International Research Journal of Pure & Applied Chemistry

22(12): 1-11, 2021; Article no.IRJPAC.84518
ISSN: 2231-3443, NLM ID: 101647669

Corn Silk as Biosorbent for Pb, Zn and Cu Removal: Batch and Fixed-bed Column Study

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Authors' contributions

This work was carried out in collaboration among all authors. Author MS did the idea, writing, coordination of the responsibilities for the research activity planning and execution. Author JP did the involvement in experimental setup, writing and editing. Author TS did the involvement in experimental setup. Author MM did the writing and reviewing. Author MK did the application of computational and mathematical study data. Author JD did the isotherm study realization. Author JM did the figure processing. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/IRJPAC/2021/v22i1230447

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/84518

Original Research Article

Received 25 October 2021
Accepted 28 December 2021
Published 30 December 2021

ABSTRACT

In this study, the minimization of heavy metal pollution was investigated. Accordingly, potential of corn silk as biosorbent of Pb, Zn and Cu from multimetal solution was considered in batch and fixed-bed column experiments. Structural changes of corn silk before and after heavy metal removal were determined using SEM-EDX and FTIR analyses. For investigation of biosorption performance the Langmuir and Freundlich isotherm models were applied at batch experimental results. Fast biosorption process and high adsorption capacity (0.382; 0.200 and 0.171 mmol g^{-1} for Pb^{2+}, Cu^{2+} and Zn^{2+}, respectively) confirmed that the corn silk is suitable for heavy metals removal. In order to produce a novel and improved column package for fixed-column bed study implementation, the corn silk was immobilized with alginate. The fixed-bed column was saturated with Pb-Cu-Zn multimetal solution. The breaktrought time is 95, 100 and 90 min for Pb^{2+}, Cu^{2+} and Zn^{2+} respectively, where 87.5, 81.9 and 95.5% Pb^{2+}, Cu^{2+} and Zn^{2+} was removed, respectively. Desorption sudy was performed in HNO_3 (p.a.) solution where high desorption efficiency (>94%) confirmed that imobilized corn silk can be used as alternative material for metal adsorption and could be applied in purification systems.

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Keywords: Biosorption; heavy metals; corn silk; batch; fixed-bed column.

1. INTRODUCTION

Industrialization and technological development are leaving an injurious influences on human life. Heavy metals from industrial effluents represent a major environmental problem, due to their harmful effect and possibility to accumulate in organisms and the food chain. Therefore, global demand is to find a new purification technology that could provide the application of low cost, renewable and efficient materials. For this purpose, widely available agroindustrial lignocellulosic waste materials have been examined over the past decades [1-3]. The surface area with a large number of micron size channels, presence of ion exchangeable cations and large number of hydroxyl, oxygen and carbonyl groups provide these materials suitable for heavy metal adsorption. Preferred characteristics of the adsorbent, which include, high efficiency, selectivity and rapid biosorption process, were confirmed for lignocellulosic materials in many studies. Geoffrey et al. 2018, find that *Moringa olifera* could be used as an effective biosorbent for Ni, Pb, Cr and Cu ion removal [4]. *Allium Cepa* seeds can remove up to 99% of Pb, Cu and Cd ions [5] while rice husk can be used as Pb and Cu adsorbent [6]. Peanut shell showed good adsorption performance for Cu and Cr removal from wastewaters [7].

Our previous investigation established that corn silk could be used as an effective adsorbent of Pb, Cu and Zn ions from a single metal solution [8,9]. Usually, the structure of industrial wastewater is complex. Their composition commonly includes a combination of several different pollutants. Previous studies showed that the competition between heavy metals in contaminated waters negatively affected the biosorption of metal of interest [10]. Physiochemical properties of heavy metals, such as ionic radius, coordination number, electronic configuration and electronegativity are important parameters that affect the biosorption process [11] (Georgievski et al). Therefore, whitin this study, we investigated the potentialy usage of corn silk for the removal of Pb, Cu and Zn ions from multi-metal solution. The FTIR and SEM-EDX of corn silk before and after metal removal were used to detect structural changes caused by biosorption process. The biosorption equilibrium was described using Langmuir and Freundlich isotherm models. Secondly, the fixed-bed column study was done in order to find out the potential application of corn silk for wastewater treatment in real industrial facilities. Biosorbents in the powder form causes some problems in a fixed-bed column, that include clogging, disintegration and separating of material after adsorption [12,13]. In order to overcome these deficiencies, the corn silk was immobilized in Ca-alginate to make an adequate biosorbent for the column reactor.

2. MATERIALS AND METHODS

2.1 Preparation of the Corn Silk

The corn silk (CS) was obtained from the local landfill near the Belgrade. The material was washed with deionized water, dried at room temperature, milled, dried until constant weight and used for batch experiments.

2.2 Immobilization of the Corn Silk within Ca-alginate

Immobilization of the CS was done according to the method described by Yan and Viraraghavan [14] Polymeric solution was prepared by dissolving 2g Na-alginate (Sigma Aldrich, p.a.) in 100 mL distilled water and shaken for 24 h (300rpm) at a mechanical shaker. In homogenous polymeric solution 8g of the CS was added in drops in 0.1M $CaCl_2$ solution forming spherical beds. The beds were left for 12h in 2% $CaCl_2$ solution, dried at 40°C until constant weight and used for fixed-bed column experiments.

2.3 Characterization of the Corn Silk

Morphological characteristics of the CS before and after Pb(II), Cu(II) and Zn(II) biosorption were done by scanning electron microscopy and energy dispersive x-ray analysis (SEM-EDX) by JEOL JSM-6610 LV SEM model.

To determine functional groups at the CS which are involved in Pb(II), Cu(II) and Zn(II) biosorption, the Fourier transform infrared spectroscopy (FTIR) of the CS before and after metal adsorption was done using Thermo Nicolet 6700 FTIR in the spectral range 4000-400 cm^{-1}.

2.4 Batch Experiments

The Pb(II), Cu(II) and Zn(II) solution of 0.1 mol L^{-1} were prepared by dilution of 43.9496 g

$Pb(NO_3)_2x6H_2O$ (p.a.), 24.1798 g $Cu(NO_3)_2x3H_2O$ (p.a.) and 28.7572 g $ZnSO_4x7H_2O$ (p.a.) in 1L distilled water, respectively. Desired pH value adduced by adding 0.1 M NaOH or 0.1M HCl in small quantities. All batch experiments were performed at room temperature, pH 5.0 for 120 min at mechanical shaker (150 rpm). For the isotherm biosorption experiments, the initial metal concentration ranged from 0.2 to 5.0 mmol L^{-1}. At the end of the experiments, the metal concentration in filtered aliquots were measured by AAS (Perkin Elmer 900T).

The amount of biosorbed Pb(II), Cu(II) and Zn(II) was evaluated using following equation:

$$q_e = \frac{C_i - C_e}{V} m \qquad (1)$$

where q_e represents the amount of metal biosorbed on the CS (mmol g^{-1}), C_i and C_e are the initial and equilibrium metal concentrations (mol L^{-1}), V is the metal solution volume (L) and m is the CS mass (g).

The influence of metal ions on the biosorption process of the ion of interest was studied in binary and ternary systems. The binary system contained a different combinations of metal: Pb-Cu, Pb-Zn and Cu-Zn while the ternary system contained all three tested metal ions (Pb-Cu-Zn). All batch experiments were performed at room temperature, pH 5.0 for 120 min at mechanical shaker (150 rpm) and metal concentration of 0.2 mmol L^{-1}. At the end of the experiments, the metal concentration in filtered aliquots were measured by AAS.

2.5 Fixed-bed Experiments

Fixed-bed column studies were performed in glass column of 1.2 cm internal diameter and 30 cm height. Immobilized corn silk (ICS) was packed into column up to desired bed high of 10 cm. The bottom of the column was covered by glass beads to achieve a uniform flow of the solution. Multi metal Pb–Cu–Zn solution of 0.2 mmol L^{-1} concentration and pH 5.0 was flowed down to the column at a flow rate 3mL min^{-1} by a peristaltic pump (Ecoline, Isomatec). The aliquot were sampled at the end of the column and metal concentrations were measured by AAS.

2.6 Desorption Fixed-bed Study

Regeneration of the ICS was performed under the same operating condition as the fixed bed metal sorption study. For this purpose, HNO_3 solution (0.1 mol L^{-1}) was used as eluting agent. At defined time intervals, the aliquots were sampled and metal content were analyzed by AAS.

Desorption efficiency was calculated by the following equation:

$$D = \frac{q_e}{q_a} x100 \qquad (2)$$

Where D is desorption efficiency (%), q_a and q_d is amount of metal adsorbed and desorbed from ICS (mmol g^{-1}), respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization of the Corn Silk

As can be seen from Fig. 1, spectroscopic analysis has shown that the CS has a rough surface area with a large number of micron sized channels and cavities. Accordingly, more sites for metal binding are available, as well as better diffusion of solution through CS was enabled. These characteristics provide the possibility of CS to be applied as suitable metal adsorbent.

The binding of Pb, Cu and Zn ions into active sites on the CS structure caused some morphological changes. As can be seen (Fig 1 (a) – (d)) the CS surface became more dissolute after metal biosorption. Similar findings have been confirmed by other researchers [15,16]. The changes on the CS surface after adsorption process indicate that some chemical changes have occurred during the interaction of metal ions and binding sites. There is no visible aggregates on the CS surface after metal biosorption indicating that there was no microprecipitation of Pb, Cu and Zn ions [17].

The EDX spectrum of the CS (Fig. 1 (e) – (h)), showed that C and O are two basic elements within the CS surface. Since lignin and cellulose have a significant part in the chemical structure of the CS high carbon and oxygen content is entirely expected. From the EDX spectrum of CS before the biosorption process (Fig. 1 (e)), high intensity picks for Ca, K and P are observed.

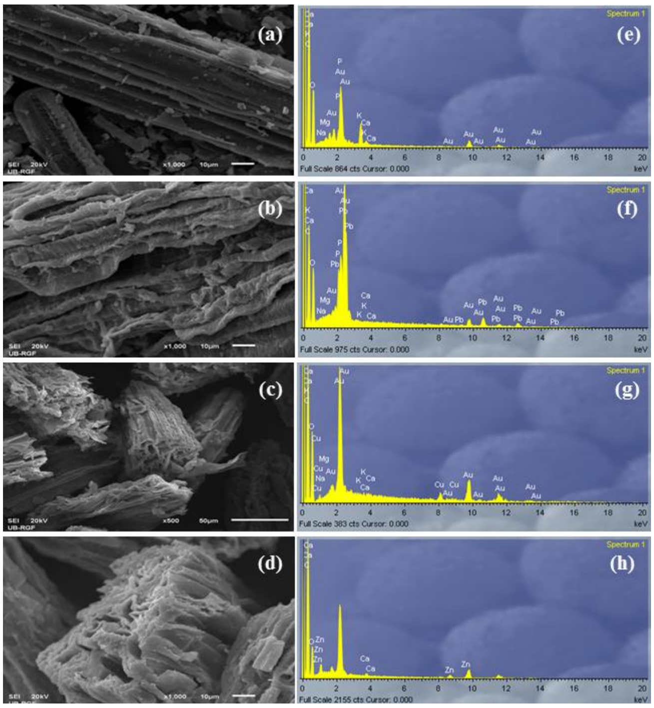


Fig. 1. SEM micrographs of the CS: (a) before and after biosorption process of (b) Pb(II); (c) Cu(II) and (d) Zn(II) ions. EDX spectrum of the CS: (e) before and after biosorption process of (f) Pb(II); (g) Cu(II) and (h) Zn(II) ions

After biosorption of Pb, Cu and Zn ions the intensity of Ca and K picks significantly decreased while the characteristic peaks of Pb, Cu and Zn were observed (Fig. 1 (e) – (h)). According to that, it can be concluded that ion exchange mechanism is responsible for binding of Pb, Cu and Zn ions on the CS surface. Milojković et al., 2014 that investigated the Pb^{2+} biosorption on the water weeds *Myriophyllum* spicatum found according to the EDX spectrum that lead ions was changed with Mg^{2+}, Ca^{2+}, K^{+} and Na^{+} ions from materials surface [18]. Similar results were shown by Mitić-Stojanović et al., 2011 [19].

Fig. 2 represents the FTIR spectra of the CS before and after Pb(II), Cu(II) and Zn(II) biosorption.

The significant changes are observed in the FTIR spectrum of the CS before and after Pb(II), Cu(II) and Zn(II) biosorption (Fig. 2). It is noticeable that intensity of some peaks decreases while the position of some peaks slightly shifted on the spectrum upon metal ions biosorption. The intensity reduction is caused due to the interaction between metal ions and functional groups on the CS surface [20,21]. From the spectrum, it can be observed that the reduction in the picks intensity increases in the range of Zn(II) < Cu(II) < Pb(II). That indicates that the CS has the highest affinity for interaction with Pb(II), then Cu(II) and finally Zn(II) ion. As can be seen (Fig. 2) intensity of all peaks was decreased and peaks at 3287 and 1376 cm^{-1} (assigned to a hydroxyl group) and at 1150 cm^{-1} (assigned to C-O-C group) were shifted after the Pb(II) biosorption. There are also, minor changes in intensity of peaks after Cu(II) and Zn(II) ions biosorption, compared to intensity changes after Pb(II) adsorption.

All these perceived changes in FTIR spectrum after the biosorption process can be attributed to the chemical interaction between Pb(II), Cu(II) and Zn(II) ions and active centers on the CS, either through the complexation and ion exchange mechanism or combination of these two mechanisms [21-23].

3.2 Isotherm Study

Biosorption experiments were conducted at room temperature at different initial concentrations of Pb(II), Cu(II) and Zn(II) ions in solution (0.2 – 5.0 mmol L^{-1}) over 120 minutes and at pH value of 5.0. The experimental results were fitted by Langmuir and Freundlich isotherm models due to investigate biosorption equilibrium between metal ion and the CS surface.

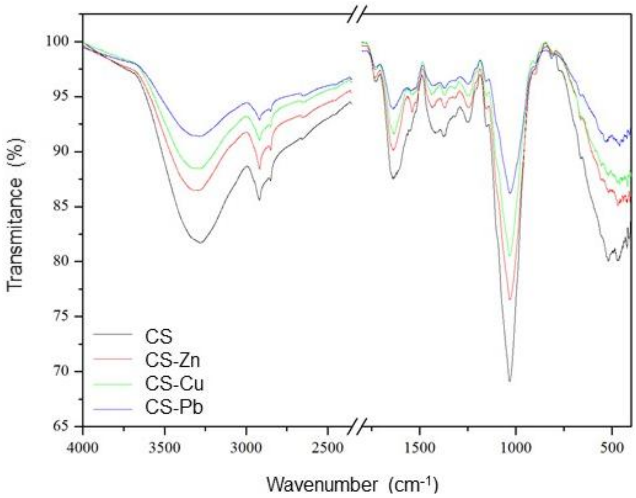


Fig. 2. The FTIR spectra of the CS before and after Pb(II), Cu(II) and Zn(II) biosorption

The Langmuir isotherm model is used to describe a monolayer biosorption process while Freundlich isotherm model describes a multilayer biosorption process on the heterogenous surface. Langmuir and Freundlich isotherm model can be calculated using equations (3) and (5), respectively [24,25]:

$$q_e = \frac{q_{max} K_L C_e}{(1+K_L C_e)} \quad (3)$$

were q_{max} is the maximum amount of metal ion biosorbed on the CS (mmol g^{-1}) and K_L is the Langmuir constant (L mg^{-1}). To describe feasibility of Langmuir model, the dimensionless constant R_L was calculated by following equation:

$$R_L = \frac{1}{(1+K_L C_0)} \quad (4)$$

where Co is the highest initial metal concentration (mmol L^{-1}).

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where K_F is the Freundlich constant and 1/n is an empirical parameter.

The Langmuir and Freundlich isotherm models as well as tabular view of isotherms parameters are presented in the Fig. 3.

As can be concluded, both models are suitable for Pb(II) equilibrium explanation (R > 0.9). This indicates that the biosorption of Pb(II) on the CS appears at heterogenous surface at multilayer biosorption. On the other hand, Langmuir model better describes biosorption of Cu (II) and Zn (II) on the CS, indicating absence of ions interaction at monolayer biosorption. According to the Fig. 3, the RL and n values are ranged between 0-1 and 1-10, respectively. This data suggesting that biosorption of Pb(II), Cu(II) and Zn (II) on the CS are favorable process. According to Langmuir isotherm model the maximum amount of the Pb(II), Cu(II) and Zn(II) ions biosorbed on the CS is 0.382, 0.200 and 0.171 mmol g^{-1}, respectively.

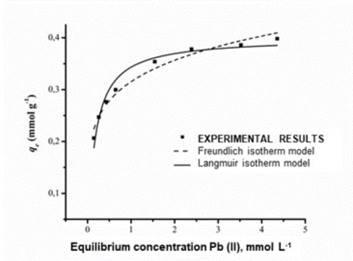
3.3 Biosorption in Multimetal Ion Solution

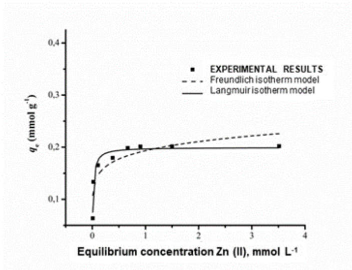
Previous studies have shown that presence of different ions in solution affected biosorption process reducing removal efficiency of ion of interest (Suh and Kim, 2000).

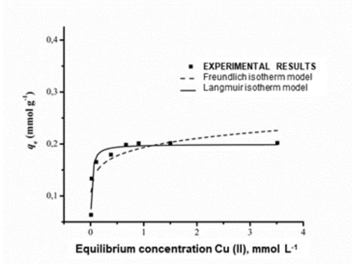
The results of amount and percentage of metal ions biosorbed in single, binary and ternary system of Pb(II), Cu(II) and Zn(II) ions on the CS are summarized in Table 1.

Tabular values are graphically presented at Fig. 4.

In a single metal solution the amount of biosorbed Pb(II), Cu(II) and Zn(II) ions on the CS were 0.184, 0.174 and 0.105 mmol g^{-1}, respectively. The percentage of removed biosorbed Pb(II), Cu(II) and Zn(II) ions on the CS were 88.0, 82.5 and 54.3 %, respectively. Base on the obtained results, it can be concluded that the CS affinity for metal uptake decreased in the following order: Pb(II) > Cu(II) > Zn(II). The influence of removal of ion of interests following at same order.







Metal ion	Langmuir isotherm model				Freundlich isotherm model		
	q_{max} mmol g^{-1}	K_L L mmol^{-1}	R_L	R^2	K_F mmol$^{1-1/n}$ L$^{1/n}$ g^{-1}	n	R^2
Pb (II)	0.382	6.07	0.45	0.968	0.315	5,64	0.976
Cu (II)	0.200	67.42	0.069	0.956	0.190	8,3	0.792
Zn (II)	0.171	59.58	0.062	0.968	0.160	7,93	0.817

Fig. 3. Langmuir and Freundlich isotherm models for Pb(II), Cu(II) and Zn(II) ion biosorption on the CS

Table 1. The amount and percentage Pb(II), Cu(II) and Zn(II) ions on the CS biosorbed in single, binary and ternary system

Ion of interest	Solution	R (%)	q_e (mmol L^{-1})
Pb(II)	Pb	88	0,184
	PbZn	76	0,128
	PbCu	55	0,117
	PbCuZn	50,6	0,085
Cu(II)	Cu	82,5	0,174
	CuZn	69,4	0,153
	CuPb	51,9	0,108
	CuZnPb	35,9	0,064
Zn(II)	Zn	54,3	0,105
	ZnCu	29,2	0,086
	ZnPb	17,8	0,037
	ZnCuPb	5,6	0,012

In binary Pb-Zn and Pb-Cu systems the capacity of Pb(II) removal decreases to 0.128 and 0.117 mmol g^{-1}, respectively while efficiency decreases to 55.0 and 60.6 %, respectively. The highest reduction of Pb(II) removal is in ternary Pb-Cu-Zn system. Similar results were obtained for Cu(II) and Zn(II) ions removal from multimetal solution (Fig. 4, Tab.2). This results are supported with previous investigation in which is concluded that the affinity of material is related to physicochemical characteristic of metal ion such as: ionic radius, electronic configuration and electronegativity [26-28].

3.4 Fixed-bed Column Study

In order to determine the breakthrough curve parameters, the experiment in the fixed-bed column system was conducted. Metal concentration in a multimetal solution was 0.2 mmol L^{-1}, the flow rate was 3 mL min^{-1} and the height of the ICS layer was 10 cm. Breakthrough curve of Pb(II), Cu(II) and Zn(II) biosorption on the ICS was shown in Fig. 5.

The small slope of the folding curves indicates that the process of biosorption of the tested metal ions on the immobilized CS is slow. The slow biosorption process in the flow system is probably caused by the difficult diffusion of Pb(II), Cu(II) and Zn(II) ions through Na-alginate which was used for immobilization of the CS. The simmilar observation also had Tsekova et al., 2010 [29]. This deficiency can be prevented by increasing the specific surface area of the beads by adding Na_2CO_3 to the Na-alginate solution.
Based on the experimental results, the parameters of the breakthrough curve were

calculated using equations 6 - 11 and shown in Table 2:

- Effluent volume, V_{ef} (mL):

$$V_{ef} = Qt_{uk} \quad (6)$$

where: tuk - total time of solution passage (min) and Q - solution flow through the column (mL min-1);

- total amount of adsorbed metal, quk (mmol)

$$q_{uk} = Q/1000 \int_{t=0}^{t=t_{uk}} C_R \, dt \quad (7)$$

where C_R represents metal concentration (mmol L^{-1});

- the amount of metal ions that have passed through the column, m_{uk}

$$m_{uk} = C_i Q t_{uk}/1000 \quad (8)$$

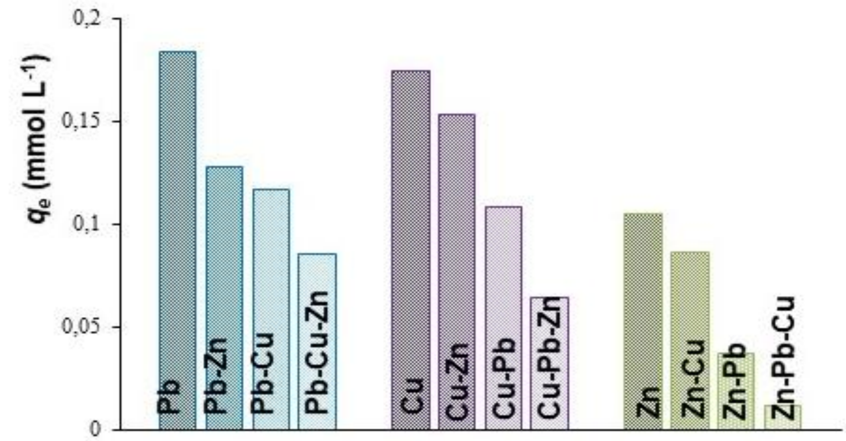
- metal removal percentage, *R* (%)

$$R = (q_{uk}/m_{uk}) \cdot 100 \quad (9)$$

- amount of adsorbed metal in equilibrium, q_e (mmol g^{-1}) and equilibrium concentration, C_e (mmol L^{-1});

$$q_e = q_{uk}/w \quad (10)$$

$$C_e = [(m_{uk} - q_{uk})/V_{ef}] \cdot 1000 \quad (11)$$



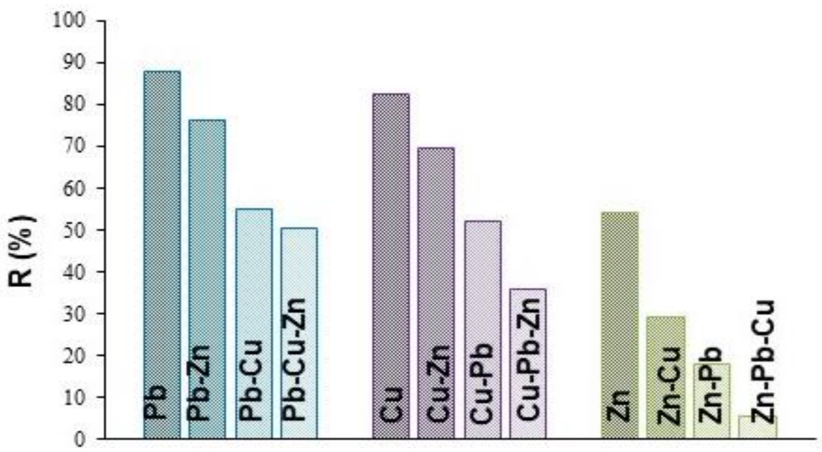


Fig. 4. Mutual impact of Pb(II), Cu(II) and Zn(II) ions on the biosorption performance of the CS

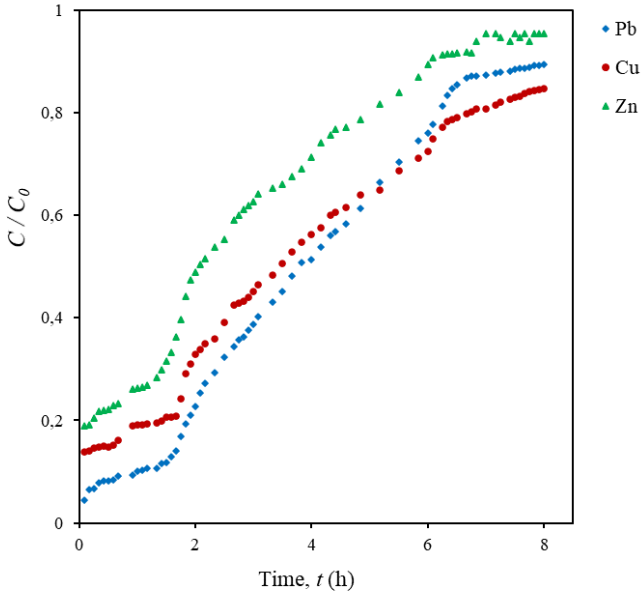


Fig. 5. Breakthrough curve of Pb(II), Cu(II) and Zn(II) biosorption on the ICS

where *w* is mass of biosorbent (g);

- amount of adsorbed metal at breakthrough point, q_p (mmol g^{-1});
- the amount of adsorbed metal at the saturation point, q_z (mmol g^{-1});
- breakthrough time of the curve, t_p (min) - is established when the concentration of metal in the effluent reaches a measurable value;
- the time required for the adsorption zone to pass through the column, t_z (min).

Results summarized in Table 2 demonstrate that biosorption of metal ions on the ICS in fixed-bed column system is very effective process. The ICS was removed 87.5, 81.9 and 95.5% of Pb(II), Cu(II) and Zn(II) ions, respectively.

The breakdown of the curves occurs after 95, 100 and 90 min for Pb(II), Cu(II) and Zn(II) ions, respectively. The amount of adsorbed Pb(II), Cu(II) and Zn(II) ions at the breakthrough point is 0.0038; 0.004 and 0.0036 mmol g^{-1}, respectively.

3.5 Desorption Process in Fixed-bed Study

Desorption process of the ICS was performed under the same operating conditions as the Pb(II), Cu(II) and Zn(II) ions biosorption in fixed-bad system. As desorption eluent was used HNO_3 solution. Acid solution was flowed down to the column through the 120 min and at defined time intervals, the aliquots were sampled and metal content were analyzed. The obtained results are presented graphically at Fig. 6.

Table 2. The parameters of the breakthrough curve of Pb(II), Cu(II) and Zn(II) ions biosorption on the ICS in fixed-bed study

Parametar		Pb	Cu	Zn
V_{ef}	(mL)	1980	1980	1980
q_{uk}	(mmol)	0.252	0.236	0.275
m_{uk}	(mmol)	0.288	0.288	0.288
R	(%)	87.5	81.9	95.5
q_e	(mmol g^{-1})	0.0252	0.0236	0.0275
C_e	(mmol L^{-1})	0.025	0.036	0.009
t_P	(min)	95	100	90
t_z	(min)	385	400	410
q_p	(mmol g^{-1})	0.0038	0.004	0.0036
q_z	(mmol g^{-1})	0.225	0.232	0.192

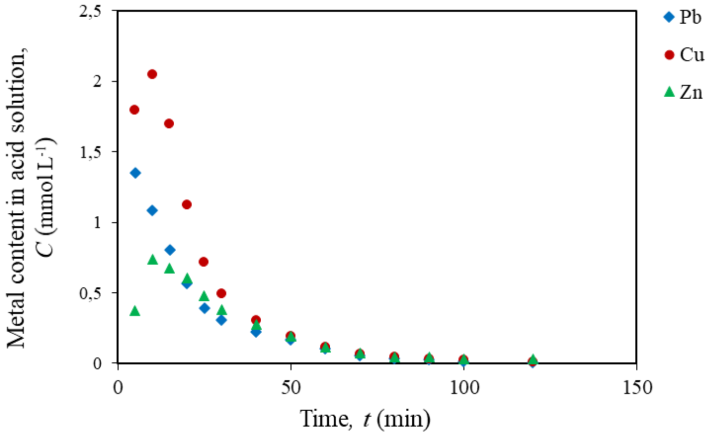


Fig. 6. The regeneration curve of ICS in fixed bed system

As can be seen (Fig. 6), biosorbed metal ions can be effectively removed from the ICS using the HNO_3 solution. Within first 60 min the most of adsorbed ions were desorbed. Desorption efficiency is 98.5, 98.3 and 94.4 % for Pb(II), Cu(II) and Zn(II) ions, respectively. This results indicates that regenerated ICS can be used for new biosorption cycle, therefore, it can be concluded that this material can be efficiently utillized during several adsorption cycles.

4. CONCLUSION

In this study corn silk was investigated as alternative material for Pb(II), Cu(II) and Zn(II) ions removal from water solutions. According to Langmuir isotherm model high adsorption capacitz 0.382; 0.200 and 0.171 mmol g^{-1} for Pb^{2+}, Cu^{2+} and Zn^{2+}, respectively was obtained indicating that the corn silk showed good adsorption performance. In order to find out the potential application of corn silk for wastewater treatment in real industrial facilities the corn silk was immobilized in alginate. Obtained results has revealed that ICS can be excellent material for metal ions removal from multimetal solution in fixed-bad column system. ICS showed high biosorption efficiency: 87.5, 81.9 and 95.5% for Pb(II), Cu(II) and Zn(II) ions removal, respectively. Desorption study was done in fixed-bad column system with diluted nitrit acid. High desorption efficiency >94% proved that ICS could be used in more biosorption cycle and could be suitable material for application in real waste water systems. On the basis of the present study the ICS can be utilized as alternative and efficient low cost material for sustainable application.

ACKNOWLEDGEMENTS

The authors are grateful to the Serbian Ministry of Education, Science and Technological Development for the financial support of this investigation (contract no. 451-03-68/2022-14/200023).

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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