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## KINETIC, EQUILIBRIUM AND THERMO-DYNAMIC STUDIES OF Ni(II) IONS SORPTION ON SULFURIC ACID TREATED *Lagenaria vulgaris* SHELL

### Article Highlights

- Sorption of Ni(II) by ccLVB is very fast and efficient in the wide pH range
- The sorption process was well described by both Langmuir and Temkin isotherms
- The biosorbent can be successfully reused multiple times
- ccLVB represents an efficient and low-cost biosorbent for heavy metals removal

### Abstract

*Chemically modified Lagenaria vulgaris shell (ccLVB) was tested as a new sorbent for the removal of Ni(II) from aqueous solution, in batch conditions. The sorption process was very fast, reaching equilibrium in about 20 min. Ni(II) sorption is almost invariant in the pH range from 3 to 6. Sorption kinetics followed pseudo-second order, intraparticle diffusion and Chrastil's models, which suggest that both surface reaction and diffusion were the rate-limiting steps. Equilibria experimental results are well fitted by Langmuir and Temkin sorption isotherm models, indicating mixed adsorption process. The maximum biosorption capacity of ccLVB for Ni(II) was found to be 84.51 mg g<sup>-1</sup>. The calculated thermodynamic parameters showed that the biosorption of nickel on ccLVB was feasible, spontaneous and exothermic at 25–45 °C. The desorption experiments showed that the ccLVB could be reused for five cycles without significant loss in sorption capacity. Release of Na<sup>+</sup> from the biosorbent during sorption of Ni(II) reveals that the main sorption mechanism is ion exchange. The presented study suggests that ccLVB can be used effectively for the removal of Ni(II) ions from aqueous solution.*

*Keywords: Lagenaria vulgaris, nickel(II), sorption, kinetic, isotherms, thermodynamics.*

Heavy metal pollution is one of the most serious environmental problems today, due to rapid industrial development and increasing release of metals into biosphere. The main sources of heavy metals pollution are wastewaters from mining activities and industries such as metal plating, pigment manufacture, battery manufacture, tanneries and petroleum refining, printing and photographic industries [1]. Since heavy metals are non-biodegradable and can be accumulated in living tissues, causing various diseases, they must be removed from wastewater before discharge.

Nickel is a heavy metal that is frequently found in wastewater streams from many industries: nickel alloys and coins manufacturing, electroplating, batteries and accumulator manufacturing, industrial plumbing, spark plugs manufacturing, machinery parts, stainless-steel and nickel-chrome resistance wires processing and catalysts manufacturing [2,3]. In drinking water, nickel may cause health problems if found in amounts greater than the health standard set. Exposure to nickel may cause gastrointestinal distress (nausea, vomiting and diarrhea), dermatitis (eczema, rash and itching) and neurological effects. Acute poisoning causes headache, dizziness, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness. Higher concentrations of nickel may cause cancer of lungs, nose and bone [3].

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Various technologies, which include chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation-flocculation, flotation and electrochemical methods, are used for removing heavy metal ions from aqueous solutions [4]. Recently, Fu *et al.* [1] reviewed the current methods with evaluation of their advantages and limitations. Some of limitations, which were mentioned, are high cost, process complexity and sludge formation. So, developing of low-cost, high efficiently and environmental friendly techniques for metal ions removal is of concern. Biosorption of heavy metals from aqueous solutions is a relatively new process which has been confirmed as a very promising. Some researchers have pointed out that the agricultural wastes and by-products, such as peanut shell, waste tea leaves, sugarcane bagasse, orange peel, maize cob, can be successfully applied for heavy metals removal [5]. Biomaterials can be used in its natural form or either physical or chemical activation can be done in order to change their sorption capacity. However, it has been established that chemical activation has several advantages in comparison to physical, required lower activation energy, so that need shorter activation time and produce higher activation yield [6]. Among various chemical activation agents reported in the literature, the most widely used are hydrochloric acid, nitric acid, zinc chloride, alkali hydroxides and organic acids [7].

In this study, concentrated sulfuric acid, which acts as dehydrating agent and oxidant for biological materials, was used for chemical modification of *Lagenaria vulgaris* shell. Chemical treatment with concentrated sulfuric acid was followed by low temperature heating in order to make the process simple and cheap. The ability of obtained chemically modified material for removal of toxic Ni(II) ions from aqueous solutions was explored. The influence of contact time, initial pH, sorbent dose and initial metal concentration on the uptake capacity was evaluated. Several kinetics models (pseudo-first, pseudo-second, intraparticle diffusion and Chrastil) were applied to understand the sorption kinetics and determine potential rate-controlling steps. On the purpose of investigating the efficacy of Ni(II) ions sorption on obtained biosorbent four isotherms (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) were employed.

## MATERIALS AND METHODS

### Sorbent preparation

*Lagenaria vulgaris* (Cucurbitaceae family) is a creeping, hardy plant, which grows mainly on alluvial sandy soil and red loam, on flat areas and moderate

slopes, and in higher-lying areas, which needs light and warmth. This plant is cultivated all over the world and its leaves and seeds are commonly used in cookery, while in many cultures its extracts are traditionally used to treat large variety of healthy problems [8]. However, the outer shell of this plant, which is hard, ligneous and covered with the spongy white pith characterized by its bitter taste, is hardly useful and creates agricultural waste.

The experiments in this study were carried out using the shell of *L. vulgaris* cultivated from April to September near the town of Niš (Serbia), in controlled conditions with irrigation and without fertilization, at an altitude of about 200 m. The *L. vulgaris* shell was air dried, crushed into small pieces, washed with deionized water several times, grounded in a crusher mill and dried in an electrical oven for 24 h at  $55 \pm 5$  °C. The dried biosorbent was fractionized using standard sieves (Endecotts, England) and particles with size from 0.8 to 1.25 mm were used for further modification. Concentrated sulphuric acid was gradually added to the biosorbent and temperature of the mixture was held at 40 °C for 2 h by water bath. At the end of the treatment, mixture was diluted by sufficient amount of deionized water and decanted. The remaining sulfuric acid was removed by washing several times with deionized water over a Büchner funnel. After that, the biosorbent was neutralized by adding small portions of 0.1/0.01 M NaOH until pH reached 6.5–7.0. Finally, the biosorbent was washed, dried in an oven at  $55 \pm 5$  °C and stored in polyethylene tubes for further experimental use [9]. The obtained black material was denoted as “cold carbonized” *Lagenaria vulgaris* biosorbent (cCLVB) and some of its physicochemical characteristics are given in Table 1.  $\text{pH}_{\text{SUS}}$  was determined by measuring the pH of biosorbent suspension in period of 24 h.  $\text{pH}_{\text{PZC}}$  was determined by drift method [9,10]. Volatile matter was determined according to method ISO 562-1981, ash content was determined by ASTM D 2866-70 method, while fixed carbon was calculated as the rest of sum of these two variables to 100%. Iodine number was determined by method ASTM D4607-14. Concentrations of sulfur and metal ions in obtained material were determined after its acid digestion ( $\text{HNO}_3 + \text{H}_2\text{O}_2$ ) in the microwave oven (MWD, ETHOS, Milestone, Italy), by using ICP-OES model iCAP 6500 Duo (Thermo Scientific, United Kingdom) equipped with a CID86 chip detector.

### Chemicals

All chemicals employed in this study were analytical grade and used without further purification. Stock Ni(II) solution ( $1000 \text{ mg dm}^{-3}$ ) was prepared by

Table 1. Physicochemical characteristics of sulfuric acid treated *Lagenaria vulgaris* shell

Parameter	Value	Parameter	Value
pH <sub>sus</sub>	5.65	K content, mass%	0.241
pH <sub>pZC</sub>	4.95	Ca content, mass%	0.331
Moisture, %	6.96	Mg content, mass%	0.0069
Volatile matter, %	49.2	Pb content, mass%	0.0004
Ash, %	15.5	Cd content, mass%	0.00005
Fixed carbon, %	48.3	Zn content, mass%	0.00021
Iodine number, mg g <sup>-1</sup>	237.4	Ni content, mass%	0.000187
S / mg g <sup>-1</sup>	38.7	Mn content, mass%	0.00004
Na content, mass%	1.732	Cr content, mass%	0.00003

dissolving weighed quantity of NiSO<sub>4</sub>·6H<sub>2</sub>O in deionized water. Working Ni(II) solutions were prepared freshly before treatment from stock solution by appropriate dilution. All solutions were made with deionized water (18.2 MΩ) obtained by water purification system Smart2Pure Standard (Thermo, USA).

### Biosorption experiments

All batch biosorption experiments were performed into glass beaker in thermostated water bath at 25.0±0.2 °C (Julabo F12-ED refrigerated/heating circulator, Germany), by stirring of 250 cm<sup>3</sup> solution containing desired metal concentration and at defined initial pH value with known amount of biosorbent. First test runs were carried out with different initial Ni(II) concentrations ranging from 10 up to 400 mg dm<sup>-3</sup>, while the other parameters were kept constant (pH 5.0, sorbent dosage 4.0 g dm<sup>-3</sup>). The second set of experiments was conducted with increasing of biosorbent dosage from 0.5 up to 8 g dm<sup>-3</sup>, while initial Ni(II) concentration was 50.0 mg dm<sup>-3</sup> and initial pH value was 5.0. The experiments on the effect of pH were carried out by varying initial pH value from 2.0 up to 6.0, which was adjusting with diluted HNO<sub>3</sub> or NaOH solution, while biosorbent dosage was 4.0 g dm<sup>-3</sup> and initial Ni(II) concentration was 50.0 mg dm<sup>-3</sup>. At regular time intervals (0, 1, 2, 5, 10, 20, 40, 60, 90, 120 and 240 min) an aliquot (3 cm<sup>3</sup>) was withdrawn, filtrated through membrane filter (Captive premium syringe filters RC 25 mm/0.45 μm, Agilent Technologies, Germany) and the remaining Ni(II) concentration in solution was determined by ICP technique.

Desorption experiments were carried out under the same conditions as the batch sorption experiments. After performing sorption experiments with 50.0 mg dm<sup>-3</sup> of Ni(II) solution and 2 g dm<sup>-3</sup> of ccLVB dose, metal loaded biomass was separated and gently washed several times with demineralized water to remove any unadsorbed Ni(II) ions. Metal loaded ccLVB was treated with 100 cm<sup>3</sup> of 0.1 M HNO<sub>3</sub> as

the desorbing agent, for 60 minutes. The suspension was centrifuged and the Ni(II) ions desorbed into the solution were analyzed. The metal-desorbed ccLVB was used as the regenerated sorbent in five repeated sorption-desorption cycles to determine reusability potential of the sorbent.

The amount of metal ions sorbed at time  $t$ ,  $q_t$  (mg g<sup>-1</sup>) and the percentage of removal (%) was calculated using the following equations:

$$q_t = \frac{(c_0 - c_t)V}{m_b} \quad (1)$$

$$\text{Removal (\%)} = 100 \frac{c_0 - c_t}{c_0} \quad (2)$$

where  $c_0$  and  $c_t$  are the initial and concentration of metal ions at the sampling time, respectively (mg dm<sup>-3</sup>),  $V$  is the volume of solution (dm<sup>3</sup>), and  $m_b$  is the weight of ccLVB biosorbent (g). Fitting and calculations of experimental data were done using OriginPro 9.0 software (OriginLab Corporation, USA).

## RESULTS AND DISCUSSION

### Effect of contact time

The effect of contact time on the sorption of Ni(II) ions on ccLVB was investigated in the time interval from 1 to 120 min, with sorbent dose 2.0 g dm<sup>-3</sup>, initial Ni(II) concentrations 10 to 400 mg dm<sup>-3</sup>, pH 5.0±0.1 and temperature 25.0±0.2 °C. As shown in Figure 1, Ni(II) uptake took place in two phases. The first phase is very rapid and occurred during the about first 5 min of biosorbent-metal interaction, resulting in the removal percentage of about 95% of the maximum removal, in the case of all investigated concentrations. During the second phase removal percentage remained almost constant over the entire sorption time range and equilibrium was reached in period from 20 to 30 min, depending on initial concentration [11]. Therefore, the contact time of 40 min was

chosen for the further sorption experiments to insure that equilibrium was reached in all applied conditions.

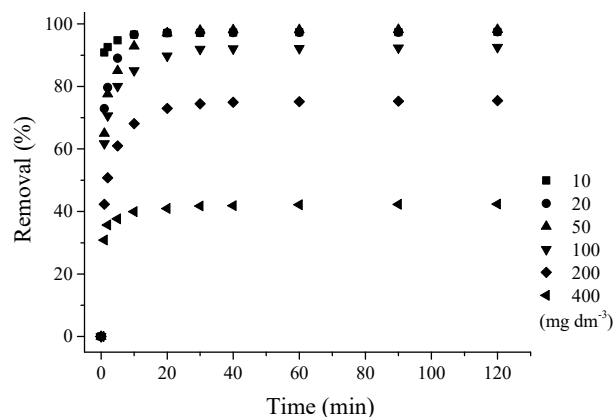


Figure 1. Effect of contact time on Ni(II) removal with cCLVB. Sorbent dose,  $2.0 \text{ g dm}^{-3}$ , initial Ni(II) concentration, 10 to  $400 \text{ mg dm}^{-3}$ , pH  $5.0 \pm 0.1$ , temperature,  $25.0 \pm 0.2 \text{ }^\circ\text{C}$ .

### Effect of initial pH

Numerous studies have shown that the pH of aqueous solution, in which biosorption is being conducted, is an important parameter [12]. Effect of initial pH value on metal uptake can be affected by both, ionization states of biosorbent functional groups and metal speciation in the solution. The experiments were studied by varying initial pH value from 2.0 up to 6.0, while other parameters were kept constant (initial Ni(II) concentration,  $50.0 \text{ mg dm}^{-3}$ , sorbent dose,  $2.0 \text{ g dm}^{-3}$ , temperature,  $25.0 \pm 0.2 \text{ }^\circ\text{C}$ ). Initial pH values higher than 6.0 did not take into consideration due to possibility of the Ni(II) ions precipitation as the hydroxides, which introduces uncertainty into the interpretation of the results. As can be seen from Figure 2, the removal percentage of Ni(II) ions increased from 87.11 to 93.66% with increasing initial solution pH from 2.0 to 3.0. Further increase in initial pH value from 3.0 to 6.0 slightly changed the percentage removal to 98.22%. Lower percentage removal in strongly acidic medium can be attributed to competition between metal ions and hydrogen ions, which concentration is higher at lower pH values, to occupy negatively charged binding sites on the biosorbent [12]. With increasing in initial pH values, the concentration of hydrogen ions decreases, as well as their competition with metal ions, thereby resulting in higher removal percentage. In the case of samples treated at initial pH 5 and 6, certain decrease of solution pH during the treatment was observed (results not shown). This phenomenon could be a result of  $\text{H}^+$  exchange with Ni(II) ions during the sorption at cCLVB groups of weak acidity, which are expected to be protonated in applied conditions. Similar trend was rep-

orted for other biosorbents, such as rose waste biomass [13] and wheat shell [14].

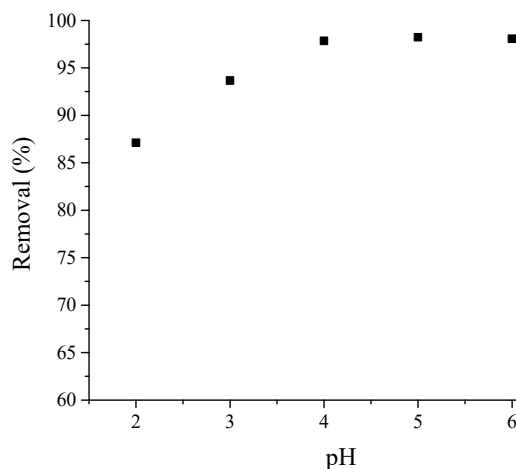


Figure 2. Effect of pH on Ni(II) removal with cCLVB. Initial Ni(II) concentration,  $50.0 \text{ mg dm}^{-3}$ , sorbent dose,  $2.0 \text{ g dm}^{-3}$ , contact time, 40 min, temperature,  $25.0 \pm 0.2 \text{ }^\circ\text{C}$ .

Results show that the sorption ability of cCLVB is very high even at pH lower of determined  $\text{pH}_{\text{pzc}}$  of biosorbent (Figure 2). Reason of this is fact that cCLVB has high amount of strong acidic sulfonic groups which are in the form of sodium salts and in conditions of drift method for  $\text{pH}_{\text{pzc}}$  determination they can not be protonated. Consequently, determined  $\text{pH}_{\text{pzc}}$  value is connected only with weak acidic functional groups on cCLVB surface, as carboxyl, lactonic, carbonyl and phenolic.

Although the removal percentage of Ni(II) ions by cCLVB in strongly acidic medium was slightly lower than at higher initial pH values, it is significantly higher in comparison with many other biosorbents [12-15]. This indicated that cCLVB can be successfully applied for metal ions removal in acidic medium. However, in this study, further nickel sorption investigations were carried out at initial pH value 5.0.

### Effect of sorbent dose

Effect of sorbent dose on the Ni(II) removal efficiency was investigated at cCLVB doses ranging from  $0.5$  to  $8.0 \text{ g dm}^{-3}$  and the results are presented in Figure 3. Removal efficiency of Ni(II) increased quickly from 66.44 to 98.22% with increasing sorbent dose from  $0.5$  to  $2 \text{ g dm}^{-3}$ , because increased active surface and the number of available binding sites. Further increment in sorbent dose to  $4 \text{ g dm}^{-3}$  slightly enhanced removal efficiency to 99.55%. Removal efficiency was almost the same at  $6.0 \text{ g dm}^{-3}$ , while beyond this value, at sorbent dose of  $8.0 \text{ g dm}^{-3}$ , a small decrease in removal percentage (98.32%) was

obtained. This is due to the binding of almost all ions to the sorbent and the establishment of equilibrium between the metal ions bound to the sorbent and those remaining in the solution. Similar results have been reported by Kumar *et al.* [16] for sorption of nickel from aqueous solution onto bael tree leaves powder. Since the sorbent dose of  $2.0 \text{ g dm}^{-3}$  was determined as sufficient, all subsequent sorption experiments were conducted at that sorbent dose.

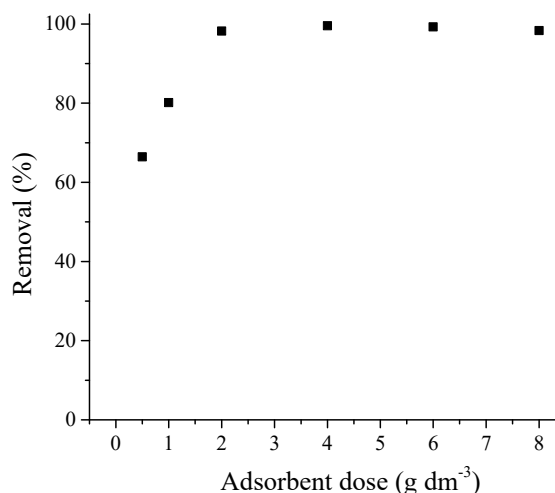


Figure 3. Effect of sorbent dose on Ni(II) removal with cCLVB. Initial Ni(II) concentration,  $50.0 \text{ mg dm}^{-3}$ , pH  $5.0 \pm 0.1$ , contact time, 40 min, temperature,  $25.0 \pm 0.2 \text{ }^\circ\text{C}$ .

### Sorption kinetics at varied initial concentrations

In order to investigate the sorption mechanism and potential rate controlling step, several models of kinetics (pseudo-first-order, pseudo-second-order, intraparticle diffusion and Chrastil's diffusion model) were applied to fit experimentally obtained data, at varied initial concentrations of Ni(II) ions.

#### Pseudo-first-order model

Lagergren's pseudo-first-order reaction kinetic model [17] considers the rate of occupation of the sorption sites to be proportional to the number of unoccupied sites, and it is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

Given the boundary conditions for:  $t = 0$ ,  $q_t = 0$ ;  $t = t$ ,  $q_t = q_t$ . Eq. (3) can be integrated to give the non-linear function:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

where  $k_1$  ( $\text{min}^{-1}$ ) is the first order rate constant,  $q_t$  and  $q_e$  are the amounts of metal ions sorbed at time  $t$  and

at equilibrium, respectively. The obtained pseudo-first-order rate constant,  $k_1$ , and the predicted  $q_e$  values by non-linear analysis of plot of  $q_e$  vs.  $t$  are given in Table 2. As an example, graph for initial Ni(II) concentration of  $50.0 \text{ mg dm}^{-3}$  was given in Figure 4. As can be seen from data presented in Table 2, the determination coefficients for the pseudo-first-order kinetics obtained by non-linear analyze are relatively high for all studied initial Ni(II) concentrations. The determined values of  $q_e$  calculated from Eq. (4) showed similarity with the experimental values.

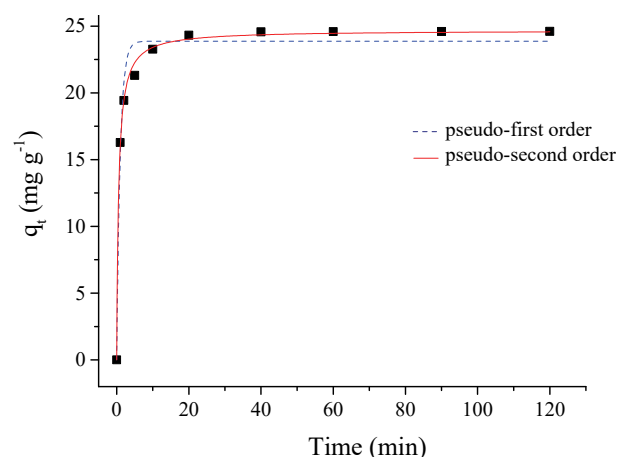


Figure 4. Pseudo-first -and pseudo-second-order kinetics of Ni(II) ions sorption on cCLVB. Initial Ni(II) concentration,  $50.0 \text{ mg dm}^{-3}$ , sorbent dose,  $2.0 \text{ g dm}^{-3}$ , pH  $5.0 \pm 0.1$ , temperature,  $25.0 \pm 0.2 \text{ }^\circ\text{C}$ .

#### Pseudo-second-order model

In contrast to the pseudo-first-order reaction kinetic model, which assumes that metal sorption process is only dependent on the number of metal ions present at the specific time in the solution, the pseudo-second-order kinetic model assumes that the metal biosorption process is dependent on the number of metal ions present in the solution as well as the free biosorption sites on the biosorbent surface [19]. The most widely used pseudo-second-order model kinetic equation has been proposed by Ho [20]:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

Integrating Eq. (5) for boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$  gives:

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \quad (6)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{ min}^{-1}$ ) is the second-order-rate constant,  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of metal ions sorbed at equilibrium, and  $q_t$  ( $\text{mg g}^{-1}$ ) is the amount of metal ions sorbed at time  $t$ .

Table 2. The values of kinetic parameters for pseudo-first-order, pseudo-second-order, intraparticle diffusion and Chrastil's diffusion model (sorbent dose,  $2.0 \text{ g dm}^{-3}$ , temperature,  $25.0 \pm 0.2 \text{ }^\circ\text{C}$ , pH  $5.0 \pm 0.1$ )

Kinetic model	Parameter	Initial metal concentration, $\text{mg dm}^{-3}$					
		10	20	50	100	200	400
Pseudo-first-order nonlinear regression	$q_{e,\text{exp}} / \text{mg g}^{-1}$	5.01	9.33	24.57	45.97	75.06	84.51
	$q_{e,\text{cal}} / \text{mg g}^{-1}$	4.91	9.16	23.86	44.41	72.44	81.50
	$k_1 / \text{min}^{-1}$	2.78	1.24	1.01	0.95	0.78	0.52
	$r^2$	0.987	0.980	0.976	0.969	0.959	0.982
Pseudo-second-order non-linear regression	$q_{e,\text{cal}} / \text{mg g}^{-1}$	5.01	9.33	24.67	45.96	75.75	83.71
	$k_2 / \text{g mg}^{-1} \text{ min}^{-1}$	2.54	0.28	0.074	0.039	0.024	0.018
	$r^2$	0.999	0.998	0.998	0.997	0.996	0.997
Intraparticle diffusion model	$k_{i1} / \text{mg g}^{-1} \text{ min}^{-1/2}$	0.133	1.03	2.19	5.20	11.66	17.46
	$C_1 / \text{mg g}^{-1}$	4.57	6.09	16.36	26.96	32.85	57.24
	$r^2$	0.969	0.973	0.999	0.896	0.946	0.979
	$k_{i2} / \text{mg g}^{-1} \text{ min}^{-1/2}$	0.002	0.004	0.036	0.182	0.337	0.414
	$C_2 / \text{mg g}^{-1}$	4.99	9.30	24.24	44.40	72.26	80.34
	$r^2$	0.853	0.882	0.897	0.873	0.826	0.859
Chrastil's diffusion model	$q_{e,\text{cal}} / \text{mg g}^{-1}$	5.021	9.36	24.58	46.05	75.35	83.90
	$k_C / \text{dm}^3 \text{ g}^{-1} \text{ min}^{-1}$	0.11	0.072	0.068	0.057	0.048	0.027
	$n$	0.021	0.038	0.114	0.155	0.184	0.269
	$r^2$	0.999	0.999	0.998	0.999	0.999	0.998

Values for the pseudo-second-order constant,  $k_2$ , and amount of the metal ion sorbed at equilibrium,  $q_e$ , determined by non-linear regression (Figure 4), for the sorption of different initial metal concentrations are listed in Table 2. The presented pseudo-second-order kinetic model fit the experimental data very well for all studied initial metal concentrations, because of extremely high determination coefficient obtained in all cases ( $r^2 > 0.99$ ), which are much closer to unity than for the pseudo-first-order kinetic model. With increasing initial metal concentration from 10 up to 400  $\text{mg g}^{-1}$ , pseudo-second-order rate constant,  $k_2$ , decreased from 2.54 to 0.018  $\text{g mg}^{-1} \text{ min}$ . Similar concentration dependence was found by Kumar and Gaur [21] for metal biosorption by *Phormidium* sp. At lower initial metal concentration almost all binding sites are free, which resulted in high pseudo-second-rate constant, while at higher metal concentration saturation of sorption sites was occurred and value of  $k_2$  decreased. Equilibrium sorption capacity,  $q_e$ , calculated by non-linear regression, increased almost linearly from 5.01 up to 75.75  $\text{mg g}^{-1}$  with increasing in initial metal concentration from 10 to 200  $\text{mg dm}^{-3}$ , and slightly to 84.51  $\text{mg g}^{-1}$  with further increasing in initial metal concentration up to 400  $\text{mg g}^{-1}$ . This also can be related with saturation of binding sites on sorbent surface. The calculated equilibrium sorption capacity is almost equal with experimental obtained value (Table 2), in all range of applied initial metal concen-

tration, which indicate that pseudo-second-order kinetic model much better fitted experimental data than pseudo-first order model, and can be successfully used for study of nickel ion sorption from solution onto ccLVB. Similar findings were reported for sorption of Ni(II) from aqueous solution on grapefruit peel and *Moringa oleifera* [11,15] and for sorption of Cu(II) on xanthate sorbents [22].

#### Intraparticle diffusion model (IPD)

The sorption process, whether physical or chemical, onto porous sorbents generally takes place through four stages: bulk diffusion, external (film) diffusion, intraparticle diffusion and finally sorption of the adsorbate onto the sorbent surface [21]. It is generally accepted that the bulk diffusion (due to rapid mixing), as well as sorption of ions to binding sites, are rapid and do not represent the rate determining step. Therefore, whether external diffusion or intraparticle diffusion can be step which control sorption process.

Intraparticle diffusion equation, proposed by Weber and Morris [23], is most commonly used model for identification is the intraparticle diffusion is rate determining step and can be expressed:

$$q_t = k_d t^{1/2} + C \quad (7)$$

where  $q_t$  ( $\text{mg g}^{-1}$ ) is amount of the metal sorbed at time  $t$ ,  $k_d$  ( $\text{mg g}^{-1/2} \text{ min}^{-1/2}$ ) is intraparticle diffusion rate constant and  $C$  ( $\text{mg g}^{-1}$ ) is constant related to the

boundary layer thickness. If the plot  $q_t$  versus  $t^{1/2}$  is linear and passes through the origin than intraparticle diffusion is sole rate limiting step. On the other side, if the plot presents multi-linearity, than two or more steps occur during the sorption process. From Figure 5 it can be seen that for sorption of Ni(II) ion onto ccLVB, regression of  $q_t$  versus  $t$  is not linear and do not pass through the origin, suggesting that the intraparticle diffusion is not the only rate-controlling step. The IPD for all studied initial Ni(II) concentrations showed multi-linearity and two stages in sorption. Similar results were shown in studies of Amin [24] and Ding *et al.* [25] where authors fitted kinetic data by two linear lines with different slope. The first, sharper portion of the plot can be attributed to diffusion of Ni(II) ions through solution to the external surface. It is a rate limiting process at the beginning of the sorption. The second portion represents the gradual sorption stage, where the intraparticle diffusion is rate-controlled. Intra-particle diffusion rate constant,  $k_{i2}$ , was determined from the slope of second portion of the plot, while increment represents constant  $C$ . The calculated intraparticle diffusion rate constants (Table 2), increased from 0.001 to 0.571  $\text{mg g}^{-1} \text{min}^{-1/2}$  with increasing initial metal concentration from 10 to 400  $\text{mg dm}^{-3}$  which can be related to faster diffusion, and biosorption, because a higher initial metal concentration produces a stronger driving force for diffusion. In addition, the constant  $C$ , which is taken to be proportional to the extent of the boundary layer thickness, increased from 2.54 to 39.69 by increasing initial metal concentration, indicating decreases of the rate of the external mass transfer and hence increases of the rate of internal mass transfer.

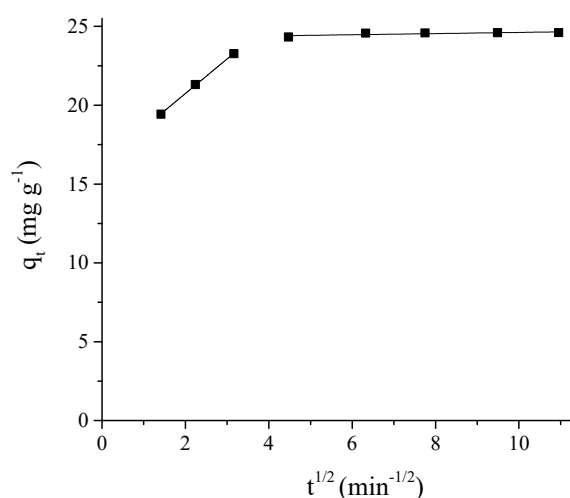


Figure 5. Intraparticle diffusion model of Ni(II) ions sorption on ccLVB. Initial Ni(II) concentration, 50.0  $\text{mg dm}^{-3}$ , sorbent dose, 2.0  $\text{g dm}^{-3}$ , pH 5.0 $\pm$ 0.1, temperature, 25.0 $\pm$ 0.2  $^{\circ}\text{C}$ .

### Chrastil's diffusion model

Chrastil's diffusion model describes sorption kinetics in diffusion controlled systems. The model can be expressed by the following equation [26]:

$$q_t = q_e \left(1 - e^{-k_C A_0 t}\right)^n \quad (8)$$

where  $k_C$  is a rate constant ( $\text{dm}^3 \text{g}^{-1} \text{min}^{-1}$ ), which depends of diffusion coefficients and sorption capacity of biosorbent,  $A_0$  is the dose of biosorbent ( $\text{g dm}^{-3}$ ) and  $n$  is a heterogeneous structural diffusion resistance constant, which can range from 0 to 1. The constant  $n$  is independent of the metal ions concentration, sorbent concentration  $A_0$ ,  $q_e$  and temperature [26,27]. In systems with small diffusion resistance, the parameter  $n$  approximates 1, while with a more significant resistance parameter  $n$  assumes small values ( $< 0.5$ ).

Plot of  $q_e$  vs.  $t$  for initial Ni(II) concentration of 50.0  $\text{mg dm}^{-3}$  is shown in Figure 6. The parameters of the model:  $q_e$ ,  $k_C$  and  $n$ , for sorption of Ni(II) at initial concentration from 10 up to 400  $\text{mg dm}^{-3}$  were determined by non-linear regression analysis of experimental data according to Eq. (8) and given in Table 2.

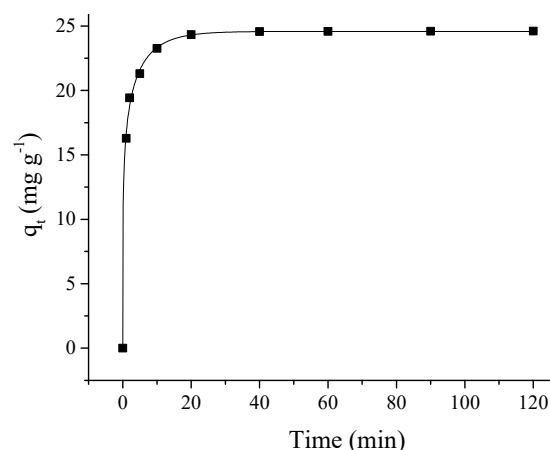


Figure 6. Chrastil's diffusion model of Ni(II) ions sorption on ccLVB. Initial Ni(II) concentration, 50.0  $\text{mg dm}^{-3}$ , sorbent dose, 2.0  $\text{g dm}^{-3}$ , pH 5.0 $\pm$ 0.1, temperature, 25.0 $\pm$ 0.2  $^{\circ}\text{C}$ .

The obtained high determination coefficients, larger than 0.99 (Table 2), indicate a very good fit of experimental kinetic data with Chrastil's model, for all tested concentrations (10–400  $\text{mg dm}^{-3}$ ). Applicability of this diffusion model also confirms similar values of the calculated  $q_e$  with experimentally determined  $q_e$  (Table 2). Extremely low values of constants  $n$  allow for the assumption that the biosorption process is strongly limited by diffusion resistance. The value of the constant  $n$  increases from 0.021 to 0.269 with increasing initial concentration of Ni(II) ions from 10 up to 400  $\text{mg dm}^{-3}$ , which is in accordance with the inf-

fluence of the driving force, concentration gradient  $\Delta c$ , on the diffusion process.

Having in mind that reaction kinetics of the sorption process is in accordance with the pseudo-second-order model, sorption of Ni(II) on ccLVB is controlled by both surface reaction and boundary layer and intraparticle diffusion, where diffusion of Ni(II) ions is more significant rate-controlling step because of low value of  $n$ . This is confirmed by the results of the study Mitić-Stojanović [27], where diffusion resistance constant,  $n$ , is significantly higher for biosorbent LVB, starting material for ccLVB synthesis, probably because the process of metal ions binding is significantly faster for chemically modified materials due to the presence of  $-\text{SO}_3^-$  groups, which has high affinity for Ni(II) ions.

### Sorption isotherms

Sorption isotherms represent distribution of metal ions between the biosorbent and solution, when the system is at equilibrium. Isotherm studies give the information important for optimization of the biosorption mechanism pathways, expression of the surface properties, capacities of biosorbents, and effective design of the biosorption systems. In this study, the experimental data were analyzed by using the following equilibrium models: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. All the isotherm parameters were evaluated with non-linear regression method by means of Origin Pro 9.0 software.

### Langmuir isotherm

The Langmuir model is based on the assumptions that there is a finite number of binding sites, which are homogeneously distributed over the sorbent surface. These binding sites have the same affinity for sorption of a single molecular layer and there is no interaction between sorbed molecules [28,29]. The non-linear form of Langmuir isotherm can be represented by the following equation:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \quad (9)$$

where  $q_e$  is the amount of sorbate sorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $c_e$  is the equilibrium concentration of sorbate in solution ( $\text{mg dm}^{-3}$ ),  $q_m$  is the maximum sorption capacity ( $\text{mg g}^{-1}$ ), and  $K_L$  is a Langmuir constant related to the energy of sorption, which reflects quantitatively the affinity between the metal ions and the sorbent. Maximum metal uptake  $q_m$  and Langmuir constant  $K_L$  can be deduced from experimental data by non-linear regression of the plot  $q_e$  versus  $c_e$  (Figure 7) and they are presented in Table 3.

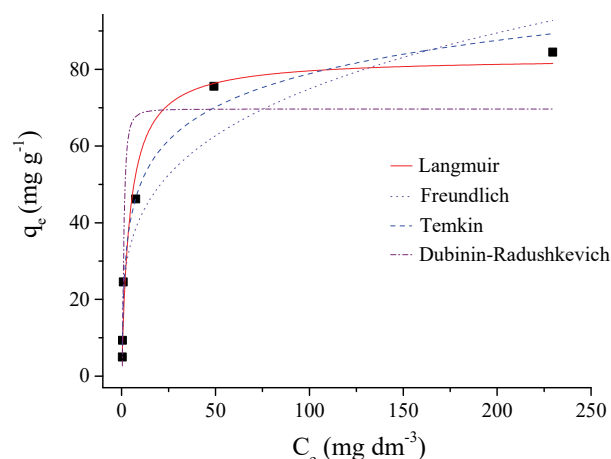


Figure 7. Isotherms of Ni(II) ions sorption on ccLVB. Sorbent dose,  $2.0 \text{ g dm}^{-3}$ , pH  $5.0 \pm 0.1$ , temperature,  $25.0 \pm 0.2 \text{ }^\circ\text{C}$ .

Table 3. Parameters of sorption isotherm models for Ni(II) sorption onto ccLVB

Adsorption isotherm	Parameter	Value
Langmuir	$K_L / \text{dm}^3 \text{ mg}^{-1}$	0.231
	$q_m / \text{mg g}^{-1}$	83.05
	$R^2$	0.964
Freundlich	$K_F / (\text{mg g}^{-1})^{1/n}$	22.96
	$n$	3.89
	$R^2$	0.877
Temkin	$K_T$	12.53
	$B / \text{J mol}^{-1} \text{ K}^{-1}$	12.53
	$R^2$	0.979
Dubinin-Radushkevich	$q_{\text{DR}}$	69.66
	$K_{\text{DR}}$	$2.9 \cdot 10^{-7}$
	$E / \text{J mol}^{-1}$	1313
	$R^2$	0.839

The high value of determination coefficient suggested that the Langmuir isotherm provides a good model of the sorption Ni(II) ions onto ccLVB. The monolayer maximum metal uptake capacity,  $q_m$ , estimated from the Langmuir model is  $83.05 \text{ mg g}^{-1}$ , which is very close to the experimental value  $84.51 \text{ mg g}^{-1}$ .

The dimensionless constant commonly known as the separation factor ( $R_L$ ), defined by Hall *et al.* [30], can be used for predicting the favorability of a sorption system:

$$R_L = \frac{1}{1 + K_L c_0} \quad (10)$$

where  $K_L$  ( $\text{dm}^3 \text{ mg}^{-1}$ ) refers to the Langmuir constant and  $c_0$  is denoted to the initial sorbate concentration ( $\text{mg dm}^{-3}$ ). The  $R_L$  value indicates the sorption nature to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ),



favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). Calculated values of  $R_L$  for the initial Ni(II) concentrations from  $10 \text{ mg dm}^{-3}$  up to  $400 \text{ mg dm}^{-3}$  are in the range from 0.295 to 0.011, confirming favorability of present process. Although the sorption process is favorable over the entire studied initial concentration range, it is more favorable at higher initial metal concentrations than at lower ones.

### Freundlich isotherm

The Freundlich isotherm is suitable for interpretation of sorption of sorbate on a highly heterogeneous sorbent surface. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation [31]. The non-linear form of this isotherm can be presented by the following equation:

$$q_e = K_f c_{\text{eq}}^{1/n} \quad (11)$$

where  $q_{\text{eq}}$  is the amount of sorbate sorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $c_{\text{eq}}$  is the equilibrium concentration of sorbate in solution ( $\text{mg dm}^{-3}$ ),  $K_f$  is Freundlich constant, related to the sorption capacity and  $1/n$  is Freundlich exponent, related to the intensity of sorption, which varies with the heterogeneity of the sorbent surface. When  $1/n = 1$  the free energy for all sorbate concentrations is constant; when  $1/n < 1$  added sorbates is added with weaker and weaker free energies, finally when  $1/n > 1$  more sorbate presence in the sorbent enhances the free energies of further sorption [32]. The experimental data for Ni(II) ions sorption on cLVB indicating favorable sorption, which is in accordance with determined  $n$  value of 3.89. However, low determination coefficient value ( $R^2 = 0.877$ ) confirmed that the Freundlich model was not suitable for well predicting sorption of Ni(II) ions onto cLVB from aqueous solution (Figure 7).

### Temkin isotherm

The Temkin isotherm, which was first developed by Temkin and Pyzhev, assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation [33]. There is no molecular interaction between the sorbed species but the free energy of surface sites varies with surface coverage. The Temkin isotherm is presented by the following non-linear equation:

$$q_e = \frac{RT}{b_T} \ln(K_T c_e) = B \ln(K_T c_e) \quad (12)$$

where constant  $B = RT/b_T$  is related to the heat of adsorption,  $R$  is the universal gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ ),  $T$  is the absolute temperature (K),  $b_T$  is the variation of

adsorption energy ( $\text{J mol}^{-1}$ ) and  $K_T$  is the equilibrium binding constant ( $\text{dm}^3 \text{mg}^{-1}$ ) corresponding to the maximum binding energy. The Temkin isotherm assumes that the heat of adsorption of all the molecules in a layer decreases linearly due to sorbent-sorbate interactions and that adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. Temkin isotherm parameters were obtained by non-linear regression of the plot  $q_e$  versus  $c_e$  and presented in Table 3. The high value of  $R^2$  (0.979) showed that in addition to the Langmuir isotherm the sorption process can also be represented by the Temkin isotherm model (Figure 7). The relatively high value of parameter  $B$ , indicated that there is a significant ionic interaction between Ni(II) ions and cLVB biosorbent and suggested predominance of chemical sorption.

### Dubinin-Radushkevich (D-R) isotherm

The Dubinin-Radushkevich model is an empirical model developed for sorption subcritical vapors in micropore solids where the sorption process follows a pore filling mechanism onto energetically non-uniform surface [34]. So, the D-R isotherm is an analog of Langmuir type but it is more general because it does not assume a homogeneous surface or constant sorption potential. The D-R model is given by the following non-linear equation:

$$q_e = q_{\text{DR}} \exp(-K_{\text{DR}} \varepsilon^2) \quad (13)$$

where  $q_{\text{DR}}$  ( $\text{mg g}^{-1}$ ) is Dubinin-Radushkevich model constant representing the theoretical monolayer saturation capacity,  $K_{\text{DR}}$  ( $\text{mol}^2 \text{kJ}^{-2}$ ) is the constant of sorption energy which is related to mean sorption energy and  $\varepsilon$  is Planyi potential, defined as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{c_e}\right) \quad (14)$$

Values  $q_{\text{DR}}$ ,  $K_{\text{DR}}$  and  $E$  should be determined from non-linear plot of  $q_e$  versus  $c_e$ . The mean sorption energy, which may provide useful information with regard to whether or not sorption is subject to chemical or physical process, can be calculated as follows:

$$E = \frac{1}{\sqrt{2K_{\text{DR}}}} \quad (15)$$

The value of mean biosorption energy, which is in the ranges of  $1\text{--}8 \text{ kJ mol}^{-1}$  and  $9\text{--}16 \text{ kJ mol}^{-1}$ , suggested the physical sorption and chemical sorption or ion exchange, respectively. According to the calculated  $E$  value, which is  $1.3 \text{ kJ mol}^{-1}$ , physical sorption can be involved in Ni(II) sorption onto cLVB. Con-

sidering determination coefficient value ( $R^2 = 0.839$ ), can be concluded that the D-R model did not fit well the experimental data (Figure 7).

High  $R^2$  values and good agreement of experimental and calculated  $q_m$  values (Table 3) suggested that the Langmuir and Temkin isotherms were the best models to describe Ni(II) sorption equilibria. The maximum sorption capacity of ccLVB for nickel was  $84.51 \text{ mg g}^{-1}$ . This high value can be explained by the fact that investigated biosorbent has significant porosity (iodine number, Table 1) and many different functional groups in lignocellulosic structure of *Lagenaria vulgaris* (R-OH, Ar-OH, -COOH and lactonic), and also  $-\text{SO}_3^-$  group, which appears after chemical modification of biosorbent [27]. It is expected that after filling of the more available sites on sorbent surface, begins an adsorption process by the inner layers, in accordance with the theory of Temkin [35]. On the other hand, functional groups on ccLVB surface have different sorption affinity for Ni(II) ions. Therefore, one can expect that sorption will start at  $-\text{SO}_3^-$  groups and after their saturation it will be carried out through carboxylic and hydroxyl groups, with lower affinity. In the both case there are difference in the sorption energy and interaction of Ni(II) ions with ccLVB is occurring by a mixed adsorption process: firstly according to the model of Langmuir isotherm and secondly as in the Temkin model.

The maximum experimental sorption capacity ( $q_{\text{max}}$ ) of the ccLVB sorbent, obtained in this study ( $83.05 \text{ mg g}^{-1}$ ) for the removal of Ni(II) ions have been compared with those of other sorbents reported in the literature [12-16,21,36-38]: *Spirogyra* raw ( $11.95 \text{ mg g}^{-1}$ ), *Spirogyra* pretreated ( $87.33 \text{ mg g}^{-1}$ ), *Chlorella vulgaris* ( $14.67 \text{ mg g}^{-1}$ ), *Eriobotrya japonica* ( $27.54 \text{ mg g}^{-1}$ ), *Moringa oleifera* bark ( $30.38 \text{ mg g}^{-1}$ ), Barley straw ( $35.6 \text{ mg g}^{-1}$ ), modified coir pith ( $38.9 \text{ mg g}^{-1}$ ), *Sargassum ilicifolium* ( $79.8 \text{ mg g}^{-1}$ ), chitosan coated on perlite ( $114.94 \text{ mg g}^{-1}$ ). It can be seen that ccLVB sorbent has higher uptake capacities for Ni(II) ions than most other materials. Also, the investigated chemically modified form of *Lagenaria vulgaris* biomass is much more efficient than untreated *Lagenaria vulgaris*, which for example has  $q_{\text{max}}$  for Zn  $6.21 \text{ mg g}^{-1}$  [27], and xantated *Lagenaria vulgaris*, which has  $q_{\text{max}}$  for Cu  $23.18 \text{ mg g}^{-1}$ , indicating that ccLVB is promising biosorbent for the effective removal of nickel from aqueous solutions.

### Thermodynamics of biosorption

Thermodynamic parameters including the change in free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) were used to describe thermodynamic behavior of the

biosorption of nickel on ccLVB. Thermodynamic parameters were calculated from the following equations [39]:

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (16)$$

$$\Delta G = -RT \Delta \ln K_L \quad (17)$$

where  $K_L$  ( $\text{dm}^3 \text{ mmol}$ ) is the isotherm constant. The experiments were carried out at 25, 35 and 45 °C. The enthalpy and the entropy change of biosorption were estimated from the slope and intercept of the linear regression of  $\ln K_L$  vs.  $1/T$  plot (Figure 8), and the results are given in Table 4 [40].

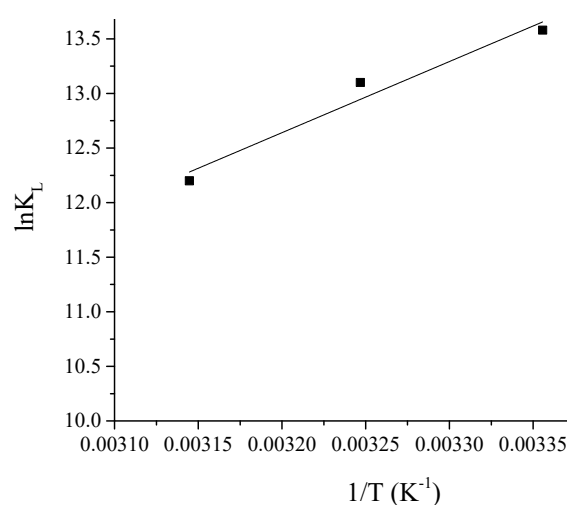


Figure 8. Plot of  $\ln K_L$  vs.  $1/T$  for the Ni(II) biosorption on ccLVB.

The free energy change ( $\Delta G$ ) was calculated to be from  $-33.78$  to  $-32.42 \text{ kJ mol}^{-1}$  for the biosorption of Ni(II) at temperature from 25 to 45 °C (Table 4). The negative values  $\Delta G$  indicates the feasibility of the biosorption process and its spontaneous nature. The decrease in  $\Delta G$  values with increase in temperature shows a slight decrease in feasibility of biosorption at higher temperatures.

Table 4. The thermodynamic parameters of Ni(II) biosorption by ccLVB

$T/^\circ\text{C}$	$\Delta G / \text{kJ mol}^{-1}$	$\Delta H / \text{kJ mol}^{-1}$	$\Delta S / \text{J mol}^{-1} \text{K}^{-1}$
25	-33.60	-54.01	-68.65
35	-32.61		
45	-32.21		

The negative  $\Delta H$  value (Table 4), implies an exothermic character of the process of biosorption within the analyzed range of temperatures. The enthalpy value within  $2.1$ – $20.9 \text{ kJ mol}^{-1}$  points to physical sorption, whereas the value from  $20.9$ – $418.4 \text{ kJ}$

mol<sup>-1</sup> indicates chemisorption [40]. The heat of Ni(II) biosorption falls into the boundary value of heat between the physical and chemical sorption, which corresponds to the heat of ion exchange process, having in mind that the heats of chemisorption generally change from 80 to 200 kJ mol<sup>-1</sup> [39]. The negative  $\Delta S$  value (Table 4) suggests a decrease in the randomness at the solid/solution interface during the biosorption of Ni(II) on ccLVB, and corroborates the previously proposed spontaneity of the biosorption process.

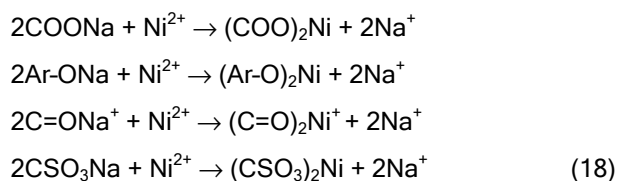
### Desorption study

In order to make the sorption process more economical through repeated use of the sorbent and recover of the metal, desorption and regeneration potential of ccLVB was investigated. In studies by Karthikeyan *et al.* [38] and Mitić-Stojanović *et al.* [27], the authors suggest that mineral acids such as HNO<sub>3</sub>, which are cheap and available, are promising desorbing agents for efficient regeneration of different biosorbents. Sorption-desorption process of Ni(II) ions was done in five repeated cycles on the same sample of ccLVB. Results in Table 5 show that desorption of the Ni(II) from loaded ccLVB was very effective in the first cycle, resulting in 98.86% of metal recovery. The desorption efficiency remained almost unchanged during the next four desorption cycles (Table 5). Also, it can be noted that a non-significant decrease in the sorption capacity of ccLVB for nickel was observed in all experiments. Re-adsorption of metal ions in the second cycle was 98.98%, and it has almost the same values in next cycles (Table 5). These results suggest very good reusability of the investigated biosorbent, as well as a good capacity for metal recovery.

### Sorption mechanism

Analysis of water solution, after the first cycle of Ni(II) ions sorption, showed presence of Na<sup>+</sup>. Release of the sodium ions during the sorption of heavy metal happens due to the fact that in the last stage of the synthesis of ccLVB, biomass was treated with NaOH. As a consequence of this treatment, the ionized oxygen-containing functional groups: carboxyl, lactonic,

carbonyl, phenolic and sulfonic, are in the form of the sodium salts (Eq. (18)). The desorption results in the present study indicated that the sorption of Ni(II) on ccLVB was reversible by acid washing (Table 5) with very high yield of biosorbent regeneration. Having in mind five efficient cycles of ccLVB regeneration and very efficient re-adsorption of Ni(II) ions, it can be assumed that the dominant mechanism of Ni(II) ions sorption might be ion exchange [19,22]. The proposed mechanism of Ni(II) sorption on ccLVB surface groups in form of sodium salts is:



The calculated equivalent amount of released sodium ions in solution approximately corresponds to amount of sorbed nickel. The equivalent amount of sorbed Ni(II) ions (0.838 meq g<sup>-1</sup>) is about 10% higher than the amount of released sodium ions (0.737 meq g<sup>-1</sup>). The difference between the presented values of Ni(II) and Na<sup>+</sup> amounts should be a consequence of partly ion exchange between hydrogen and Ni(II) ions that takes place because of some groups on ccLVB surface protonated at pH 5, which release H<sup>+</sup> by dissociation [11].

### CONCLUSIONS

This study demonstrates the ability of using concentrated sulfuric acid treated *Lagenaria vulgaris* shell as biosorbent for the removal and recovery of Ni(II) ions from aqueous solution. The biosorption rate is very fast and depending on the initial metal concentration equilibrium is accomplished from 20 to 30 min. The kinetics of the process is well described using the pseudo-second-order and the diffusive models (IPD and Chrastil's model), which indicate that limiting factors are both surface reaction and diffusion in the boundary layer and pores. Langmuir and Temkin isotherm models gave the best fit to the sorption data of Ni(II), which is the result of difference in the availability and the binding energies of the active

Table 5. Sorption-desorption capability of ccLVB sorbent for Ni(II) ions

Cycle	Sorbed Ni(II), mg g <sup>-1</sup>	Desorbed Ni(II), mg g <sup>-1</sup>	Desorption efficiency, %	Readsorption efficiency, %
1	24.60	24.32	98.86	/
2	24.35	24.12	99.05	98.98
3	24.20	23.95	98.96	98.37
4	24.25	24.04	99.13	98.57
5	24.12	23.86	98.92	98.04

sites, giving a mixed adsorption process. The thermodynamic parameters indicated the feasibility, exothermic and spontaneous nature of the biosorption process in temperature range 25–45 °C. The recovery tests indicate that the biosorbent could be regenerated and reused for at least five cycles. Releasing of the sodium ions during Ni(II) sorption proves the significance of the ion exchange binding mechanism. It may be concluded that cCLVB has the potential to be used as an efficient and low-cost sorbent for Ni(II) from water.

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## KINETIČKA, RAVNOTEŽNA I TERMODINAMIČKA ISPITIVANJA SORPCIJE NI(II) JONA NA KORI *Lagenaria vulgaris* TRETIRANOJ SULFATNOM KISELINOM

Hemijski modifikovana kora *Lagenaria vulgaris* (ccLVB) je ispitivana kao novi sorbent za uklanjanje Ni(II) jona iz vodenog rastvora, u šaržnim uslovima. Proces sorpcije je veoma brz i postiže ravnotežu za 20-30 min, zavisno od inicijalne koncentracije. Sorpcija Ni(II) jona na ccLVB je skoro bez uticaja pH u opsegu od 3 do 6. Kinetika sorpcije se može opisati modelima pseudo-drugog reda, međučestične difuzije i Krastilovim modelom, što ukazuje na to da reakcija na površini i difuzija unutar čestica određuju brzinu procesa. Eksperimentalni rezultati ravnotežnih ispitivanja se najbolje mogu opisati pomoću modela Langmuir i Temkin sorpcione izoterme, što ukazuje na mešovitu prirodu sorpcionog procesa. Maksimalni kapacitet biosorpcije ccLVB za Ni(II) jone iznosi 84,51 mg g<sup>-1</sup>. Izračunati termodinamički parametri su pokazali da je biosorpcija Ni(II) jona na ccLVB spontana i egzotermna u temperaturnom opsegu 25-45 °C. Eksperimenti regeneracije sorbenta su pokazali da se ccLVB može ponovo koristiti u 5 ciklusa, bez značajne promene sorpcionog kapaciteta. Oslobađanje Na<sup>+</sup> iz biosorbenta tokom sorpcionog vezivanja Ni(II) jona ukazuje da je jonska izmena glavni mehanizam sorpcije. Navedena istraživanja sugerišu da se ccLVB može koristiti kao jeftin i dostupan sorbent za efikasno uklanjanje Ni(II) jona iz vode.

*Ključne reči:* *Lagenaria vulgaris*, nikel(II), sorpcija, kinetika, izoterme, termodinamika.