Copper ions biosorption onto bean shells: Kinetics, equilibrium and process optimization studies

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Abstract: The removal of copper ions from aqueous solutions using bean shells as an adsorbent is presented in this paper. The influence of the solution pH on the biosorption capacity was investigated. The biosorption capacity increased with the increase in the solution pH. The pseudo-second order kinetic model showed the best agreement with the analysed experimental data, indicating that chemisorption could be a possible way of binding the copper ions to the surface of the bean shells. The Langmuir isotherm model best fitted the analysed isotherm data. The SEM-EDS analysis was performed before and after the biosorption process. The change in the morphology of the sample after the biosorption process was evident, whereby K, Mg, Si and Ca were possibly exchanged with copper ions. Response surface methodology (RSM) based on the Box–Behnken design (BBD) was used to optimize the biosorption process, with the selected factors: the solution pH, initial copper ions concentration and contact time. The optimum biosorption conditions were determined to be: pH 3–4, initial copper ions concentration, 100 mg dm^{-3}, and contact time, 10–30 min.

Keywords: biosorption; copper ions; bean shells; kinetics; Box–Behnken design.

INTRODUCTION

Concentrations of heavy metal ions in wastewaters originating from various industrial systems are often significant. These wastewaters can pose a serious threat to the surrounding ecosystems when discharged without previous treatment.[1]

Wastewaters polluted with heavy metals are treated by well-known conventional technologies, such as: adsorption, coagulation and flocculation, ion exchange, membrane filtration, precipitation and others.[2–4]

Biosorption is a possible alternative method for heavy metal ions removal. This process is considered "user-friendly" with various advantages, including specific affinity, low cost and simple design. It is based on adsorption with agricultural or industrial by-products being used as adsorbents. These by-products are convenient for the described use due to their abundant availability, favourable physical, chemical and surface characteristics, and their low cost.[4]

Copper is a widely used metal due to its excellent electrical and thermal conductivity, excellent corrosion resistance, and good resistance to strength and fatigue. Pure copper is widely used in the production of cables and wires and many other parts in the electrical industry. Due to its excellent anti-corrosion properties, copper is used for pipes, valves, and fittings in systems that carry drinking water, process water or some other type of water. Copper extraction, as well as its production, is the main source of pollution with this heavy metal. The excessive copper concentrations in the environment are highly toxic for living organisms. It inhibits cell growth, impacts metabolism, and other processes. For this reason, it is very important to develop a sustainable, green remediation technique for copper removal, that is also economical, efficient and environment-friendly.[5]

The aim of this work is to determine whether bean shells can be used as an adsorbent for copper ions biosorption from aqueous solutions.

The successful use of bean shells as an adsorbent for lead ions biosorption produced the idea of investigating the potential use of this biomass as an adsorbent for other heavy metals.[6]

For this purpose, kinetics, isotherm and SEM-EDS analyses of the data were obtained and shown in this paper. The process was also modelled by response surface methodology using Box–Behnken design to analyse the influence of three variables on the biosorption process and to determine their optimal values.

EXPERIMENTAL

Bean shells collected on the fields in the village Rudna Glava (Eastern Serbia) were used as an adsorbent for copper ions biosorption experiments.

0.5 g of been shells were used as samples for biosorption experiments. The bean shells samples were rinsed with 200 mL of distilled water, prior to the biosorption experiments, in order to remove the physical impurities.

Biosorption experiments were conducted using synthetic copper ions solutions prepared with $CuSO_4·5H_2O$ (*p.a.* purity). The solutions were prepared by mixing different amounts of the copper sulfate with distilled water, in order to obtain the concentrations needed for the specific experiment. The stock solution concentrations varied based on the specifics of the experiment. The solution pHs was adjusted with 0.1 M HNO_3 and 0.1 M KOH solutions.

All experiments were performed in batch conditions. Cu(II) content was determined on a spectrophotometer (Spectroquant Pharo 300 – Merck, Rahway, NJ, USA), by forming a complex with NH_4OH (*p.a.* purity), at 610 nm wavelength. The SEM-EDS analysis was performed on a SEM scanning electron microscope (Vega 3 LMU, Tescan, Brno, Czech Rep-

ublic) with an integrated energy-dispersive X-ray detector (X act SDD 10 mm^2, Oxford Instruments, Abingdon, UK).

The full characterization and preparation of the biosorbent are reported in a previous publication.[6]

Process parameters, such as: process time, initial copper ions concentration, initial solution pH and temperature were adjusted depending on the performed experiment.

The biosorption capacity and the Removal in % were calculated using the following equations:

$$q_t = \frac{V(c_i - c_t)}{m} \tag{1}$$

$$Removal = 100\left(1 - \frac{c_t}{c_i}\right) \tag{2}$$

where q_t is the adsorbent capacity defined as mass of the adsorbed metal per unit mass of the adsorbent (mg g^{-1}) at time t; c_i is the initial metal ion concentration in the solution; c_t is the metal ion concentration in the solution at time t; m is the adsorbent mass; V is the volume of the solution; Removal is the degree of the adsorbed copper ions.

RESULTS AND DISCUSSION

The influence of the solution pH on the adsorption capacity

To determine the influence of the solution pH on the biosorption capacity (Fig. 1), a number of experiments were performed, and the initial solution pHs was adjusted in the range from 2 to 5. 50 mL of copper ions solutions (initial concentration 200 mg dm^{-3}) was brought into contact with 0.5 g of been shells for 60 min. The experiments were performed in batch conditions, at room temperature, on a magnetic stirrer (with the stirring rate set at 300 rpm).

As can be seen from Fig. 1, the solution pH had a significant effect on the biosorption capacity. An increase in the biosorption capacity with the increase of the solution pH could be noted. At pH 2, the biosorption capacity was 1.739 mg g^{-1}, while the maximum capacity of 12 mg g^{-1} was achieved at pH 5.
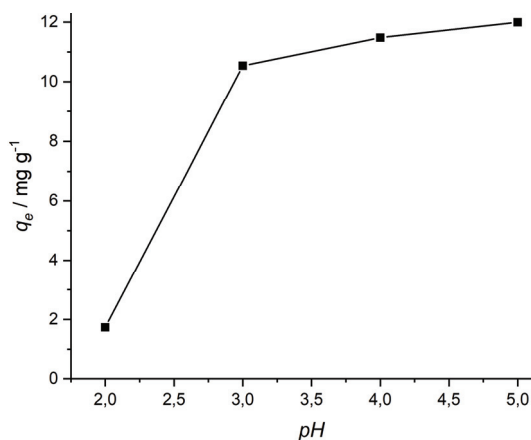

Fig. 1. The influence of solution pH on the adsorption capacity.

A lower biosorption capacity at lower solution pH could be a result of a higher concentration of H$^+$, which occupied the active sites in the structure of bean shells and suppressed the already adsorbed Cu^{2+}. At higher pH, the concentration of H$^+$ in the solution were lower, resulting in a higher biosorption capacity.[7]

Adsorption kinetics

Kinetic models are often used for analysing the experimental data to determine the biosorption rate, the step that dictates the rate of the process and its mechanism.[8]

In this paper, pseudo-first order kinetic model, pseudo-second order kinetic model, intraparticle diffusion (Webber–Morris) kinetic model and Elovich kinetic model were used to analyse the obtained experimental data. Details are presented in Supplementary material to this paper.

In order to obtain the biosorption kinetic data, 50 mL of copper ion solutions (initial concentration 200 mg dm^{-3}) were brought into contact with 0.5 g of bean shells, for different process time (ranging from 1 to 90 min). The change in the biosorption capacity with time is shown in Fig. 2. It can be noted that the biosorption capacity increased rapidly at the beginning of the process (first 5 min), as a result of a large number of available active sites in the structure of the bean shells.[9] After this initial period, a slower increase in the biosorption capacity was noted (10–90 min), reaching a constant value after 90 min of the process.
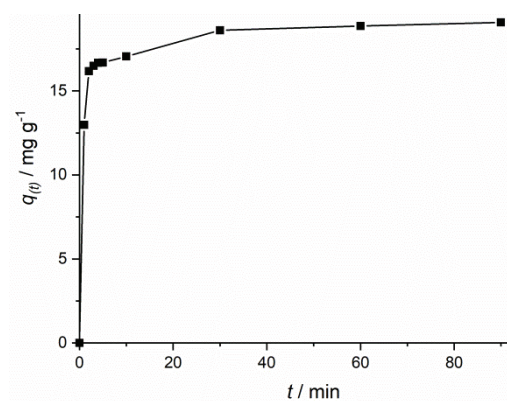

Fig. 2. Change in the adsorption capacity with time.

Pseudo-first order kinetic model

This model is based on the assumption that adsorption is a reversible process.[10]

The plot log (q_e–$q_{(t)}$) *vs.* t gives a linear dependence that serves as a base to determine the first-order kinetic model parameters. The obtained experimental data shown in Fig 2 were linearized and the obtained plot is shown in Fig. 3a. The obtained kinetic parameters corresponding to this model are given in Table I.
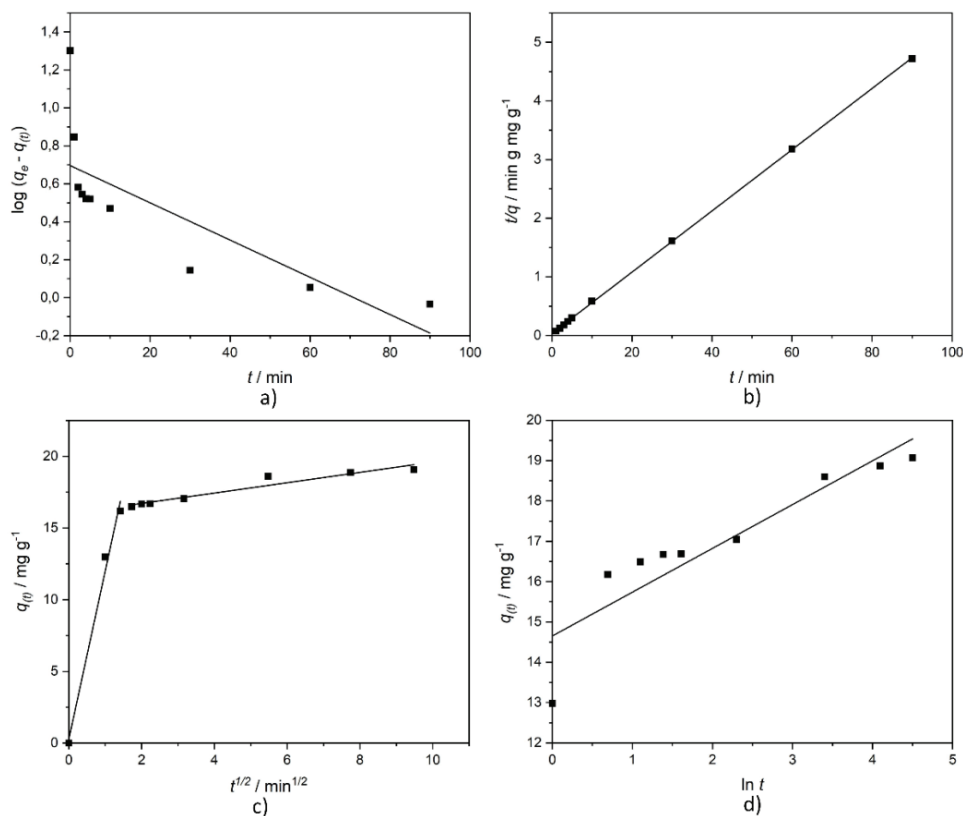
Fig. 3. a) Pseudo-first order kinetic model; b) pseudo-second order kinetic model;
c) intraparticle diffusion kinetic model; d) Elovich kinetic model.

Pseudo-second order kinetic model

Pseudo-second order kinetic model is based on the assumption that adsorption and ion exchange take place on the surface of the adsorbent, and that the adsorbate is bound to the adsorbent surface by chemisorption.[11]

Plot $t/q_{(t)}$ *vs.* t, shown in Fig. 3b, was used to determine the kinetic parameters for this model, which are given in Table I.

Intraparticle diffusion kinetic model (Webber–Morris model)

This model assumes that the adsorption does not occur only on the surface of the adsorbent, but that the diffusion and adsorption inside the adsorbent structure are also present.[12]

The plot $t^{1/2}$ *vs.* $q_{(t)}$, shown in Fig. 3c, is used to obtain the intraparticle diffusion kinetic model parameters shown in Table I.

Elovich kinetic model

This model was primarily used to analyse gas chemisorption onto solid adsorbents, but was later successfully applied on the adsorption of toxic materials from aqueous solutions.[13]

From the plot $q_{(t)} = f(\ln t)$, shown in Fig. 3d, the Elovich kinetic model parameters were determined and given in Table I.

TABLE I. Kinetic model parameters for copper ions biosorption onto bean shells

Model	Parameter	Value
Pseudo-first order kinetic model	k_1 / min^{-1}	0.023
	$q_{e,exp}$ / mg g^{-1}	19.07
	$q_{e,cal}$ / mg g^{-1}	4.97
	R^2	0.596
Pseudo-second order kinetic model	k_2 / g mg^{-1} min^{-1}	0.077
	$q_{e,exp}$ / mg g^{-1}	19.07
	$q_{e,cal}$ / mg g^{-1}	19.16
	R^2	0.999
Intraparticle diffusion kinetic model	k_{i1} / g mg^{-1} min$^{-0,5}$	11.722
	C_{i1} / mg g^{-1}	0.285
	R_1^2	0.989
	k_{i2} / g mg^{-1} min$^{-0,5}$	0.360
	C_{i2} / mg g^{-1}	15.995
	R_2^2	0.929
Elovich kinetic model	α / mg g^{-1} min^{-1}	14.652
	β / g mg^{-1}	1.086
	R^2	0.837

Based on the obtained correlation coefficients, it can be concluded that the adsorption kinetics could be fairly modelled with the pseudo-second order kinetic model, which led to the conclusion that chemisorption was a possible way of binding copper ions onto active sites in the adsorbent structure. This statement was also supported by the negligible difference in the values of calculated and experimentally obtained adsorption capacity ($q_{e,cal}$ and $q_{e,exp}$).

Adsorption isotherms

Adsorption isotherms are used to gain insight into the mechanism of the adsorption process, as well as to determine the maximum adsorption capacity.[14]

In this paper, the linear Langmuir, Freundlich and Temkin isotherm models were used to describe copper ions biosorption onto bean shells. Details are presented in Supplementary material.

Biosorption isotherm data was obtained by performing the following experiment: 0.5 g of bean shells samples were brought into contact with 50 mL of copper ions solutions, of different initial Cu^{2+} concentrations (in the range from 50

to 500 mg dm^{-3}). The suspension was stirred on a magnetic stirrer, at room temperature for 90 min.

The obtained experimental adsorption isotherm data for copper ions adsorption onto bean shells is shown in Fig. 4a.
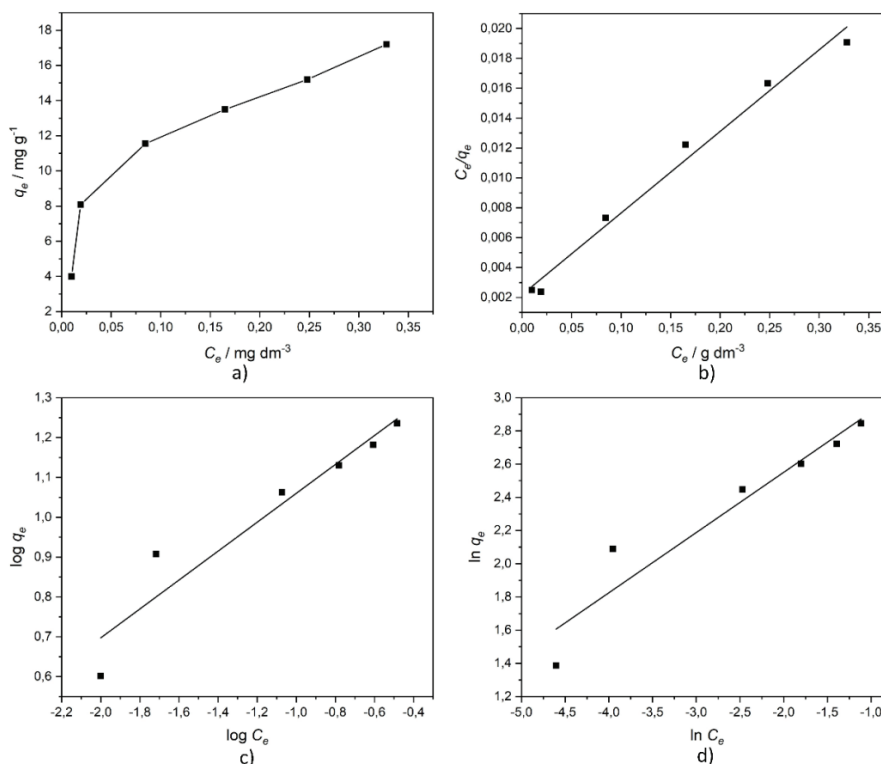

Fig. 4. a) Experimental adsorption isotherm data; b) Langmuir adsorption isotherm model; c) Freundlich adsorption isotherm model; d) Temkin adsorption isotherm model.

Langmuir isotherm model

This model is based on the assumption that the adsorption process occurs on specific homogenous sites inside the adsorbent structure.[15]

The Langmuir isotherm data were calculated from the plot C_e *vs.* C_e/q_e shown in Fig. 4b, and given in Table II.

Freundlich isotherm model

Freundlich model represents the earliest known relationship that describes the non-ideal and reversible adsorption. This model can also be used to study multilayer adsorption.[16]

The plot log q_e *vs.* log C_e (Fig. 4c) provided the required data for the Freundlich model isotherm data calculation, which are shown in Table II.

Temkin model

This model assumes that the heat of sorption of all molecules linearly increases with the coverage of the adsorbent surface and that there is a uniform distribution of binding energies up to maximum binding energy.[16]

Temkin constants B and K_T were determined from the plot $\ln C_e$ *vs.* q_e (Fig. 4d), and given in Table II.

Based on the analysed data and the obtained results (Table II), it can be concluded that the Langmuir isotherm model was the best fit for the experimental data ($R^2 = 0.986$), which indicated that the surface of the adsorbent was homogenous, and the biosorption of copper ions onto bean shells occurred in a monolayer.[17]

TABLE II. Adsorpton isotherm model parameters for copper ions biosorption onto bean shells

Langmuir				Freundlich			Temkin		
K_L / dm^3 mg^{-1}	q_{exp} / mg g^{-1}	q_m / mg g^{-1}	R^2	K_F	$1/n$	R^2	B / J mol^{-1}	K_T / dm^3 g^{-1}	R^2
24.9	17.2	18.3	0.99	1.42	0.36	0.92	0.36	3.28	0.92

The performance of the adsorbent is usually defined by the maximum biosorption capacity. Based on the results in copper removal with various biosorbents reported in other works (shown in Table III), it can be concluded that bean shells could play an important role as a cost-effective biosorbent for the copper ions removal.

TABLE III. Cu^{2+} biosorption on bean shells in comparison with other adsorbents

Biosorbent	Maximum biosorption capacity (q_m / mg g^{-1})	Data
Bean shells	18.3	This work
Wheat straw	4.30	[18]
Sawdust of deciduous trees	9.90	[19]
Myrica esculenta	39.4	[20]
Activated sawdust powder	10.4	[21]
Rosa damascena leaves	25.1	[22]
Carbonized sunflower stem	20.0	[23]
Combretum indicum	12.1	[24]

SEM-EDS analysis

The SEM-EDS analysis was performed on samples before and after the biosorption of copper ions. The obtained results are shown in Fig. 5. Before the biosorption of copper ions (Fig. 5a) a porous structure was noticed, with visible cavities and macro-pores. The presence of these pores and cavities facilitated the penetration of the aqueous phase into the adsorbent structure.[25] The EDS spectrum of the sample before biosorption of copper ions (Fig. 5b) suggested the presence of O, Mg, Si, K and Ca.
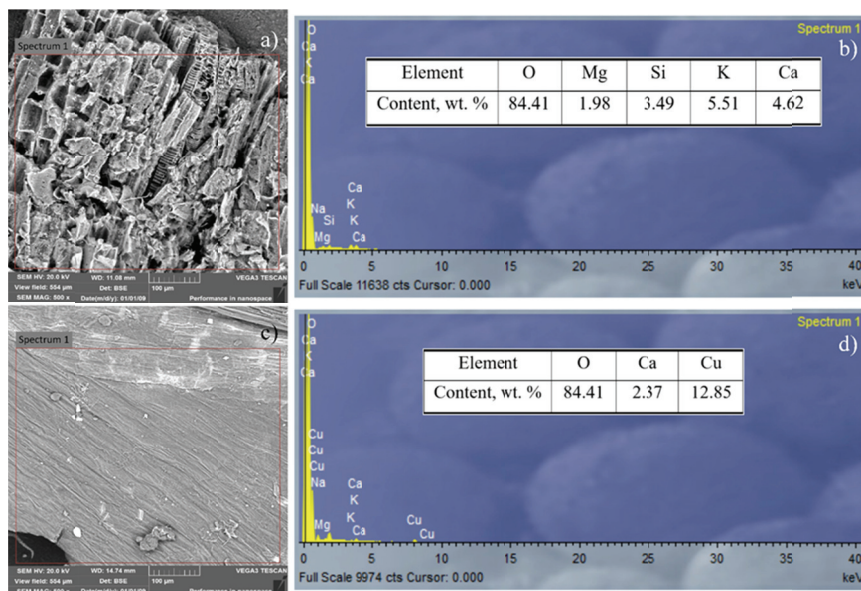
Fig. 5. SEM-EDS analysis before and after the biosorption of copper ions.

After the biosorption process, the SEM analysis (Fig. 5c) showed a more compact structure, with the absence of macro-pores and cavities, as a result of the incorporation of copper ions into the molecular structure of the bean shells. The obtained EDS spectrum after the biosorption of copper ions (Fig. 5d) demonstrated the presence of O, Ca and Cu. The absence of Mg, Si, K and detected lower levels of Ca, indicated that any of these ions could be exchanged with copper ions during the biosorption process.

Optimization of the biosorption conditions – Box–Behnken experimental design

Copper ions biosorption onto bean shells was optimized using an experimental design, in order to determine the effects of three selected independent variables on the percentage of Cu^{2+} removal (dependent variable).[26] The optimum biosorption conditions were determined by the means of Box–Behnken design (BBD) and response surface methodology (RSM). The RSM is a set of techniques useful for evaluating the relationships between a number of experimental factors and measured responses.[27] The BBD was applied, comparing three factors: solution pH (X_1), initial copper ions concentration (X_2), and contact time (X_3). The chosen experimental ranges and levels in the design are given in Table IV. The experimental design matrix, as well as the response Y (adsorption degree), are given in Table V. All the experiments are performed in batch conditions, at room temperature, on a magnetic stirrer (with the constant stirring rate, set at 300 rpm).

TABLE IV. Experimental ranges and levels in the experimental design

Factor	Range level		
	−1	0	1
X_1 – solution pH	2	3	4
X_2 – Initial metal ion concentration, mg/L	100	500	1000
X_3 – Contact time, min	10	30	60

TABLE V. Box–Behken Design matrix for three factors along with observed response for Cu^{2+} biosorption onto bean shells

Run	X_1: solution pH	X_2: Initial Cu^{2+} concentration, mg dm^{-3}	X_3: Contact time, min	Y: Removal, %
1	2	100	30	32.95
2	4	100	30	86.52
3	2	1000	30	22.58
4	4	1000	30	11.89
5	2	500	10	30.55
6	4	500	10	23.84
7	2	500	60	20.86
8	4	500	60	39.75
9	3	100	10	87.79
10	3	1000	10	6.922
11	3	100	60	69.70
12	3	1000	60	7.102
13	3	500	30	25.07
14	3	500	30	31.36
15	3	500	30	38.86

The correlation between the independent variables are given in Supplementary material.

The statistical significance of the model was evaluated by the analysis of variance (ANOVA) and presented in Table VI. The significance of each coefficient was determined by the magnitude of the *F*-values and *P*-values, given in Table VI. The larger the *F*-value, and the smaller *P*-value, the corresponding coefficient was more significant. *P*-values less than 0.0500 indicated high significant regression at 95 % confidence level.[27]

The suitability of the model was confirmed by the regression coefficients of the predicted and experimental responses (R^2 = 0.924 and adj-R^2 = 0.787). This suggested that 96 % of the responses were explained by the used model. The corresponding *F*-value (6.76) and *P*-value (0.024) indicated that the model was significant. *P*-values lower than 0.0500 in the cases of X_2 (initial Cu^{2+} concentration) and X_1X_2 (solution pH combined with the initial Cu^{2+} concentration) indicated that these were the significant model terms.

The relationship between the experimental responses and the responses predicted by the model is shown in Fig. 6.

TABLE VI. ANOVA analysis for response surface model in relation to Cu^{2+} biosorption onto bean shells

| Source	DF	Adj-SS	Adj-MS	F-Value	P-Value
Model	9	8676.69	964.08	6.76	0.024
Linear	3	6920.46	2306.82	16.17	0.005
X_1	1	378.85	378.85	2.66	0.164
X_2	1	6524.53	6524.53	45.74	0.001
X_3	1	17.08	17.08	0.12	0.743
Square	3	476.86	158.95	1.11	0.426
X_1^2	1	50.70	50.70	0.36	0.577
X_2^2	1	401.23	401.23	2.81	0.154
X_3^2	1	1.76	1.76	0.01	0.916
2-Way interaction	3	1279.36	426.45	2.99	0.135
X_1X_2	1	1032.05	1032.05	7.23	0.043
X_1X_3	1	163.87	163.87	1.15	0.333
X_2X_3	1	83.45	83.45	0.58	0.479
Error	5	713.24	142.65	–	–
Lack-of-Fit	3	617.94	205.98	4.32	0.194
Pure error	2	95.30	47.65	–	–
Total	14	9389.93	–	–	–
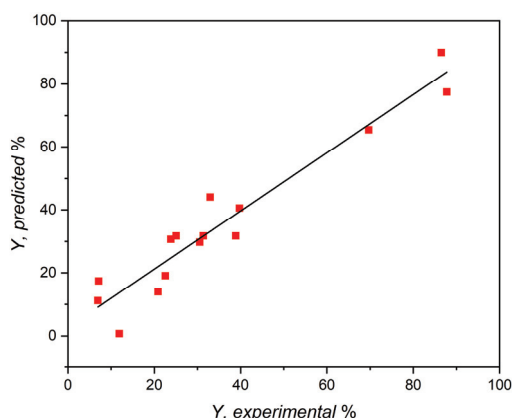
Fig. 6. Plot of experimental and predicted responses.

As can be seen from Fig. 6, there was a good relationship between the experimental and predicted responses, based on the correlation coefficient ($R^2 = 0.924$).

The contour plots showing the influence of the analysed process parameters on the adsorption degree are presented in Fig. 7. Fig. 7a indicates that the higher solution pH and lower initial Cu^{2+} concentration in the solution leads to higher metal ions removal. Further, the biosorption process was more favourable at lower initial Cu^{2+} concentration combined with shorter contact time (Fig. 7b). Lastly, Fig. 7c shows that a high solution pH combined with medium-to-longer contact time led to a higher Removal.
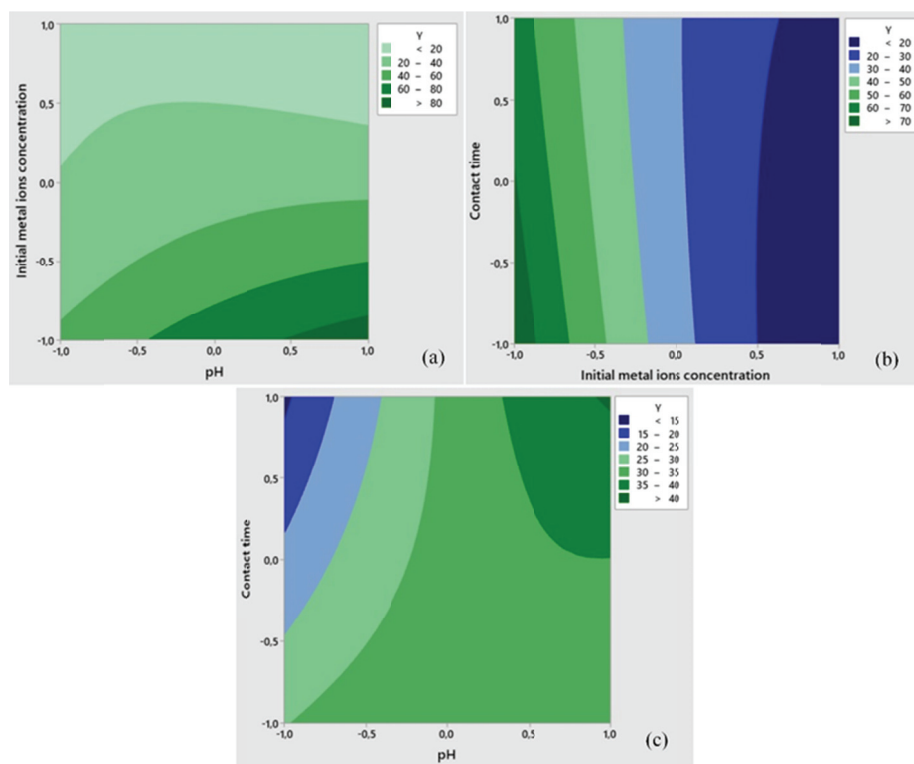
Fig. 7. Contour plots showing the interaction and the influence on the adsorption rate (*Y*) of: solution pH and the initial metal ions concentration (a); initial metal ions concentration and contact time (b) and solution pH and contact time (c).

RSM based on BBD was used to optimize the process of copper ions biosorption onto bean shells. The influence of three parameters (solution pH, initial metal ions concentration and contact time) was investigated. The obtained data indicated that the used model was statistically significant. The data showed that the initial metal ions concentration, as well as the combination of initial metal ions concentration and solution pH, had a significant influence on the biosorption efficiency. Using this model, the optimum biosorption conditions were determined to be: pH 3–4, initial metal ions concentration 100 mg/L and contact time 10–30 min.

CONCLUSIONS

The study of biosorption, as a potential method for copper ions removal from aqueous solutions, is presented in this paper. Bean shells were investigated as potential adsorbent. For that purpose, kinetics, equilibrium, SEM-EDS and process optimization studies were performed.

The solution pH was determined to have a significant influence on the biosorption capacity. An increase in the biosorption capacity with the increase in the solution pH from 2 (1.739 mg g^{-1}) to 5 (12 mg g^{-1}) was noted.

Experimentally obtained kinetics data were analysed using four adsorption kinetic models (the pseudo-first order kinetic model, pseudo-second order kinetic model, intraparticle diffusion kinetic model and Elovich kinetic model). The obtained kinetics parameters indicated that the pseudo-second order kinetic model best fitted the analyzed experimental data, which further suggested that chemisorption was a possible way of binding the copper ions to the surface of bean shells.

Experimental biosorption isotherm data were fitted using the Langmuir, Freundlich and Temkin adsorption isotherm models. Obtained results indicated that the Langmuir model served as the best fit for the analysed data, leading to the conclusion that the surface of the adsorbent was homogenous, and the biosorption of copper ions onto bean shells occurred in a monolayer.

The SEM-EDS analysis was performed on a bean shells sample before and after the biosorption of copper ions. The obtained SEM micrographs showed that the surface morphology of the sample changed after the biosorption process, from a porous to a more compact structure, possibly as a result of the incorporation of copper ions into the structure of the bean shells. The EDS spectrums of the samples before and after the biosorption process indicated that Mg, Si, K and Ca could potentially be involved in the biosorption process and exchanged with copper ions.

Process optimization studies were performed by the means of response surface methodology based on the Box–Behnken design. The influence of solution pH, initial metal ions concentration and contact time was investigated and modelled.

The used model was determined to be statistically significant. The data suggested that the initial metal ions concentration, as well as the combination of initial metal ions concentration and solution pH, had a significant influence on the biosorption efficiency. Using this model, the optimum biosorption conditions were determined to be: pH 3–4, initial metal ions concentration 100 mg dm^{-3}; and contact time 10–30 min.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/12110, or from the corresponding author on request.

ИЗВОД

БИОСОРПЦИЈА ЈОНА БАКРА НА ЉУСКАМА ПАСУЉА: ИСПИТИВАЊА КИНЕТИКЕ, РАВНОТЕЖЕ И ОПТИМИЗАЦИЈА ПРОЦЕСА

МИЉАН МАРКОВИЋ, МИЛАН ГОРГИЕВСКИ, НАДА ШТРБАЦ, КРИСТИНА БОЖИНОВИЋ, ВЕСНА ГРЕКУЛОВИЋ, АЛЕКСАНДРА МИТОВСКИ И МИЛИЦА ЗДРАВКОВИЋ

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У овом раду приказана је анализа уклањања јона бакра из водених раствора коришћењем љуски пасуља као адсорбенса. Испитан је утицај pH вредности раствора на капацитет биосорпције. Добијени резултати су показали да капацитет биосорпције расте са повећањем pH вредности раствора. Кинетичка испитивања су показала да модел псеудо-другог реда најбоље описује анализиране податке, што указује да је хемисорпција могућ начин везивања јона бакра за површину љуски пасуља. Испитивања равнотеже процеса су показала да Ленгмиров модел адсорпционе изотерме најбоље описује анализиране податке. SEM-EDS анализом су испитани узорци пре и након извођења процеса биосорпције. Ова анализа је показала евидентну промену у морфологији узорка након процеса биосорпције, при чему су EDS спектри указали на могућу измену K, Mg, Si и Ca јона са јонима бакра. Модел *response surface methodology* (RSM) базиран на Box–Behnken дизајну (BBD) је коришћен за оптимизацију процеса биосорпције, са изабраним факторима: pH вредности раствора, почетна концентрација јона бакра у раствору и време контакта. Помоћу модела су одређени оптимални услови за извођење процеса биосорпције, и то: pH вредности између 3 и 4, почетна концентрација јона бакра од 100 mg dm^{-3} и време контакта између фаза 10-30 min.

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