keywords: Biosorption, *Egeria densa*, Copper ion.

Introduction

Environmental pollution with metals and xenobiotics is a global problem, and the development of new cost effective technologies for metal removal from waste waters is therefore of significant interest. Copper is introduced in the ecosystem as a result of different industrial activities such as automobile industries, and construction works. Many attempts have been made to remove and recover metal elements from waste waters, in order to keep clean environment and protect human health and aquatic animals and plants [19, 20].

In metal-contaminated wastewater treatments, many methods that involve a variety of physical, chemical, and biochemical processes such as ion exchange, reverse osmosis, electrolysis, precipitation and adsorption are available [15]. Bio-treatment technologies have been developed based on the biosorption (heavy metal removal capacity) features of biological materials such as filamentous fungus, bacteria, leavenings, seaweed and different biomass [6, 11, 12, 21].

The industrial potential of the biosorption process depends on many factors, such as biosorption capacity, efficiency and selectivity of metal sequestration and mainly, equal

performance and cost compare with traditional processes [14]. An industrial application of particular biosorbent requires also an equipment design competitive to the market. Biosorption studies have been reported for bacteria [13], seaweed [3, 4, 7, 17], green algae [1], fungus [16], aquatic macrophytes [18] and plants [5]. Based on this technique non-living plants can be used for heavy metal removal due to the low costs, free availability and easy regeneration.

The goal of this work was to study the copper removal potential of non-living aquatic macrophyte *Egeria densa*. In order to obtain maximum information about biosorbent response for the given experimental conditions several adsorption kinetics and equilibrium experiments were performed. The process of copper removal was modelled and the adsorption equilibrium and kinetic parameters were estimated.

Material and methods

Biomass Sampling

Aquatic macrophytes *E. densa* were collected from artificial ponds, washed in tap water, and rinsed many times with deionized water. In laboratory conditions, a part of the samples was dried at room temperature (30°C), and the rest was dried by using an electrical oven at 50°C. All samples were grounded using steel-knives electrical mill and sieved to different fraction sizes.

Chemicals

The used chemicals were of analytical-reagent grade. Deionized water was used as a dilution medium. Several stock solutions with Cu^{2+} ion concentrations in the range from 2.0 to 4.5 mequiv·l⁻¹ were prepared from water-soluble metallic salt ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Merck pro analysis) and stored in l⁻¹ volumetric flasks for posterior metal adsorption experiments. Base and acid solutions of 1 M NaOH and 1 M HCl, respectively, were used for pH adjustment. The calibrate curve for atomic absorption spectrometer were obtained by using copper ions standard solution (1.0 g·l⁻¹ for AAS, Merck) and different diluted-Cu concentrations from 0.1 to 1.5 mg·Cu·l⁻¹.

AAS Measurements

After each test or biosorption experiment, the liquid phase was separated from the adsorbent by a vacuum filtration system using 0.45 μm-membranes. Further, the metal concentration was measured by using previously calibrated Absorption Atomic Spectrometry (AA 932–GBC, Analytica).

Preliminary tests

In order to find the pH value of metal precipitation, one litter of copper solution with concentration 3.34 mequiv·Cu²⁺·l⁻¹ was used and distributed in small aliquots (duplicate) with adjusted pH between 3 and 8. The metal precipitation test was performed without mixing at room temperature for 48 h experimental time. The copper concentration in each filtrate was measured by AAS. In order to improve the biosorption kinetic and equilibrium experimental conditions, the temperature effect on plant drying was tested by using two temperatures: 30 and 50°C (while the solution temperature effect was evaluated at four controlled temperatures between 25 and 45°C). Both tests in duplicates were performed in 125 ml Erlenmeyer flask as follows: liquid volume of 50 ml Cu²⁺ solution and 250 mg dry plant. The mixtures were

agitated on a rotary shaker for 12 h and at each setting temperature. The copper concentration was measured by AAS. On the bases of these results plants dried at 30°C were used as a biosorbent.

The effect of biosorbent grain size was also studied, using three grain fractions sizes between 0.1 to 0.6 mm and a mixture of them. The test was carried out by using the same procedure as described for temperature effect test ($T = 30^{\circ}\text{C}$ of copper solution and 12 h contact time).

Kinetic test

For kinetic experiments, 250 mg dry biomass quantity was added to 50 ml metal solution with approximately $4.52 \text{ mequiv}\cdot\text{Cu}^{2+}\cdot\text{l}^{-1}$ at initial $\text{pH} = 5$. The mixtures were agitated on a rotary shaker at 30°C controlled temperature. During the sorption experiments the $\text{pH} = 5$ was controlled by adding alkaline and acid solutions. In order to determine the equilibrium time the adsorption experimental points were set up for nine short contact times in the range from 0 to 6 h. The initial and final copper concentrations in each liquid phase were determined by AAS.

Equilibrium concentration

In order to obtain the equilibrium concentration and to assess the pH effect, several batch Cu^{2+} – sorption experiments using 20 to 550 mg dry *E. densa* were carried out in a constant volume of 50 ml copper solutions containing different Cu^{2+} concentrations (from 2.0 to 4.5 $\text{mequiv}\cdot\text{l}^{-1}$). All equilibrium sorption experiments were carried out in duplicates. The experimental conditions were as follows – mixing in a rotary shaker at 30°C controlled temperature, monitoring and adjustment of pH at 4 and 5, and 12 h contact time. The equilibrium copper ions concentrations were measured by AAS.

Results and discussion

Preliminary tests

The pH-based Cu^{2+} precipitation data was fitted by a Logistic-type function, with a good correlation coefficient and residual χ^2 (Fig. 1).

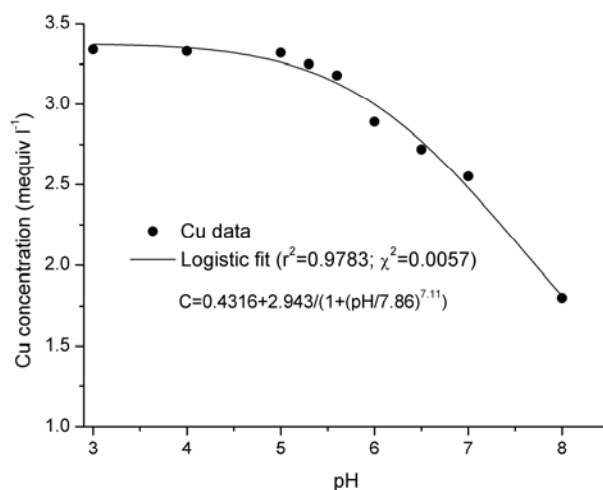


Fig. 1 Copper ions concentration as a function of pH. Standard deviations are less than the symbol size. Solid curve represent the Logistic-type fitting.

Simulations with the model were helpful to find the critical pH value of metal precipitation. pH threshold was found to be about 5.2 when the copper precipitation started. Consequently, to avoid unacceptable pH region, all next copper sorption experiments were performed adjusting the pH below this threshold.

In both dry temperature tests, it was achieved exactly the same copper removal percentage close to 70%, suggesting that temperature effect (in this range) on biosorption can be neglected. Hence, a room temperature (30°C) was used for all copper sorption experiments and other tests.

In the interval from 25°C to 45°C controlled temperatures, the highest copper removal percentage was observed at 30°C solution temperature, corresponding to 70% Cu²⁺ removal, which was approximately 15% above achieved by the our other tests.

The copper-sorption experiments based on the different *E. densa* grain fraction sizes showed small differences (<5%) when the removal of copper ion was considered as a grain sizes function. Thus, the grain size effect on biosorption removal capacity of the biomass can be neglected, as well.

Kinetic test

The dry *E. densa* biomass-based biosorption kinetic data using Cu²⁺ solutions at pH = 5 was fitted by a Logistic-type function with good correlation coefficient (0.9992) and χ^2 (0.0011). The results are shown in Fig. 2, where one can see a fast metal biosorption behavior of the biomass at the beginning of the process.

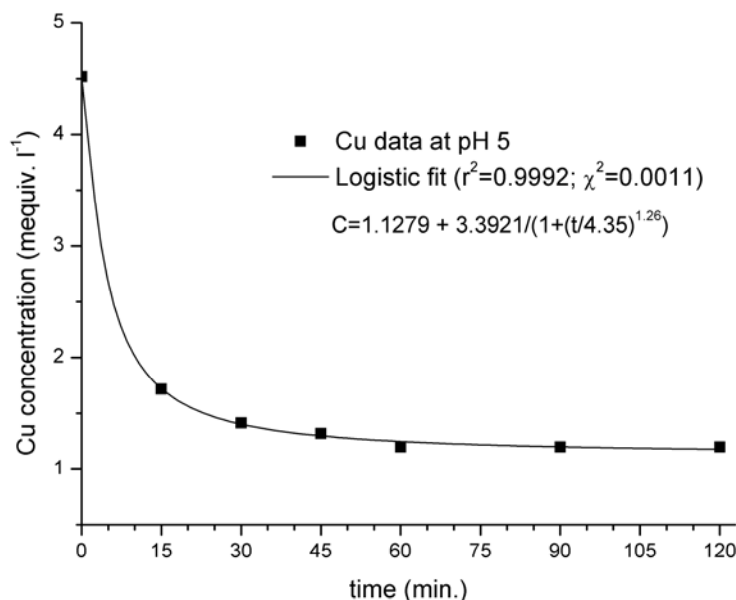


Fig. 2 Effect of the contact time on Cu²⁺ ions sorption by *E. densa*, using an initial concentration of 4.52 ± 0.04 mequiv·Cu²⁺·l⁻¹, pH = 5, T = 30°C. Solid curve represents the Logistic-type fitting.

The metal removal rate and equilibrium time were determined, as well. As can be seen in Fig. 2, the biosorption process has increased sharply at contact times less than 15 min and slowed gradually when approaching the equilibrium state, resulting in an equilibrium time of about 60 min, and 70% – Cu²⁺ removal. Such system response was expected for a strong metal biosorption, which is characterized by no energy exchange reaction and thus the metal removal is considered to be a purely physical-chemical interaction between the biosorbent mass surface and the metal in the solution [4].

The biosorption kinetic data obtained for *E. densa* were compared with the results of other scientists, where the experimental conditions such as temperature, pH, and initial metal concentration were the same, but the biosorbent was the non living straw of wheat *Triticum aestivum* [5]. In that study, the equilibrium state was reached at about 60th min, which was approximately two times longer than the time achieved in the present work. In other work, where *Chlorella vulgaris* [1] was studied as a biosorbent, the copper equilibrium time was about 15 min. Indeed, these results support our understanding that the aquatic macrophytes *E. densa* have a competitive copper removal potential in comparison with other plants. Due to its low equilibrium time, the biosorbent *E. densa* could reduce the mass transfer zone in a continuous system compared to the other biosorbents or take the biosorption-based effluent treatment systems for a long experimental time.

Adsorption kinetic

The copper ions concentration in solid phase in time, labeled as q_t was calculated (see Eq. (1)) from the initial concentration (C_0 in mequiv·l⁻¹) and the final concentration (C_t in mequiv·l⁻¹) in time, accumulated by *E. densa* biomass.

$$q_t = \frac{V(C_0 - C_t)}{m_s} \quad (1)$$

In order to analyze the sorption kinetics of copper, the pseudo-first order and pseudo-second order kinetic models were applied to the data. A simple pseudo first-order equation, which was proposed by Lagergren is described by Eq. (2) [2, 9]. A plot of $\log(q_{eq} - q_t)$ versus t would provide a straight line for the first order adsorption kinetics, which allows to obtain the adsorption rate constant K_1 [16].

$$\log(q_{eq} - q_t) = \log(q_{eq}) - \left(\frac{K_1}{2,303} \right) t \quad (2)$$

On the other hand, the Ho's second-order rate equation, which has been called a pseudo-second order kinetic expression, has also been applied widely [8-10] and described by Eq. (3). The experimental data were plotted as t/q_t against t , which showed a linear tendency of the data and allowed determination of the sorption rate constant K_2 in a simple way.

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{1}{q_{eq}} t \quad (3)$$

The second order kinetic model was evaluated (the correlation coefficient value $r^2 = 0.9999$) to fit best the experimental data at 30°C and pH = 5 (see Fig. 3).

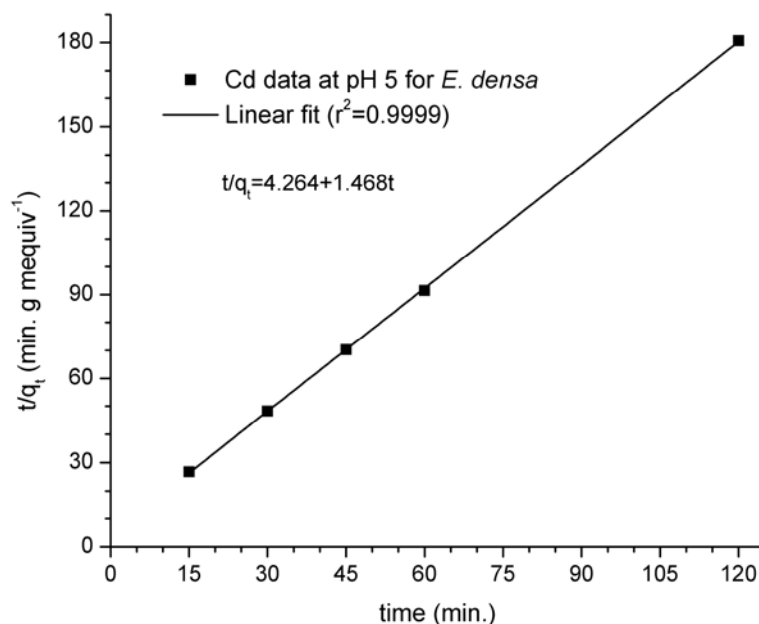


Fig. 3 Copper adsorption kinetic data by applying *E. densa*, at $T = 30^{\circ}\text{C}$ and $\text{pH} = 5$, and simulation data of the pseudo second order model. Standard deviations are less than the symbol size. Solid curve represents the linear fitting and intercept and slope values of $4.26 \pm 0.48 \text{ min}\cdot\text{g}\cdot\text{mequiv}^{-1}$ and $1.468 \pm 0.007 \text{ min}\cdot\text{g}\cdot\text{mequiv}^{-1}$, respectively.

Hence, based on the second order kinetic model, it was possible to determine the q_{eq} parameter value $q_{eq} = 0.681 \pm 0.003 \text{ mequiv}\cdot\text{Cu}^{2+}\cdot\text{g}^{-1}$, and the sorption rate constant value $K_2 = 0.51 \pm 0.06 \text{ g}\cdot\text{mequiv}^{-1}\cdot\text{min}^{-1}$.

Sorption isotherm

Usually, the isotherms in use to fit the biosorption data are the Langmuir and Freundlich which are described by the Eq. (4) and (5), respectively. Adsorption isotherm is represented by Eq. (4).

$$q^* = q_{\max} \left(\frac{bC^*}{1 + bC^*} \right) \quad (4)$$

$$q^* = a(C^*)^n \quad (5)$$

The Langmuir and Freundlich isotherms have two parameters to be adjusted to the Cu^{2+} equilibrium biosorption data of *E. densa*. The metal adsorption modelling parameters for each isotherm type were obtained using the Origin[®] software. The adsorption experimental data for copper ions removal at $\text{pH} = 4$ and 5 by using *E. densa* dry biomass are shown in Fig. 4 and Fig. 5, respectively, including the both Langmuir and Freundlich isotherms.

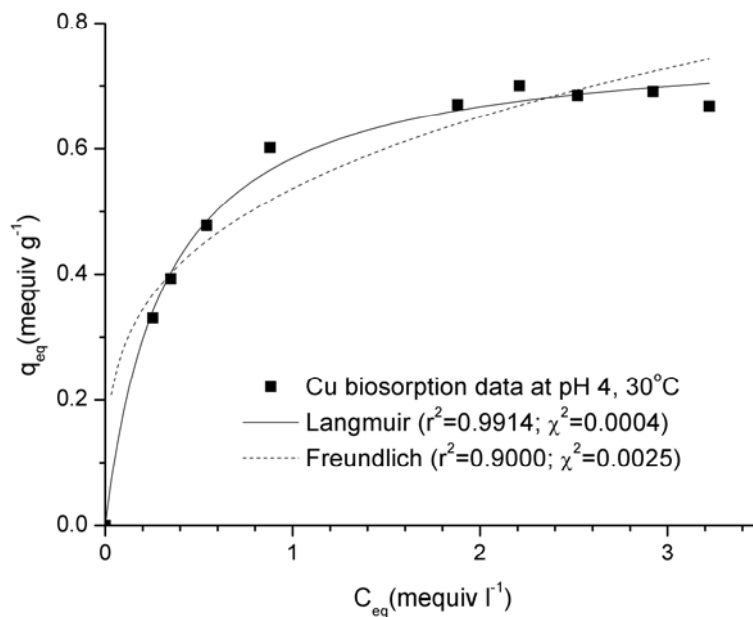


Fig. 4 Copper sorption isotherm applied to fit the experimental data for *E. densa* at pH = 4. Solid and dotted curves are calculated with the Langmuir and Freundlich equations, respectively.

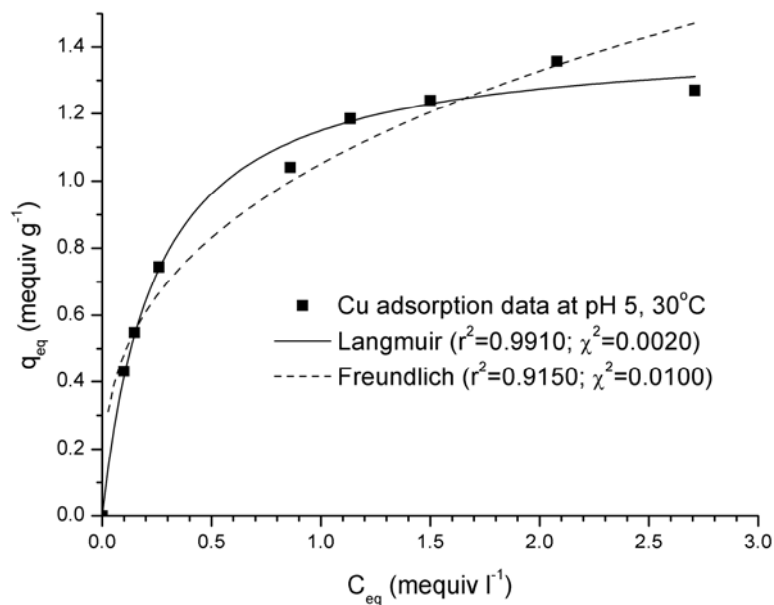


Fig. 5 Copper sorption isotherm applied to fit the experimental data for *E. densa* at pH = 5. Solid and dashed curves are calculated with the Langmuir and Freundlich equations, respectively.

Our data were fitted better by the Langmuir isotherm which is better than Freundlich one in order to characterize the *E. densa* biomass as a new metal adsorbent, according to the correlation coefficient and χ^2 values for each model.

The curves in Figs. 4 and 5 were drawn using the couple of adjustable Langmuir (q_{max} , b) and Freundlich (a , n) parameters, which are summarized in Table 1.

Table 1. Copper adsorption modelling parameters of Langmuir and Freundlich isotherms

pH	Langmuir		Freundlich	
	q_{max} [mequiv·g ⁻¹]	b [l·mequiv ⁻¹]	a	n
4	0.78 ± 0.02	3.10 ± 0.28	0.54 ± 0.02	0.28 ± 0.04
5	1.43 ± 0.04	4.11 ± 0.42	1.05 ± 0.03	0.34 ± 0.04

In comparison between Langmuir parameters values for both pH values, it was possible to find the best maximal copper accumulation in *E. densa*, corresponding to q_{max} value equal to 1.43 ± 0.04 mequiv·g⁻¹ at pH = 5. Similar result was obtained using *Chlorella vulgaris* algae [1], which maximum copper content was 0.94 mequiv·g⁻¹ at pH 5, indicating that *E. densa* is an alternative biosorbent with a great metal removal capacity.

From the low equilibrium time (60 min), the quick copper removal rate (55% in 10 min), and the high copper uptake, the *E. densa* as a biosorbent can be used in effluent treatment systems due to its great adsorption potential.

Conclusions

In this work, the biosorption removal of Cu²⁺ ions by non-living aquatic macrophytes *E. densa* was studied as possible metal purification from industrial effluents. The results from the preliminary tests can be summarized as follows:

1. The pH threshold for copper precipitation was pH = 5.2.
2. A high copper ions removal was obtained without applying an artificial thermal pre-treatment of *E. densa* biomass.
3. Maximum copper removal was achieved at 30°C experimental temperature.
4. Biomass size distribution has no effect on copper sorption experiments.
5. Moreover, from the kinetic test, due to its low equilibrium time, the *E. densa* as biosorbent could take a reduction of effluent treatment continuous system dimensions. Because of its good characteristics on copper removal such as low equilibrium time, fast copper removal rate, and maximal copper uptake similar or better than other biosorbent, the *E. densa* can be considered as alternative biosorbent toward the implementation of biosorption technology in industrial and environmental remediation.

Abbreviations

- a Constant in Eq. (5)
 b Constant in Eq. (4), [l·mequiv⁻¹]
 C^* Metal concentration at the equilibrium, [mequiv·l⁻¹]
 K_1 Rate constant for the pseudo first-order adsorption process, [min⁻¹]
 K_2 Rate constant for the pseudo second-order adsorption process, [g·mequiv⁻¹·min⁻¹]
 m_s biosorbent dry weight, [g]

n	Constant in Eq. (5)
q^*	Metal uptake concentration, [mequiv·g ⁻¹]
q_{eq}	Metal uptake concentration at the equilibrium, [mequiv·g ⁻¹]
q_{max}	Maximal metal uptake concentration, [mequiv·g ⁻¹]
q_t	Metal uptake concentration in time t , [mequiv·g ⁻¹]
V	Volume of the metal solution, [l]

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