



Comparison of Biosorbents and Ion-Exchanger Efficiency for Copper Ions Removal

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Abstract

Copper ions removal by different sorbents from model aqueous solutions was investigated. The decrease of copper ions after addition of biosorbents prepared from mosses *Sphagnum* sp., *Polytrichum commune* and a green alga *Parachlorella kessleri* was compared to copper removal by commercial cationic exchanger Amberlite IR 120. The maximum sorption capacity obtained was 7.4 mg.g⁻¹ (96.1%) and 71 mg.g⁻¹ (95.3%) for ion-exchanger at a solution with concentration of copper ions 16 mg.l⁻¹ and 160 mg.l⁻¹, respectively. A significant copper (II) uptake was achieved within 10 min after addition of biomass *Parachlorella kessleri* and *Sphagnum* sp. Their maximal uptake efficiency 92.8% and 85.4%, respectively is comparable to efficiency of ion-exchanger at low copper (II) concentration in solutions. However, at higher copper concentration ion-exchanger was more efficient in copper removal. The advantage of biomass is high biosorption capacity, high efficiency achieved very quickly and cost-effectiveness especially for solutions with low metal concentration (under 100 mg.l⁻¹). These parameters determine biomass as economical alternatives for metal removal from solution during final, polishing step or drinking water preparation.

Keywords: mosses, green alga, cationic exchanger, copper (II) removal

Introduction

Copper is known to be one of the heavy metals most toxic to living organisms and it is one of the more widespread heavy metal contaminants of the environment. Copper-containing wastewater arises from industrial activities as printed circuit board manufacturing, electronics plating, wire drawing, copper polishing, paint manufacturing, wood preservatives and printing operations (Aksu and İšoğlu, 2005; Farooq et al., 2010; An et al., 2013).

The removal of copper from the waste effluents has received considerable attention because of their association with various health problems. The excessive intake of copper is accumulated in the livers of human and animals, which results in hemochromatosis and gastrointestinal catarrh diseases. It is especially toxic to fish rather than other living organisms when it is available even in a small quantity in natural water (Gundogan et al., 2004; Farooq et al., 2010; An et al., 2013).

There are many different methods for treating wastewaters. Current methods for wastewater treatment include precipitation, coagulation/flotation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, adsorption and ion exchange. Conventional technologies for the removal of toxic metal ions from wastewaters are proving expensive due to non-regenerable materi-

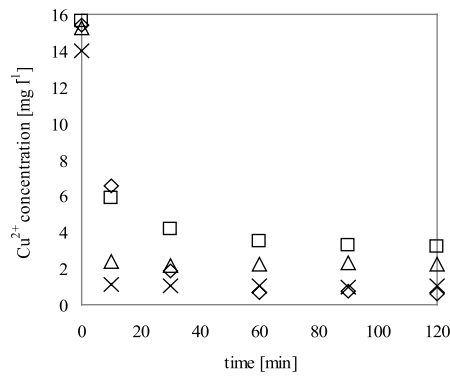
als used and high costs. Biosorption is offering the use of economical alternate and renewable biological materials with high efficiency, high biosorption capacity for metal removal and waste remediation (Volesky, 2003; Pamukoglu and Kargi, 2007; Rengaraj et al., 2007; Jha et al., 2009; Wang and Chen, 2009; Farooq et al., 2010).

The objective of the paper is to compare the utilization of cationic exchanger and biosorbents for the removal/minimization of copper ions from model solutions.

Materials and methods

Sorbents

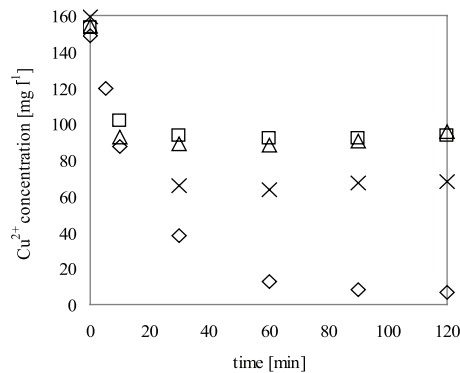
The research was carried out with commercially produced cationic exchanger (Amberlite-IR-120) and three types of biosorbents. Two of them were originated from mosses *Polytrichum commune* and *Sphagnum* sp obtained from the forests near Rožňava (Slovak Republic), washed several times by deionised water, air-dried and homogenized. Dried powdered biomass *Parachlorella kessleri*, an unicellular green alga, obtained from the Institute of Botany of Slovak Academy of Science was used as the third type of biosorbent. The resin was purified and activated by immersing in 4M HCl and 1M NaOH, then it was washed with deionised water several times until the resulting water become neutral and dried at 60°C for 24h.



◇ Ionexchanger □ Polytrichum commune △ Sphagnum sp. × Parachlorella kessleri

Fig. 1. Decrease of copper ions concentration after addition of studied sorbents, $c_0=16 \text{ mg l}^{-1}$

Rys. 1. Spadek stężenia jonów miedzi po dodaniu badanych sorbentów $c_0=16 \text{ mg l}^{-1}$



◇ Ionexchanger □ Polytrichum commune △ Sphagnum sp. × Parachlorella kessleri

Fig. 2. Decrease of copper ions concentration after addition of studied sorbents, $c_0=160 \text{ mg l}^{-1}$

Rys. 2. Spadek stężenia jonów miedzi po dodaniu badanych sorbentów $c_0=160 \text{ mg l}^{-1}$

Metal sorption experiments

For sorption experiments, two model solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with initial concentration 16 mg l^{-1} and 160 mg l^{-1} of Cu^{2+} ions were prepared. The amount of all types added of sorbents was 2 g l^{-1} . The pH of solutions was adjusted to 4–4.5 using 10% solutions of H_2SO_4 and NaOH . The pH of solutions was adjusted to 4–4.5 using 10% solutions of H_2SO_4 and NaOH . These samples were shaken for 24 hours. Solution samples were withdrawn at desired intervals, filtrated and the concentration of copper ions in solutions was determined by atomic absorption spectrometry (Varian AA20+). All samples were triplicated.

The sorption capacity q and the copper ions uptake efficiency Q were calculated using the following relationships:

$$Q_e = \frac{c_0 - c_e}{c_0} \times 100 \quad (1)$$

$$q_e = \frac{(c_0 - c_e) \times V}{m} \quad (2)$$

where:

q_e – the equilibrium sorption capacity (mg.g^{-1}),

Q_e – the copper ions uptake efficiency in equilibrium (%),

c_0 – the initial concentration of copper ions (mg.l^{-1}),

c_e – the equilibrium concentration of copper ions (mg.l^{-1}),

V – the volume of the solution (l),

m – the weight of the sorbent/biosorbent (g).

Results and discussion

The effect of contact time on the decrease of copper ions at initial 16 and 160 mg.l^{-1} Cu^{2+} concentration after the addition of mosses *Polytrichum commune*, *Sphagnum sp.*, the green alga *Parachlorella kessleri* and ion-exchanger are presented in Fig. 1 and Fig. 2.

The experimental data revealed that maximum amount of copper adsorbed by *Parachlo-*

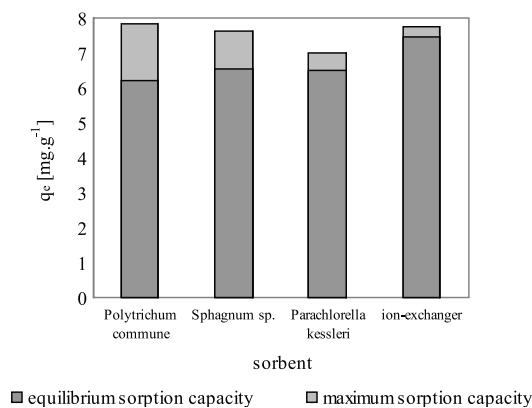


Fig. 3. Comparison equilibrium sorption capacities for studied sorbents, $c_0=16 \text{ mg l}^{-1}$

Rys. 3. Porównanie wydajności sorpcji przy stanie równowagi dla badanych sorbentów $c_0=16 \text{ mg l}^{-1}$

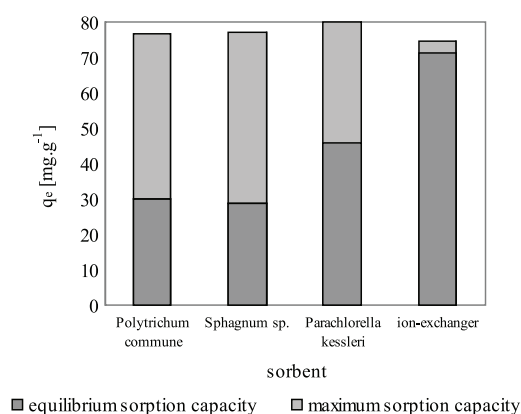


Fig. 4. Comparison equilibrium sorption capacities for studied sorbents, $c_0=160 \text{ mg l}^{-1}$

Rys. 4. Porównanie wydajności sorpcji przy stanie równowagi dla badanych sorbentów $c_0=160 \text{ mg l}^{-1}$

rella kessleri and *Sphagnum sp.* from both model solutions increases rapidly with contact time up to 10 min. *Polytrichum commune* achieves maximum sorption capacity at higher concentration of solution up to 30 min, at lower concentration of solution up to hour. The maximum decrease of the copper (II) concentrations by ion-exchanger was detected after one hour. After 10 min of the process ion-exchanger removed 57.6% of copper ions from solution with Cu^{2+} concentration 16 mg.l^{-1} and 41.1% of copper ions from solution with Cu^{2+} concentration 160 mg.l^{-1} , respectively.

Comparison of equilibrium sorption capacities against maximum sorption capacities theoretically calculated for studied conditions are depicted at input copper(II) concentrations 16 and 160 mg.l^{-1} in Fig. 3 and Fig. 4. Comparison of maximum uptake efficiencies in equilibrium after 2 hours of sorption experiments for both model solutions is plotted in Fig. 5. of copper ions.

The results obtained, as illustrated in Fig. 3–5 clearly showed that in the equilibrium the best sorbent with 96.1% and 95.3% removal of copper ions is commercially produced ion-exchanger for model solutions with lower and higher Cu^{2+} concentration.

To remove copper ions from solution with lower concentration, biosorbents are suitable too. The removal efficiency decreased in the order 92.8% for *Parachlorella kessleri*, 85.4% for *Sphagnum sp.*, 79.5% for *Polytrichum commune*. Biosorbents have lower copper ions removal efficiency from solution with higher concentration in comparison to ion-exchanger. *Parachlorella kessleri* sequestered 57.5% of copper(II), *Polytrichum commune* 39% and *Sphagnum sp.* 37.7%.

The biosorption equilibrium was reached by all studied sorbents up to 2 hours. But biosorbents needed less than 30 minutes (generally 10–15 min) to reach the equilibrium while ion-exchanger more than 1 hour. This fact makes biosorption

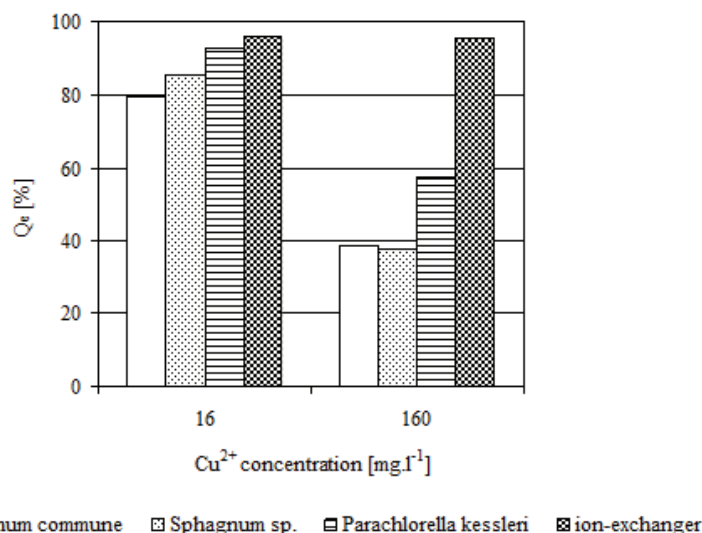


Fig. 5. Comparison of copper ions removal in equilibrium by studied sorbents and different initial concentration of copper ions

Rys. 5. Porównanie usuwania jonów miedzi w stanie równowagi dla badanych sorbentów oraz różnych wstępnych stężeń jonów miedzi

more attractive process for the use in columns. High biosorption capacity, high efficiency, high biosorption rate and cost-effectiveness assign biosorbents as economical alternative materials for metal removal from solution at lower metal concentrations.

Conclusions

The maximum decrease of copper(II) concentration was detected in both model solutions for cationic exchanger. Copper removal efficiency of green alga *Parachlorella kessleri* was comparable to efficiency of commercial ion-exchanger under conditions of lower copper(II) concentration in solution.

The biosorption equilibrium, in both model solutions with low and high Cu²⁺ concentrations, was established within 10 min for green alga *Pa-*

rachlorella kessleri and moss *Sphagnum sp.* and within 30 minutes for moss *Polytrichum commune* which was shorter time compared with commercial cationic exchanger. The results obtained demonstrated that *Parachlorella kessleri*, *Sphagnum sp.* and *Polytrichum commune* could be used as suitable biosorbents for continuous flow water treatment of copper (II) ions from solutions with lower concentration due to the very fast biosorption.

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Porównanie wydajności biosorbentów oraz wymienników jonowych dla usuwania jonów miedzi

Zbadano usuwanie jonów miedzi za pomocą różnych sorbentów z modelowego roztworu wodnego. Zmniejszenie liczby jonów miedzi po dodaniu biosorbentów przygotowanych z mchów *Sphagnum* sp., *Polytrichum commune* oraz zielonych alg *Parachlorella kessleri* porównano z usuwaniem miedzi za pomocą kationowych wymienników Amberlite IR 120. Maksymalna wydajność sorpcji została osiągnięta przy poziomie, odpowiednio, $7.4 \text{ mg} \cdot \text{g}^{-1}$ oraz $160 \text{ mg} \cdot \text{g}^{-1}$. Znaczący wychwyt miedzi (II) został osiągnięty w czasie 10 minut po dodaniu biomasy *Parachlorella kessleri* oraz *Sphagnum* sp. Ich maksymalna skuteczność, odpowiednio 92.8% oraz 85.4% jest porównywalna do skuteczności wymienników jonowych przy niskim stężeniu miedzi (II) w roztworach. Jednakże, przy wyższym stężeniu miedzi wymiennik jonowy był bardziej skuteczny w usuwaniu miedzi. Przewagą biomasy jest wysoka wydajność biosorpcji, skuteczność osiągnięta bardzo szybko przy niskich kosztach, zwłaszcza dla roztworów o niskim stężeniu metali (poniżej $100 \text{ mg} \cdot \text{l}^{-1}$). Parametry te determinują biomasę jako ekonomiczną alternatywę do usuwania metali z roztworu podczas finalnego kroku lub przygotowania wody pitnej.

Słowa kluczowe: mchy, zielone glony, wymiennik kationowy, usuwanie miedzi (II)