



Biosorption of the Copper and Cadmium Ions – a Study through Adsorption Isotherms Analysis

Marcia R. Fagundes-Klen, Luiz G. L. Vaz, Marcia T. Veit,
Carlos E. Borba, Edson A. Silva, Alexander D. Kroumov*

West Paraná State University-Toledo, Department of Chemical Engineering,
645 Faculty Str., Garden “La Salle”, 85903-000, Toledo, Paraná, Brazil
E-mails: fklen@bol.com.br edsondeq@unioeste.br
marcia_veit@yahoo.com.br adkroumov@yahoo.com

*Corresponding author

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Abstract: In this work, the biosorption process of copper-cadmium ions binary mixture by using marine algae *Sargassum filipendula* was investigated. A set of experiments was performed to obtain equilibrium data for the given batch operational conditions – $T = 30^{\circ}\text{C}$, $\text{pH} = 5$. The interpretation of equilibrium data was based on the binary adsorption isotherms models in the Langmuir and Freundlich forms. To evaluate the models parameters, non-linear identification procedure was used based on the Least Square statistical method and SIMPLEX local optimizer. An analysis of the obtained results showed that the marine algae biomass has higher affinity to copper ions than to cadmium ones. The biomass maximum adsorption capacity for the binary system was about 1.16 meq/g.

Keywords: Biosorption, Equilibrium, Copper, Cadmium.

Introduction

Biosorption process

The metal ions represent forms of contamination of water resources and decrease continuously and permanently their quality [4]. Removal of Cadmium, Zinc, Lead, and other ions from water effluents is extremely important, because of their high toxicity on the fauna and flora. Hence, the majority of the industrialized countries have an ambient legislation that establishes limits on the effluents containing heavy metals ions. In Brazil, the federal legislation (Resolution n0 357, of 17/03/05 of the National Advice of Environment – “CONAMA”), classifies the water quality, directs their applications, and establishes the conditions and standards for effluents launching. Article #24 from the Resolution establishes that: “The direct or indirectly effluent discarding any polluting source in the water environment could only be permitted after a treatment which is in accordance with the conditions, standards and requirements written in this Resolution and other applicable norms from environmental protection agencies.” In this article, the standards of launching some inorganic pollutants, such as heavy metals, are established. The allowed maximum concentrations for cadmium and copper launchings are 0.2 mg/L, 1.0 mg/L, respectively.

Diverse processes of separation are currently used with the objective to reduce the metals concentration to the acceptable levels. However, the majority of heavy metal salts are water-soluble and consequently, they cannot be separated by using conventional physical processes of separation [8]. Hence, the conventional processes, as precipitation, ionic exchange and reverse osmosis are very costly and inefficient for low concentrations levels.



The biosorption process involving living organisms (macrofits, algae, fungus, etc.) is a promising low-cost solution for the heavy metals removal. It is especially useful for heavy metal removal from diluted water solutions in the range from 1 to 100 mg/L [3].

The studies of biosorption metals removal have to be focused on the following fields of inquiry: types of biomass, mechanisms of captation, sorption equilibrium study in batch operation, acidity effect on the equilibrium study, the influence of biosorbent form (entire, particle) on the metals removal, physical-chemical treatment of the biomass to obtain greater mechanical resistance of the biosorbent, and study of heavy metals removal in columns.

The authors [12] have investigated the influence of pH, agitation rate and initial metal concentration in charcoal, and obtained a removal capacity of 18.98 and 20.92 mg/g for copper and cadmium ions, respectively. The other researchers [11] have studied the removal and biosorption kinetics of copper and cadmium in lignines – products from the paper industry – taking in consideration variations of temperature, particles size and pH. The authors have obtained a high biosorbent removal capacity of metals (87.05 mg/g and 137.14 mg/g for copper and cadmium ions, respectively) at 25°C. The authors [1] have applied the kinetics models with competitive, non-competitive and partially competitive inhibition effects to describe the biosorption equilibrium data of the copper-cadmium ions binary mixture. The authors have obtained the best representations of experimental data by using the non-competitive model. Moreover, the model appropriately described the pH influence on the biosorption process of these metals by the macroalgae. Amongst the great variety of available biosorbents, the brown algae have shown a higher potential for removal in relation to the other biomasses. Moreover, its use is favored as the algae are a cheap renewable source which can be found in the abundant Brazilian coasts.

The algae biosorption capacity is mainly attributed to the cellular wall, which structure is composed of fibers deeped in an amorphous matrix of some polisaccharides. Alginates and some sulfated polisachcarides are important components of the *Phaeophyta* brown alga cellular walls [18]. The brown algae of *Sargassum sp.* are constituted mainly by the alginates, generally calcium and sodium alginates, which posses a higher potential for heavy metal accumulation, in comparison to other algal biomasses [6]. The alginates of the brown algae are found in the cellular wall and into the intercellular substances. Its presence in the cellular wall can reach up to 40% of dry weight [18].

The biosorption process has mainly been applied to treat synthetic solutions containing a single metallic ion. It is important to notice, the metal removal can be influenced by the presence of other metals. Usually, the industrial water residues contain various pollutant composite species, therefore the multi-component systems need detailed studies. The biosorbent selectivity is a fundamental aspect of the columns and separation reactors design applied for the multi-component system [19].

In industrial scale, the biosorption effectiveness depends on many factors, such as biosorption capacity, efficiency, selectivity, easiness of the metal recovery, which is compared with traditional processes by using two criteria-performance and total costs. On the other hand, the biosorption process does not necessarily need to be a substitution to the existing methodologies, but it can prevent using some processes that are not completely efficient [5]. In the industrial applications and the equipment design of the adsorption/biosorption separation processes, it is essential to determine the biosorbent removal capacity. Generally, this information can be obtained from the experiments on the system equilibrium data.

Hence, the main objective of this work was to investigate the copper and cadmium ions removal by using marine algae biomass of *Sargassum filipendula* at temperature of 30°C and pH = 5. The equilibrium experimental data of the system have been studied by using different adsorption isotherms models. Non-linear identification procedure and least square statistical method were applied to evaluate model parameters values. Based on these results, the best Langmuir-Freundlich isotherm model describing biosorption process was chosen.

Binary adsorption isotherms

The evaluation of the biosorbent removal capacity is made through the analysis of the applied isotherms models with the attainment of the equilibrium data in batch systems. In the biosorption process of heavy metals removal, several mechanisms are involved, and the distinguished one is based on an ion exchange where a stoichiometric exchange of ions keeps the biosorbent load. Usually, the marine alga strains are used in calcium, magnesium and sodium ions exchange with the fluid phase. In the adsorption isotherms, the equilibrium relation between chemical species in the liquid phase is established, therefore chemical species liberated by biosorbent don't influence the concentration of adsorbed metals ions.

The most applicable mathematical forms, which are used to describe biosorption phenomenon, are the Langmuir and Freundlich isotherms. The Langmuir isotherm is based on the following theoretical assumptions:

- Adsorption is in monolayer;
- All the active sites are equivalents and the adsorption process is uniform;
- The adsorption of a molecule by a free site does not depend on the occupied neighboring sites.

The mathematical expression of the Langmuir binary isotherm can be written:

$$q_1^* = \frac{q_m C_1^* b_1}{1 + b_1 C_1^* + b_2 C_2^*} \quad (1)$$

where: q_m , b_1 , and b_2 are the Langmuir binary isotherm constants; q_1^* is the amount of the adsorbed ion in meq/g; C_1^* and C_2^* are the equilibrium concentrations of copper and cadmium ions, respectively.

The Langmuir isotherm constants have a physical meaning, and b_j parameter represents the ratio of sorption-desorption rates. Therefore, the high values of this parameter indicate a strong affinity of the ions to the adsorbent material sites, while q_m parameter represents the total number of available sites in the biosorbent material [7].

Chong and Volesky [3] and Sánchez et al. [16] have used a model originally developed by Bailey and Ollis [2], to represent the equilibrium binary data of biosorption process. The original model was developed to describe the non-competitive inhibition in enzyme kinetics. This model is represented by the following equation:

$$q_1^* = \frac{q_m C_1 b_1 [1 + (K/b_1)C_2^*]}{1 + b_1 C_1^* + b_2 C_2^* + 2K C_1^* C_2^*} \quad (2)$$

where: q_m , b_1 , b_2 and K are the model constants.



Parameter K correlates with the equilibrium constants. The parameters q_m , b_1 and b_2 have the same meaning as the Langmuir isotherm, while the high values of K parameter indicate a favorable formation of the [B-M₁-M₂] complex.

Chong and Volesky [3] and Sánchez et al. [16] have used the Langmuir isotherm modified models to represent the biosorption equilibrium data in binary mixtures. These models have been developed through the incorporation of new parameters into the Langmuir isotherm original model (see Eq. (1)). An incorporation of new constants (k_1 , k_2) in the Langmuir isotherm results in the following expression:

$$q_1^* = \frac{q_m C_1^* b_1}{1 + b_1 (C_1^*)^{k_1} + b_2 (C_2^*)^{k_2}} \quad (3)$$

Adding the constants (k_1 , k_2) in the form of power to the numerator and the denominator of the Langmuir isotherm, results in Langmuir-Freundlich isotherm [13], which can be written as follows:

$$q_1^* = \frac{q_m b_1 (C_1^*)^{k_1}}{1 + b_1 (C_1^*)^{k_1} + b_2 (C_2^*)^{k_2}} \quad (4)$$

Sag and Kutsal [15] have applied the empirical model of Freundlich to describe biosorption equilibrium in binary systems, which mathematical representation is given by the following equations:

$$q_1^* = \frac{a_1 (C_1^*)^{n_1 + \alpha_{11}}}{(C_1^*)^{\alpha_{11}} + a_{12} (C_2^*)^{\alpha_{12}}}, \quad q_2^* = \frac{a_2 (C_2^*)^{n_2 + \alpha_{22}}}{a_{21} (C_1^*)^{\alpha_{21}} + (C_2^*)^{\alpha_{22}}} \quad (5)$$

where: (a_1 , n_1) and (a_2 , n_2) are the Freundlich isotherm constants obtained from the equilibrium data of the single components. These constants were obtained by Fagundes-Klen [7], where the experiments of the biosorption process of copper and cadmium ions in mono-component system were conducted at 30°C and pH = 5. The other constants (α_{11} , α_{12} , α_{21} , α_{22} , a_{12} , a_{21}) were determined by using the equilibrium binary data.

In the original Langmuir isotherm model for a binary system, the chemical species M₁ and M₂ compete between itself for the occupation of the same biosorbent active site. Jain and Snowyink [9] have considered an adsorption model for binary mixtures based on the hypothesis that when $q_{m_1} \neq q_{m_2}$, the adsorption process occurs without competition. For $q_{m_1} > q_{m_2}$, the number of sites where the competition does not exist is given by the difference ($q_{m_1} - q_{m_2}$). The mathematical representation of Jain and Snowyink model [9] is given by:

$$q_2^* = \frac{q_{m_2} C_2^* b_2}{1 + b_1 C_1^* + b_2 C_2^*} \quad (6)$$

The first term of the right-hand side of Eq. (6) is the expression of Langmuir isotherm for the molecule number of species 1 that adsorb without competition and is proportional to the

number of sites ($q_{m_1} - q_{m_2}$). The second term of the right-hand side represents the molecule number of species 1 that adsorb q_{m_2} sites in competition with species 2, and it is based on the competitive adsorption Langmuir model. The term q_2^* in Eq. (6) represents the molecule number of species 2 that adsorb on the sites of q_{m_2} in competition with species 1. This model was developed originally by Jain and Snowyink [9] and used to predict the behavior of sorption equilibrium in activated carbon for the binary systems.

The presented binary adsorption isotherm models have been used to describe the equilibrium data of the copper and cadmium ions sorption process by the biomass of *S. filipendula*.

Materials and methods

During the experimental assays, the marine algae biomass of *Sargassum filipendula* was used. Initially, it was washed with tap water to remove the impurities and sand, followed by drying in the oven at 60°C for 24 hours. Further, the biomass was submitted to the chemical treatment with a calcium chloride solution for 24 hours, followed by a washing with deionized water and dried in the oven. The copper and cadmium ions solutions were prepared by dissolving copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and cadmium chloride ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$) in deionized water. The prepared solutions were with the initial concentrations in the range from 40 to 450 mg/L. In the biosorption equilibrium study of copper (II) and cadmium (II) ions by *S. filipendula* biomass, batch experiments were carried through at pH = 5, which is optimal value for the biosorption process of many metallic species. Erlenmeyer flasks containing 0.23 g biomass (dry weight) and 50 mL of solution of the metals binary mixture were agitated continuously in a shaker with controlled temperature at 30°C. For pH correction, 0.01 N NaOH and 0.01 N HCl solutions were used. The equilibrium duration time was determined by comparing the values of three consecutive samples. At the end of each assay, the liquid phase was separated from biosorbent by using 0.45 µm Millipore membrane. The initial and equilibrium metal ions concentrations in each flask were determined by atomic absorption spectrophotometer. The assays were carried through in duplicates.

The equilibrium concentration q_j^* of j metallic ion in the biosorbent material was calculated by using the following equation:

$$q_j^* = \frac{V(C_j^0 - C_j^*)}{m_s} \quad (7)$$

where: C_j^0 is the initial concentration of j metallic ion in the solution; C_j^* is the equilibrium concentration of j metallic ion in the solution (at the end of the experiment); V is the solution volume in Erlenmeyer flask and m_s is the biosorbent mass (dry weight).

The equilibrium experimental data have been used for an evaluation of the adsorption isotherms models parameters. The Simplex method of local optimization was used to minimize the objective function (F_{OBJ}) written in the following form:

$$F_{OBJ} = \sum_{j=1}^n \left(\frac{q_{1j}^{Exp} - q_{1j}^{Mod}}{q_{1j}^{Exp}} \right)^2 + \left(\frac{q_{2j}^{Exp} - q_{2j}^{Mod}}{q_{2j}^{Exp}} \right)^2 \quad (8)$$

where: q_{ij}^{Exp} is the experimental equilibrium concentration of the i species in the biosorbent; q_{ij}^{Mod} is the model equilibrium concentration of the i species; n is the number of experimental data; indexes 1 and 2 stand for copper and cadmium ions, respectively.

Results and discussions

Modeling through the adsorption isotherms

The experiments were design for biosorption of the copper and cadmium ions binary mixture by using *S. filipendula* biomass at temperature of 30°C and pH = 5.0. The obtained data were fitted by applying six Langmuir and Freundlich adsorption isotherms models, which mathematical expressions were discussed in section 1.

The model parameters evaluated values have been obtained on the bases of experimental data by minimizing the objective function (see Eq. 8) and are shown in Table 1. For the Cu-Cd binary system, the analysis of obtained results showed that the copper ions were preferentially caught by *S. filipendula* biomass, which is confirmed by the superior values of the parameter b_1 (see models 1, 3 and 4).

Table 1. Estimated parameters values of the binary adsorption isotherms

Model	Eq.	Parameters
Langmuir	(1)	$q_m=1.16$ (meq/g), $b_1= 6.92$ (L/meq), $b_2= 0.69$ (L/meq)
Langmuir with inhibition	(2)	$q_m = 1.11$ (meq/g), $b_1= 0.031$ (L/meq), $b_2= 0.379$ (L/meq), $K= 5.00$ (L/meq) ²
Langmuir modified	(3)	$q_m = 1.27$ (meq/g), $b_1= 7.14$ (L/meq), $b_2= 0.708$ (L/meq), $k_1= 1.04$, $k_2= 1.18$
Langmuir-Freundlich	(4)	$q_m = 1.14$ (meq/g), $b_1= 12.2$ (L/meq), $b_2= 1.10$ (L/meq), $k_1= 0.844$, $k_2= 0.946$
Freundlich	(5)	$a_{11}= 1.62$, $a_{12}= 5,03$, $\alpha_{11}= 0.000097$, $a_{12}= 0.179$, $a_{21}= 0,866$, $\alpha_{22}= 0.619$
Jain and Snowyink	(6)	$q_{m_1} = 1.12$ (meq/g), $q_{m_2} = 0.679$ (meq/g), $b_1= 21.6$ (L/meq), $b_2= 4.03$ (L/meq)

Indexes 1 and 2 stand for copper and cadmium ions, respectively.

The K constant of model (2) is related with the ratio between the formation and consumption rates of the B-M₁-M₂ complex. Results presented in Table 1 show that the value of the constant K is superior compare to the b_2 value, indicating that the formation of B-M₁-M₂ complex is more favorable. In model (3), the k_1 value is close to the unit, while k_2 value is deviated from it. Values of k_1 and k_2 constants close to unit indicate that model (3) is similar with Langmuir original model. The adsorption isotherm model applied by Jain and Snowyink, [9] involved a non-competitive mechanism of the adsorption process. A fraction of biosorbent sites where the copper ions are adsorbed without competition with cadmium ions, is proportional to the ratio $(q_{m_1} - q_{m_2}) / q_{m_1}$ which is equal to 39%. This value represents the fraction of sites that can be occupied exclusively from copper ions. Based on the objective function values, relative average deviation (RAD) and a correlation coefficient, statistical analysis was carried through to evaluate the models behavior.

In Table 2, the objective function values, the relative average errors and the correlation coefficient for copper and cadmium ions are presented.

Analyzing the objective function and relative average deviation values, one can see that the best model to represent the equilibrium data of Cu-Cd binary mixture was the, Langmuir-Freundlich one.

Table 2. Objective function values, RAD stands for binary mixture deviation (Isotherms)

Model	F _{Obj}	Cu (%)	Cd (%)	Correlation Cu (%)	Correlation Cd (%)
1	0.81	10.6	8.5	98.19	98.42
2	0.50	8.5	7.9	99.01	99.45
3	0.71	9.1	8.0	98.63	99.14
4	0.43	9.1	5.3	98.92	99.63
5	1.28	17.3	5.8	95.48	99.52
6	0.51	9.2	6.7	98.92	99.44

The relative average deviation (RAD) was calculated using the following expression:

$$RAD = \frac{100}{N} \sum_{j=1}^n \left(\frac{q_j^{Exp} - q_j^{Mod}}{q_j^{Exp}} \right)^2 \quad (9)$$

In the adsorption binary systems, the removed metal amount of one particular species depends on the equilibrium concentrations of both species in the fluid phase $q_1 = f_1(C_1, C_2)$ and $q_2 = f_2(C_1, C_2)$. Therefore, the representation of the data generates reply surfaces, which direct interpretation for analysis of the competition effects is difficult. Analyzing a binary system, Silva [19] has observed that the concentration effect of one metal provokes the capture of another metal of interest and he has proposed to fix the concentration of the desired metal ion for better evaluation. Hence, based on Langmuir-Freundlich model (best one) it is possible to fix copper equilibrium concentration and to vary the cadmium one. Therefore, it is possible to determine the sorption capacity values of copper and cadmium ions by using Eq. (4). Analogically it can be done for any species of a binary mixture to determine its ions adsorbed amount.

In our experiments, the copper ions equilibrium concentration was fixed at 0.5 and 6.0 meq/L while the cadmium one was varied, where the q_1 and q_2 values of Freundlich isotherm were calculated. The same procedure was applied for cadmium ions, where its concentration was fixed in two levels, varying the concentration of copper ions. In Figs. 1a and 1b cadmium ions concentration effect on the copper ions biosorption capacity is shown, when *S. filipendula* biomass and Langmuir-Freundlich isotherm were applied. It is observed, that the amount of copper ions caught by biosorbent decreased with the increase of the cadmium ions concentration for both applied levels. It was verified, that when the equilibrium copper ions concentration was bigger than (6.0 meq/L), a small amount of cadmium ions was biosorbed. The maximum adsorbed amount of copper ions in the presence of cadmium was about 10%. These results demonstrate a high biomass affinity to the copper ions in a Cu-Cd binary system.

Figs. 1c and 1d show the copper ion concentration effect on cadmium biosorption capacity of *S. filipendula* in equilibrium state, when applied Langmuir-Freundlich binary isotherm. It is observed, that the caught amount of cadmium by the biosorbent decreased with an increase of the copper ions concentration for both chosen levels. It can be noticed, that for low cadmium concentrations the reduction of cadmium adsorbed amount was very significant. When applied equal copper and cadmium ions concentrations, the cadmium removal reached 97% and this fact is explained by the ions competition for the biomass active sites.

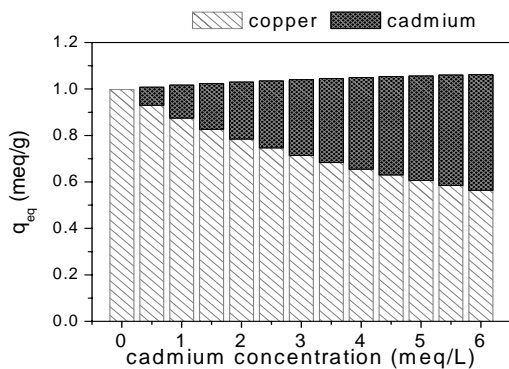


Fig. 1a Section of the binary sorption isotherms surface: sorption capacity of metal ions as a function of cadmium concentration where copper concentration is fixed – 0.5 meq/L (T = 30°C; pH = 5.0)

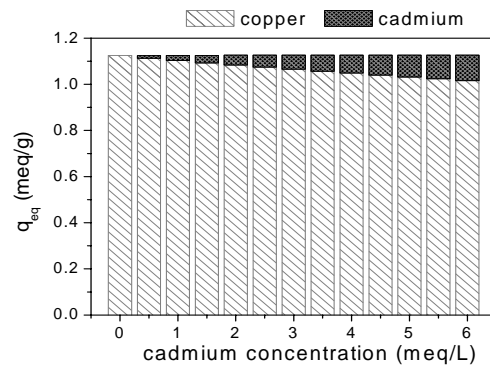


Fig. 1b Section of the binary sorption isotherms surface: sorption capacity of metal ions as a function of cadmium concentration where copper concentration is fixed – 6.0 meq/L (T = 30°C; pH = 5.0)

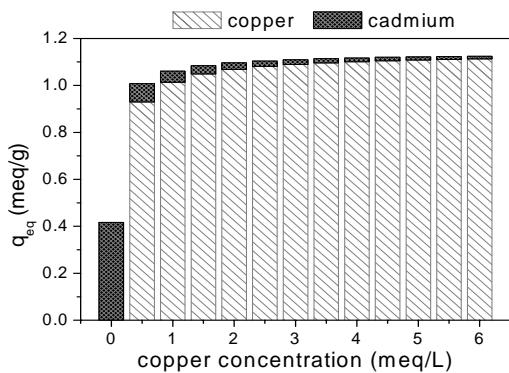


Fig. 1c Section of the binary sorption isotherms surface: sorption capacity of metal ions as a function of copper concentration where cadmium concentration is fixed – 0.5 meq/L (T = 30°C; pH = 5.0)

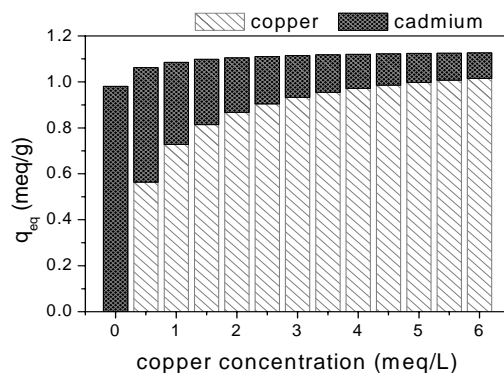


Fig. 1d Section of the binary sorption isotherms surface: sorption capacity of metal ions as a function of copper concentration where cadmium concentration is fixed – 6.0 meq/L (T = 30°C; pH = 5.0)

In Fig. 2 the experimental results fitted by the best Langmuir-Freundlich isotherm model are shown.

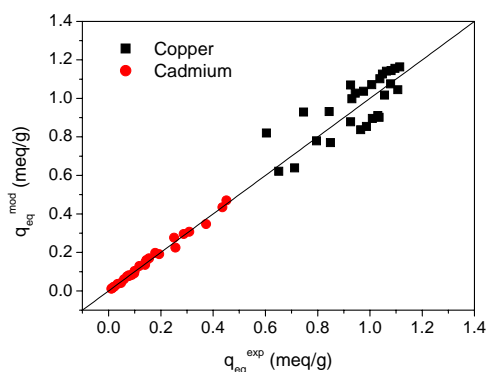


Fig. 2 Langmuir-Freundlich isotherm

During biosorption process, some factors affect the biosorbent preference for metallic ions in solution and they are related to the physical-chemical parameters of the solutions (pH, temperature, etc.), surface specific properties of biosorbent (functional groups, structure, etc.) and the metals properties (electron configuration electronegativity ionic radius and reduction potential, etc.). In Table 3, some physical and chemical properties of Cd and Cu ions are shown.

Table 3. Comparison of some physical-chemical properties of Cd and Cu metal ions

PROPERTIES	Cd (II)	Cu (II)
Electrical configuration	[Kr]4d ¹⁰ 5s ²	[Ar]3d ¹⁰ 4s ¹
Electronegativity	1.69	1.90
Ionic radius (Å)	0.95	0.73
Ionization potential	8.99	7.72
Coordination Number	4.6x10 ⁸	2x10 ⁴
Standard reduction potential (V)	-0.40	0.34

The properties of metallic ions can be significant in biosorption behavior of different biosorbents. The ionic properties such as electronegativity, ionization potential, ionic radius, and standard reduction potential are good indicators of biosorption capacity of mono-component and multi-components systems. Metallic ions with high negative charge will be attached strongly to the biosorbent surface. A small ion radius implies that more molecules may be adsorbed to a biosorbent superficial area. The adsorption capacity increases with an increase of the standard reduction potential. In the binary system the copper (II) ions presented a higher biosorption capacity than cadmium ones because of the mentioned ionic properties.

In Table 3 analyzing the copper (II) ions paramagnetic electronic configuration one can see that these ions have the biggest trend to be attached to the biosorbent magnetic field. In contrast, the diamagnetic electron configuration of cadmium (II) ions shows trend of repelling them by the magnetic field.

In a binary system, the physical-chemical properties of copper ions confirm its affinity and preference during the biosorption process compare to the cadmium ones. However, the order of biosorption preference of the metal ions cannot necessarily follow the described general trends above as some exceptions can be based on a combination of all factors.



To evaluate the biosorption capacity of calcium, copper, cadmium, iron, and zinc ions in multi-component cadmium. Kratochvil and Volesky [10] have used the biomass of *Sargassum sp.* chemically pretreated with CaCl_2 . The authors have observed the following affinity order: $\text{Cu} > \text{Ca} > \text{Cd} > \text{Zn} > \text{Fe}$. For the fungal biomass of *Phanerochaete chrysosporiu*, in competitive conditions Say et al [17] have observed the following biosorption affinity order: $\text{Cu} > \text{Pb} > \text{Cd}$. Saeed et al. [14] have studied the biosorption capacity of copper, cadmium and zinc ions in $\text{pH} = 5$ for the papaya biomass and have obtained similar affinity order: $\text{Cu} > \text{Cd} > \text{Zn}$. The results of all cited above authors have proved our results and understanding that copper ions are preferable in biosorption process compare to the cadmium ones for the studied biosorbents and experimental conditions.

Conclusions

In this work, the equilibrium experimental data of batch biosorption process of copper and cadmium ions binary mixture were obtained by using chemically pre-treated biomass of *S. filipendula* at 30°C and $\text{pH} = 5$. The biomass maximum adsorption capacity for the chosen Cu-Cd binary system was about 1.16 meq/g. Based on performed experiments it was verified that the biomass posses greater affinity to copper ions. Several adsorption isotherm models were used to describe overall biosorption system behavior. Non-linear identification procedure based on statistical least square method and SIMPLEX local optimizer was applied to obtain model parameters values. The Langmuir-Freundlich isotherm was the model that best represented the Cu-Cd equilibrium data.

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