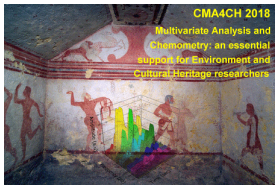

Biosorption of Cu^{2+} Ions Using *Mentha Spicata L.* and *Ruta Graveolens L.*

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Abstract

In the present study the feasibility of two biomaterials based on *Mentha spicata L.* (denoted as MS) and *Ruta graveolens L.* (denoted as RG) from the group of ethereal oil plants for the removal of Cu^{2+} ions from aqueous solution was investigated. Batch experiments were performed to evaluate the effect of contact time, acidity and initial metal concentration on Cu^{2+} removal from aqueous solutions. Pseudo-first order, pseudo-second order and intraparticle diffusion models were used to analyse kinetic data. Equilibrium experimental data were fitted to linear Langmuir, Freundlich and Dubinin-Radushkevich isotherm models and maximum adsorption capacities were calculated.

Introduction

The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, no additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery. The removal of metal ions using biological materials have been widely studied in the last decade due to its potential, particularly in wastewater treatment [1, 2].

There are many potential sources of copper pollution. Although copper is regarded as an essential element at low concentrations, it becomes toxic at higher concentrations and therefore is classified in the second group of toxicity of metal ions [3]. Thus, being a threat to living organisms and especially for humans, copper has to be removed from industrial wastewaters before discharging them in the environment [4, 5].

The present study explores the utilization of MS and RG available in abundance in nature as potential biosorbents for Cu^{2+} ions removal from aqueous solutions. The influence of different parameters on adsorption properties of MS and RG towards Cu^{2+} ions was also investigated.

Materials & Methods

The plant materials were washed with distilled water several times and dried at 60°C for 48 h. The materials were then milled in an electric grinder to a size below 0.1 mm. No other physical or chemical treatment was performed. The initial and equilibrium copper concentrations were determined by means of inductively coupled plasma optical emission spectrometry (ICP-OES) on the PRODIGY 7 ICP-OES spectrometer (Teledyne Leeman Labs, USA). The effect of the acidity on metal removal efficiency was investigated with Cu^{2+} concentration of 200 mg L^{-1} over the pH range 1.8–5.0 (pH-meter model pH 211, Hanna instruments, Germany). This allowed for establishing optimal pH value and for avoiding precipitation of copper (II) hydroxide. To determine the effect of the initial metal ion concentration on the adsorption capacity, Cu^{2+} concentrations in the range 50 - 500 mg L^{-1} at pH 4.0 were chosen. The Cu^{2+} concentrations measured in real surface water samples (collected from water sources located in a copper-mining region in South Bulgaria) are within the selected concentration range. The effect of contact time on the amount of adsorbed Cu^{2+} ions with concentrations of 200 mg L^{-1} was studied at pH 4.0.

Results

The acidity of the aqueous solution is an important controlling parameter in biosorption processes. The optimum pH value was found to be at pH 4 for both samples. The extent of Cu^{2+}

removal increased with the increase in agitation time and reached a maximum value within 10 min. The short time period required to attain equilibrium suggests an excellent affinity of the investigated biosorbents towards Cu^{2+} ions in aqueous solution. In order to determine the rate-controlling mechanism of the biosorption, three kinetic models were applied to the experimental data (pseudo-first order, pseudo-second order and intraparticle diffusion models). The adsorption data were also analyzed with the linearized forms of Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. The calculated kinetic parameters and isotherm constants are presented in Table 1.

It can be concluded that Cu^{2+} adsorption onto both investigated biomaterials could be described better by the pseudo-second-order kinetic model, i.e. the chemisorption is the rate-limiting step. The adsorption isotherm exhibits mainly Freundlich behaviour, which confirms the existence of different types of possible adsorption sites on biosorbent surface with considerable difference in energy. The calculated n-values indicate favourable adsorption onto both investigated biomaterials. It is seen that the biosorbent MS show better adsorption efficiency towards Cu^{2+} than RG. On the other hand, both plant materials show higher adsorption capacities towards Cu^{2+} ions as compared with Cd^{2+} (reported in our previous investigation [6]). This is probably due to the complexation properties of copper ions.

Further investigations will focus on the search of other appropriate plants for the removal of toxic ions from waste waters including statistical data treatment as well as planning of the experiment.

Table 1. Kinetic parameters and isotherm constants for Cu^{2+} adsorption onto the investigated biosorbents

Biosorbent	Pseudo-first order constants			Pseudo-second order constants			Intra-particle diffusion constants		
	Qe (mg g^{-1})	**k_1** (min^{-1})	**r^2**	**Qe** (mg g^{-1})	**k_2** (g $mg^{-1}min^{-1}$)	**r^2**	**k_{id}** (mg g^{-1} $min^{-1/2}$)	**C** (mg g^{-1})	**r^2**
MS	1.58	0.014	0.9837	16.86	3.734	1.0000	0.311	15.11	0.9262
RG	1.16	0.019	0.9530	12.26	3.419	0.9995	0.198	11.12	0.8808
	Langmuir parameters			**Freundlich parameters**			**Dubinin-Radushkevich parameters**		
	Q_0 (mg g^{-1})	**K_1** (L mg^{-1})	**r^2**	**k_F** ($mg^{1-n}L^n$ g^{-1})	**n** (L mg^{-1})	**r^2**	**$Q_{m(o)}$** (mg g^{-1})	**E** (kJ mol^{-1})	**r^2**
MS	46.10	0.009	0.7921	3.02	2.01	0.9754	27.44	0.146	0.7989
RG	38.20	0.009	0.9496	0.90	1.61	0.9819	21.12	0.051	0.7551

Conclusions

The results from the kinetic studies confirmed that the pseudo-second-order mechanism was predominant for the Cu^{2+} adsorption on both investigated biomaterials and best fit was obtained with the Freundlich isotherm model, which indicates heterogeneous surface binding. Maximum adsorption capacities for MS and RG were found to be 46.10 mg g^{-1} and 38.20 mg g^{-1} respectively, thus showing that they could be used as effective biosorbents for the removal of copper ions from aqueous media.

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