

Equilibrium and Kinetic Studies on the Biosorption of Cu(II) onto *Aspergillus niger* Biomass

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*The solid and liquid waste with heavy metal content that are discharged direct or indirect in environment determine negative effects for organisms, and environment. The main heavy metals found in wastewaters and solid wastes are cadmium, chromium, lead, nickel, zinc, copper, mercury, and arsenic. From these heavy metals, copper in high concentrations determines significant health problems such as hemochromatosis, gastrointestinal diseases, and "Wilson's Disease". Usually, copper toxicity increases in the presence of small amounts of Mo^{+2} ions, Zn^{+2} and SO_4^{2-} . Therefore copper must be removed from wastewaters using various methods. Sorption is one of the most important processes involved in heavy metals, metals and metalloids removal from wastewaters. For sorption can be used synthetic, natural, and biological materials. Biological materials are preferred in heavy metals biosorption because they have many advantages such as: the presence of a large variety of functional sites (imidazole, carboxyl, amino, phosphate, sulphhydryl, phenol, thioether, amide, carbonyl and sulphate) that can be used to bond and to retain pollutants, especially heavy metals from aqueous synthetic solutions or real wastewaters. Compared with conventional methods used in heavy metal removal from wastewaters, biosorption is a more effective alternative to decrease the concentration of heavy metal ions in solution from ppm to ppb level by using low cost materials. Usually this process is one faster than the other heavy metals removal processes. Among the promising biosorbents for heavy metals removal we chose the strain *Aspergillus niger* ATCC 22343 in order to remove Cu(II) from synthetic waters which contain copper sulfide nanoparticles. The kinetic data obtained for the Cu(II) biosorption onto *Aspergillus niger* ATCC 22343 were analyzed using the pseudo-first-order kinetic, pseudo-second-order kinetic, and intraparticle diffusion equations. Kinetic parameters, like rate constants, equilibrium adsorption capacities, and correlation coefficients for Freundlich and Langmuir kinetic models were calculated and discussed. The Langmuir model agreed better with the biosorption of copper ions onto *Aspergillus niger* ATCC 22343.*

Keywords: copper removal, Aspergillus niger, biosorption

Heavy metals are non-degradable and harmful to a variety of living organisms, and for the environment. Through the food chain they can accumulate in organisms [1]. Wastewaters contain heavy metals in dissolved form and as nanoparticle suspensions [2-6].

Nanoparticles have dimensions close to the cellular components, and can interact with protein and nucleic acids. These interactions have negative effects on vital processes such as enzyme function, and gene transcription and translation.

Therefore, removal of heavy metals (dissolved or in suspension) from industrial effluents is essential not only to protect natural ecosystems, but also to slow down the fast depletion of heavy metals sources.

For the removal of copper from wastewaters can be applied the following methods: chemical precipitation, electrochemical treatment, ion exchange processes, solvent extraction, membrane separation and evaporation [7]. Some of these conventional methods are ineffective and unfavorable because they generate large volumes of sludge that have to be removed and processed, and some of them are expensive and determine heavy metal incomplete removal [8].

Biosorption is an alternative method to conventional treatment methods. Biomaterials are used in heavy metals removal from wastewaters because they have many advantages such as reusability, low operating cost, improved selectivity for specific metals of interests, removal of heavy metals found in low concentrations in wastewaters, short operation time, and no production of secondary compounds which can be toxic [9]. As biomaterials used in heavy metal removal from synthetic and real wastewaters can be mentioned: fungi, yeast and bacteria.

Fungal biomass is capable of treating metal-contaminated effluents with efficiencies several orders of magnitude superior to conventional adsorbent materials such as activated carbon, clays, zeolites. Its high biosorption capacity is due to the fact that fungal cell walls contain compounds such as polysaccharides, proteins and lipids whose functional groups can be involved in heavy metals bonding. They also can tolerate adverse conditions like low pH medium.

Mechanisms involved in heavy metal removal by biosorption may be one or a combination of the following: adsorption, electrostatic interaction, complexation, coordination, chelation, ion exchange and microprecipitation.

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Fungal species such as *Aspergillus niger* [2], *Aspergillus flavus* [10], *Aspergillus versicolor* [11], *Fusarium* [12], *Gliomastix murorum* [13], *Cladosporium cladosporioides* [13], *Pleurotus ostreatus* (a macro-fungus) [4], *Pleurotus pulmonarius* [14], *Trametes versicolor* [7], *Penicillium* [15], *Schizophyllum commune* [14], *Rhizopus arrhizus* [16], *Pycnoporus sanguineus* (a white-rot fungus) [17] have been used in copper removal from wastewater.

The present work aims to investigate the ability of *Aspergillus niger* ATCC 22343 biomass to remove Cu(II) from wastewaters which contain copper sulfide nanoparticles by batch system. It was chosen this filamentous fungus with many applications in fermentation industry because of its ease of culturing and lack of pathogenicity to humans and animals [18]. It is preferred over other organisms in bioremediation because it is easier to remove from liquid phase [19, 20].

In this case Cu(II) removal involves in a first stage bioleaching followed by biosorption. The optimum biosorption conditions were determined as a function of initial pH, initial metal ion concentration, and contact time.

Experimental part

Materials and methods

The fungus strain was propagated on potato dextrose agar (PDA) 39 g·L⁻¹ and malt extract 0.1 g·L⁻¹ for 5-7 days at 30°C. Copper(II) uptake studies were carried out in liquid minimal medium containing 30 g·L⁻¹ dextrose, 10 g·L⁻¹ peptone, 0.4 g·L⁻¹ KH₂PO₄, 0.2 g·L⁻¹ KH₂PO₄, 0.2 g·L⁻¹ MgSO₄·7H₂O. The pH of the growth medium was 6.24. After inoculation, flasks were incubated at 150 rpm for 8 days at 30°C using Thermoshake (an Incubator Shaker).

In this study copper was used in the form of copper sulfide nanoparticles. These nanoparticles were previously obtained and characterized [21 - 23]. CuS nanoparticles used have an average diameter of about 20-30 nm [22].

The copper content in final solution was determined using atomic absorption spectroscopy (AAS) (ANALYTIKJENA – AAS Multi-Element with Continuum Source ContraAA®700). In this purpose the contents of the flasks were separated by filtration, and residual copper concentration was determined in the filtrates.

Medium pH was determined using type C830 a multiparameter analyzer.

Biosorption experiments were carried out by batch method using a Thermoshake (an Incubator Shaker) at the speed rotation 150 rpm (rotation per min). The solution volume used was 100 mL, and the copper concentration in solution was in the range of 25 – 100 mg/L. All the experiments were carried out in duplicate.

For the kinetic study *Aspergillus niger* fungal strain was inoculated into 100 mL copper solution with an initial concentration of 25 mg Cu(II)·L⁻¹ obtained in liquid minimal medium containing 30 g·L⁻¹ dextrose, 10 g·L⁻¹ peptone, 0.4 g·L⁻¹ KH₂PO₄, 0.2 g·L⁻¹ KH₂PO₄, 0.2 g·L⁻¹ MgSO₄·7H₂O. The pH of the growth medium was 6.24. Controls were run with a fungal biomass system without copper. Samples were shaken at 150 rpm at 30±1°C for 24, 48, 72, 96, 120 h. After the biosorption experiments samples were filtered. The supernatant was used to analyze the residual copper ion concentration. Equilibrium time and its conditions were determined through the kinetic studies.

Different concentrations of Cu(II) solutions (25, 50, 75, and 100 mg·L⁻¹) were mixed with *Aspergillus niger* fungal strain. The solutions were shaken at 150 rpm and 30±1°C until the equilibrium was reached. The residual copper ion concentration was determined after the biomass filtration.

Aspergillus niger fungal strain was inoculated into 100 mL solutions containing 25 mg Cu(II)·L⁻¹ with an initial pH of 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7 and 7.5. The pH was varied using HCl 1M, and NH₄OH 25% solutions. The mixtures were shaken at 150 rpm until reaching the equilibrium.

At the end of biosorption, biomass of *Aspergillus niger* was contacted with 100 mL of 0.05 HNO₃ in deionized water. The mixture was shaken at 150 rpm on Thermoshake at 30±1°C for 24 h. After elution, the mixture was filtered, and the copper ion concentration of supernatant was determined.

Results and discussions

Copper uptake

Bioleaching and bioaccumulation of copper ion was investigated as a function of initial copper concentration and biomass growth.

Fungal strain of *Aspergillus niger* ATCC 22343 was growing rapidly in the presence of CuS. This fungal strain is characterized by disperse filamentous hyphae (fig. 1).

From this figure it can be seen that the hyphae have a diameter of 10-20 µm, and the length varied between 30-120 µm.

The initial copper ion concentrations in the batch flasks varied between 25 and 100 mg·L⁻¹. Copper was used in the form of copper sulfide (CuS) nanoparticles. The contact time between biomass and solution with CuS was 8 h. It was observed an inverse correlation between copper concentration and biomass growth (table 1). From this table it can be seen that increasing the copper ion concentration reduced the final biomass substantially.

Results obtained for Cu(II) biosorption process are expressed as units of dried cell mass (X_m : g·L⁻¹),

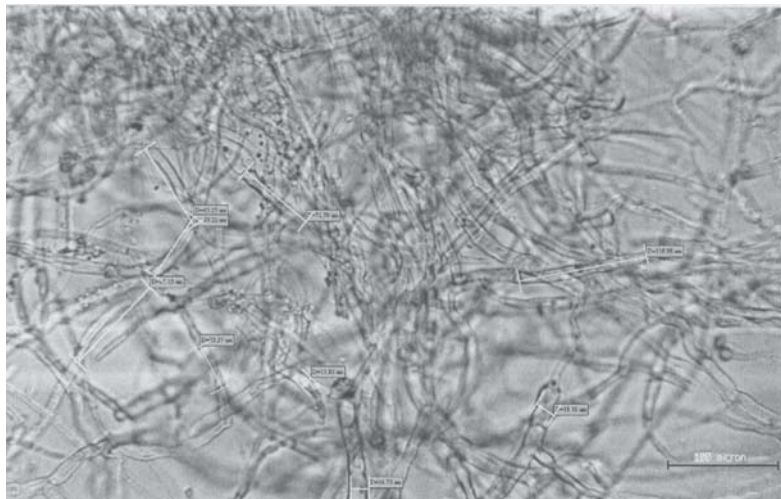


Fig. 1. Morphology of mycelium of *Aspergillus niger* grown in presence of CuS

Table 1
QUANTITY (G) OF BIOMASS OBTAINED WITHOUT AND WITH COPPER IN GROWTH LIQUID MEDIUM

Fungus strain	Initial copper concentration (mg·L ⁻¹)				
	0	25	50	75	100
<i>Aspergillus niger</i> ATCC 22343	16.4529	22.3113	21.7933	19.2967	14.5323

Table 2
REMOVAL OF COPPER BY FUNGAL STRAINS, INCUBATED FOR 8 DAYS AT 30°C WITH SHAKING AT 150 RPM

Fungus strain	Initial copper concentration (mg·L ⁻¹)	X _m (g·L ⁻¹)	C _{acc} (mg·L ⁻¹)	q _m (mg·g ⁻¹)	Uptake efficiency (%)
<i>Aspergillus niger</i> ATCC 22343	25	14.26	23.56	1.65	94.24
	50	16.87	44.32	2.63	88.64
	75	15.11	55.3	3.66	73.73
	100	14.1	77.9	5.53	77.9

bioaccumulated metal ion concentration at the end of growth (C_{acc}: mg·L⁻¹), specific copper uptake as a function of copper ions per unit of dry weight (q_m: mg·g⁻¹), and the percentage uptake efficiency (table 2). This parameter (percentage uptake efficiency is defined as the ration of bioaccumulated copper ion concentration at the end of the growth period to the initial copper concentration.

For the fungus strain *Aspergillus niger* ATCC 22343 it was observed that copper uptake decreases with increasing of copper ion concentration in solution, but for the copper concentration equal with 100 mg·L⁻¹ was observed that the uptake efficiency was higher than determined for solution with 75 mg Cu(II)·L⁻¹.

The maximum uptake efficiency of the copper ions (94.24%) was registered in case of growing of *Aspergillus niger* ATCC 22343 in presence of 25 mg Cu(II)·L⁻¹.

Kinetic studies

Kinetic studies of *Aspergillus niger* fungal strain were performed as batch tests, with the sample removed from the Thermoshaker between 24 and 120 h. These tests were performed in order to establish the factors which influence copper removal processes from wastewaters by *Aspergillus niger* fungal strain.

These experiments were performed in order to verify sorption kinetic models and to investigate the mechanism of sorption and potential rate controlling steps. These parameters are useful for selecting optimum operating conditions for the full-scale batch process. In this context pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models were used.

The kinetic data obtained for copper biosorption by *Aspergillus niger* fungal strain were fitted to the models mentioned above by linear regression analysis.

The pseudo-first-order kinetic model equation [24] is expressed as:

$$\frac{dQ_t}{dt} = k_1 \cdot (Q_e - Q_t) \quad (1)$$

The linear form of the pseudo first-order model is given in eq. (2):

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} \cdot t \quad (2)$$

Equation (3) establishes the mass balance of process at equilibrium condition:

$$Q = \frac{(C_i - C_e) \cdot V}{m} \quad (3)$$

Straight line plots of $\log(Q_e - Q_t)$ against t were used to determine the rate constant, k₁ and correlation coefficient, R² values.

Value of the rate constant k, and correlation coefficient value R² for biosorption of Cu(II) by *Aspergillus niger* ATCC 22343 determined from the experimental value are presented in table 3.

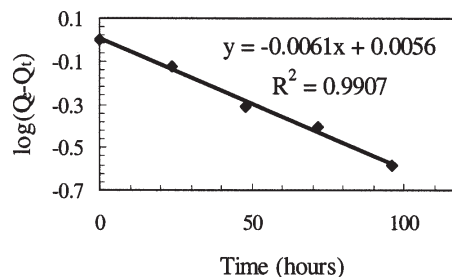


Fig 2. Pseudo-first order sorption kinetics of Cu(II) onto *Aspergillus niger* ATCC 22343

The second-order equation [25] may be expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2 \cdot Q_e^2} + \frac{t}{Q_e} \quad (4)$$

Straight-line plots t / Q_t against t was tested to obtain rate parameters and the results suggested the applicability of this kinetic model to fit the experimental data.

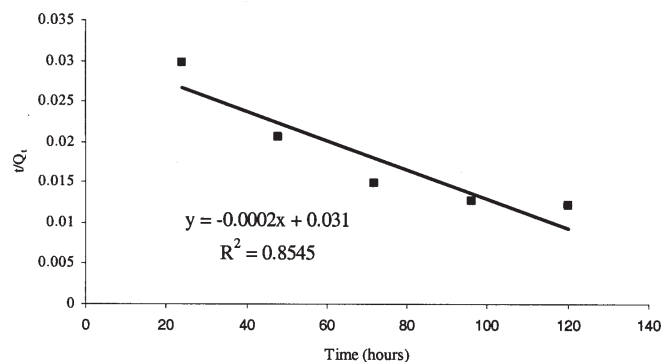


Fig 3. Pseudo-second order sorption kinetics of Cu(II) onto *Aspergillus niger* ATCC 22343

The rate parameters obtained are shown in table 3.

The intraparticle diffusion model can be expressed by following equation:

$$Q_t = k_i \cdot t^{0.5} \quad (5)$$

The k_i is the slope of straight-line portions of the plot of Q_t against t^{0.5}.

Data obtained for intraparticle diffusion kinetics are presented in table 3.

Results presented in table 3 show that the pseudo-first order equation best described the biosorption process followed by intraparticle diffusion.

The applicability of pseudo-first order equation shows that the rate limiting steps is adsorption and the biosorption rate depends on the Cu(II) concentration.

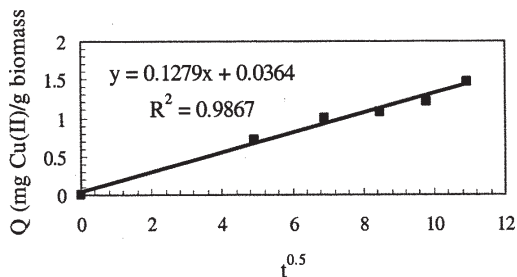


Fig 4. Intraparticle diffusion kinetics of Cu(II) onto *Aspergillus niger* ATCC 22343

Table 3
SUMMARY OF KINETIC PARAMETERS AND CORRELATION COEFFICIENTS FOR THE Cu(II) BIOSORPTION PROCESS

Biosorption kinetics	Rate constant	Correlation coefficient (R ²)
Pseudo-first order kinetic	1.3956·10 ⁻² (min ⁻¹)	0.9907
Pseudo-second order kinetic	1.4887·10 ⁻⁴ (g·mg ⁻¹ ·min ⁻¹)	0.8545
Intraparticle diffusion kinetic	3.6341·10 ⁻² (mg·g ⁻¹ ·min ^{-0.5})	0.9867

Biosorption isotherm

The biosorption capacity of *Aspergillus niger* fungal strain, Q, is calculated by means of equilibrium studies and then summarized using the equilibrium equations of Langmuir and Freundlich.

The most simple sorption isotherm is based on the assumption that every sorption center is equivalent and the capacity of the particles to bond some components is independent of how many adjacent centers are occupied or not with sorbat.

Results obtained from copper retaining on *Aspergillus niger* fungal strain are correlative with Langmuir and Freundlich models in function of the next equations [26, 27]:

$$Q = K_F \cdot C_e^{1/n} \quad (6)$$

or

$$Q = \frac{K_L \cdot C_e}{1 + a \cdot C_e} \quad (7)$$

These models are made in linear form by logarithmation.

$$\log Q = \log K_f + n \log C_e \quad (8)$$

$$\frac{C_e}{Q} = \frac{1}{K_L} + \left(\frac{a}{K_L} \right) \cdot C_e \quad (9)$$

Data obtained for these two models were used to draw the following graphics: $\ln(Q) = f(\ln(C_e))$, and $C_e/Q = f(C_e)$.

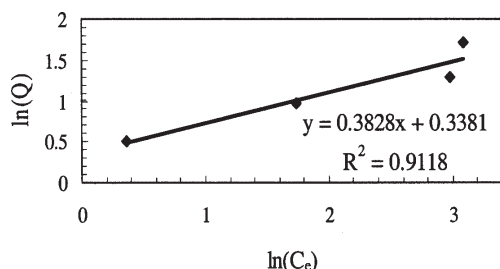


Fig 5. Freundlich linearized sorption isotherms for Cu(II) biosorption on *Aspergillus niger*

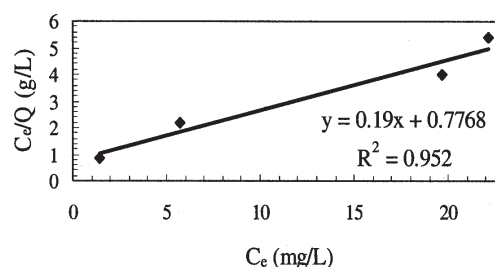


Fig 6. Langmuir linearized sorption isotherms for Cu(II) biosorption onto *Aspergillus niger*

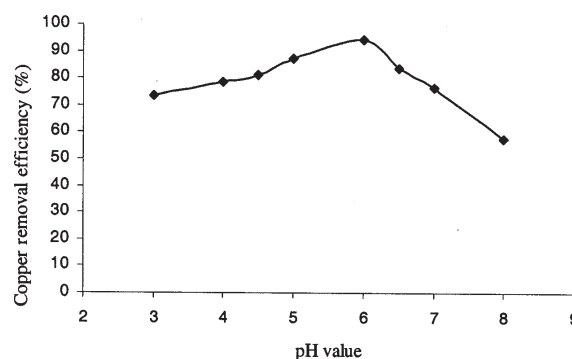


Fig. 7. Effect of pH value on the copper removal efficiency of *Aspergillus niger* ATCC 22343

The table 4 presents the value of the constant and the correlation coefficients (R²) of the Langmuir and Freundlich isotherms determined from intercepts and slopes of linear plots of the Langmuir and Freundlich equations for Cu(II) sorption on *Aspergillus niger*.

The correlation regression coefficient shows that the Cu(II) biosorption onto *Aspergillus niger* can be well defined by Langmuir equation. This model predicts the formation of an adsorbed solute monolayer [28]. There are no interactions between the adsorbed ions, and it is assumed that it occurs the adsorption of one ion per binding site on the homogeneous sorbent surface.

Effect of pH

The removal efficiency was determined over a pH range 3.5-8. Results obtained are presented in figure 7.

Table 4
THE FREUNDLICH AND LANGMUIR PARAMETERS FOR THE BIOSORPTION OF CU(II) ONTO ASPERGILLUS NIGER

MODEL	FREUNDLICH			LANGMUIR		
PARAMETER	K _F	n	R ²	K _L	a	R ²
	1.4022	2.6121	0.9118	1.2873	0.2445	0.9520

From this figure it can be seen that the copper removal efficiency increases with increasing of pH from 3.5 to 6. Maximum biosorption occurs at pH 6. After this value of pH, biosorption capacity decreases due to the formation of copper hydroxides.

These results are in concordance with literature data which mentioned the following values of pH for maximum Cu(II) adsorption: 6.5 for *Aspergillus niger* [4], 5 for *Trametes versicolor* [2], 6 for pretreated *Aspergillus niger* biomass [29].

Elution study

The elution study shows that high desorption and recovery of adsorbed Cu(II) ions could be achieved using acidic solutions. In this case biomass of *Aspergillus niger* was contacted with 100 mL of 0.05 HNO₃ in deionized water, and the copper elution was more than 80%.

Conclusions

Aspergillus niger ATCC 22343 can be considered as an efficient microorganisms for copper biosorption from solutions containing nanoparticles of copper sulfide. The process was mainly influenced by pH, time and copper concentration in initial solution. At pH 6 the removal efficiency was 94.24%. The experimental data were analyzed using Langmuir and Freundlich isotherm model. The equilibrium data for copper biosorption fitted well with the Langmuir isotherm. The maximum biosorption capacity of ATCC 22343 biomass for Cu(II) was found to be 5.53 mg·g⁻¹. The kinetic data were analyzed using pseudo-first order, pseudo-second order and intraparticle diffusion models. Among the kinetic models studied, the pseudo-first order equation was the best applicable model to describe the Cu(II) sorption process.

From these it can be concluded that *Aspergillus niger* ATCC 22343 can be evaluated as an alternative adsorbent for the treatment of wastewater containing Cu(II) ions, being a low-cost adsorbent and having a considerable sorption capacity.

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Nomenclature

a- Langmuir biosorption constant, L·mg⁻¹;
 C_e - equilibrium concentration of copper in solution, mg·L⁻¹;
 C_i - initial concentration of copper in solution, mg·L⁻¹;
 k₁ - rate constant of pseudo-first order sorption, min⁻¹;
 k₂ - rate constant of second-order biosorption, g·mg⁻¹·min⁻¹;
 k_i -intraparticle diffusion rate, mg·g⁻¹·min^{-0.5};
 K_F - equilibrium constant indicative of biosorption capacity for Freundlich model;
 K_L - the saturated monolayer sorption capacity, mg·g⁻¹;
 m - amount of dry biosorbent, g;
 n - equilibrium constant indicative of biosorption intensity for Freundlich model;
 Q -copper uptake per unit of dry biomass, mg·g⁻¹;
 Q_e - biosorption capacity at equilibrium, mg·g⁻¹;

Q_t - amount of metal ions adsorbed at any given time t, mg·g⁻¹;
 V - suspension solution volume, L;

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