

## REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTION BY EXTRACTED ONION PROCESSING WASTE

Tsvetko V. Prokopov<sup>1</sup>, Milena I. Nikolova<sup>1</sup>, Donka S. Taneva<sup>1</sup>,  
Nadezhda T. Petkova<sup>2\*</sup>

<sup>1</sup>University of Food Technologies, Department of Environmental Engineering, 26 Maritsa Blvd., 4000 Plovdiv, Bulgaria

<sup>2</sup>University of Food Technologies, Department of Organic and Inorganic Chemistry, 26 Maritsa Blvd., 4000 Plovdiv, Bulgaria

\*Corresponding author: [petkovanadejda@abv.bg](mailto:petkovanadejda@abv.bg)

Received: October, 07, 2019

Accepted: October, 22, 2021

**Abstract:** The aim of the present study was to examine the performance of residue from extracted onion processing waste for the ability to remove Cr (VI) ions from aqueous solutions. The characterization of applied biosorbent was conducted by FT-IR analysis. Batch experiments were carried out and the effects of different adsorption process parameters were determined. Maximum removal efficiency of  $98.29 \pm 0.17$  % was obtained at  $pH = 1.0$ , adsorbent dose  $0.5 \text{ g} \cdot \text{L}^{-1}$ , initial Cr (VI) concentration  $50 \text{ mg} \cdot \text{L}^{-1}$ , temperature  $25.0 \pm 0.5$  °C, agitation speed 200 rpm and contact time of 30 min. The pseudo-second order model and Langmuir model provided the best fit to experimental kinetics and equilibrium isotherm data, respectively. Based on the values determined for the maximum adsorption capacity ( $q_{max} = 47.17 \text{ mg} \cdot \text{g}^{-1}$ ) the extracted onion processing waste could be applied as a low cost biosorbent for removal of Cr (VI) ions from polluted water.

**Keywords:** chromium, isotherms, kinetics, onion, removal, waste, water

## INTRODUCTION

Heavy metals polluted waters have become one of the major environmental problems nowadays. The raw and wastewaters that consist of heavy metals have to be treated because it will harm the ecosystems and public health. It is well established that heavy metals are non-degradable and causing various diseases and disorders [1 – 4].

Chromium (VI) is commonly used in industrial applications and has been considered among the top sixteen toxic pollutants with harmful effects on human health [3 – 8]. The conventional wastewater treatment methods used for removal of Cr (VI) were reported to be expensive and not efficient for the initial Cr (VI) concentration ranged from 10 to 100 mg·L<sup>-1</sup> [9].

Recently, the biosorption method for heavy metal removal from aqueous solution has become more applicable. Most of the biosorption studies considered plant waste materials which have the ability to remove metal ions [2 – 4, 10].

The onion processing industry generated solid waste rich in biologically active substances which can be subjected to utilization by extraction of existed phenols, flavonoids and etc. [11]. However, the extraction process resulted in a significant amount of solid residue which creates considerable environmental problem.

Adsorption of Cr (VI) has been reported in many studies [2 – 9, 12 – 16], including the use of onion skins as biosorbent of different heavy metals [17 – 21].

There were no data about the use of extracted onion processing waste (EOPW) for removal of chromium (VI) from aqueous solution. Therefore, the main goal of the present study was to examine the ability of the EOPW to remove Cr (VI) ions from aqueous solution.

## MATERIALS AND METHODS

The raw onion processing waste material used in this study was obtained and treated as described in our previous study [11]. The extracting onion processing waste was obtained as the follows procedure was performed. Firstly, the resultant onion processing waste powder was removed from biologically active substances by the extraction with 80 % methanol at 1 : 25 (w·v<sup>-1</sup>) for 60 min at 25 °C. Then the obtained solid residue was washed twice with distilled water (1 : 10 w·v<sup>-1</sup>) for 10 min at 25 °C. Finally, the EOPW was oven-dried at 60 °C for 2 h to the constant moisture content 6.00 ± 0.20 % and after cooling was stored in a plastic bag for further use [2].

Functional groups characterization of onion waste raw material and EOPW was conducted by VERTEX 70v FTIR Spectrometer Bruker (Germany) in pellets with KBr (Honeywell/Fluka FT-IR grade > 99 %). The spectra were recorded according to our previous studies [2 – 4].

Stock and working solutions of Cr (VI) was prepared according to [3 – 5] and the pH value of the samples was adjusted by adding 0.1 M NaOH or HCl solutions [2 – 5].

Batch adsorption experiments were carried out for determination of the effects of pH (1.0 - 4.0), initial Cr (VI) concentration (5-100 mg·L<sup>-1</sup>), EOPW biosorbent dose (0.25-1.5 g·L<sup>-1</sup>) and contact time (5 - 35 min) on the removal of Cr (VI) from aqueous solution according to procedure described in our previous studies [3 – 5].

Analytical determination of Cr (VI) concentration in the samples was performed at 540 nm by using standard Diphenylcarbazide method [3 – 5, 22].

The metal uptake  $q$  ( $\text{mg}\cdot\text{g}^{-1}$ ) and the removal efficiency  $RE$  (%) were calculated according to our previous studies [2 – 5, 22 – 26].

The equilibrium time of Cr (VI) biosorption was determined by conducting of kinetic experiments ( $pH$  1.0, biosorbent dose 0.05 g, initial metal concentration  $50 \text{ mg}\cdot\text{L}^{-1}$  and contact time 5 to 35 min) as described in our previous studies [2, 3, 5]. The modelling of the obtained kinetic experimental data was carried out by using of pseudo-first-order kinetic model [33] and pseudo-second-order kinetic model [24] in their linearized forms according to [2, 3, 5, 23, 25].

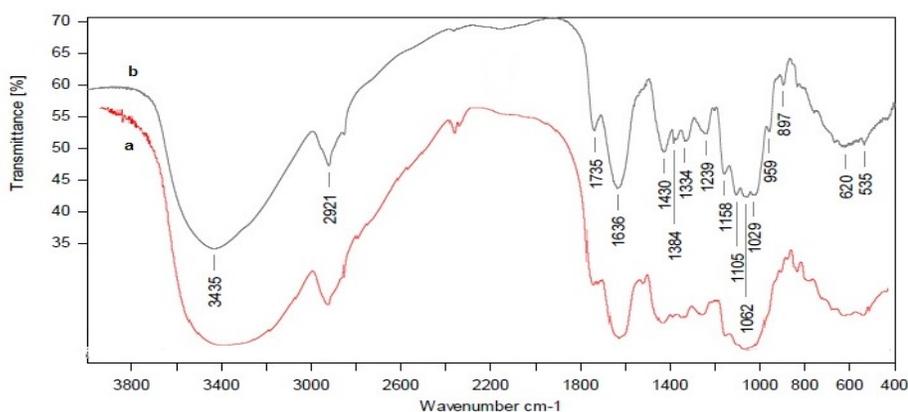
Isotherm study was performed ( $pH$  1.0, biosorbent dose 0.05 g, initial metal concentration  $5.0 - 100.0 \text{ mg}\cdot\text{L}^{-1}$  and equilibrium time 60 min) and the Freundlich [27] and Langmuir [28] isotherms in their linearized forms were applied for modeling of the experimental equilibrium data for Cr (VI) removal as described in [2 – 5, 23, 26].

All experiments were run in triplicate. The data were analyzed and presented as mean values. Statistical techniques, incl. ANOVA and Duncan's Multiple Range Test were applied to determine the significant differences at 95% confidence ( $P < 0.05$ ) level [2 – 5].

## RESULTS AND DISCUSSION

### FT-IR characterization of onion processing waste (OPW) raw material and EOPW biosorbent

The yield after treatment with 80 % methanol was 86 % dry weight. The IR-FT spectra of OPW raw material (a) and EOPW biosorbent (b) were presented in Figure 1 and some of the bands for typical functional groups were summarized in Table 1. Typical bands for carbohydrates (cellulose, pectin and inulin), as well as quercetin (Figure 1), were observed in OPW raw material and biosorbent FT-IR spectra.



**Figure 1.** FT-IR spectra of OPW raw material (a) and EOPW biosorbent (b)

Moreover, the quantity of dietary fiber in OPW was previously described [11], that could explain better sorption properties of biosorbent.

The broad band at  $3388\text{ cm}^{-1}$  was assigned to the (O–H) stretching vibrations of the intermolecular H - bridge between the OH groups, hydrogen-bonded and free hydroxyl groups of the alcohols and phenol groups of the compounds [27, 28]. After treatment (Figure 1b) this band shortened and maximum at  $3435\text{ cm}^{-1}$  was observed that is typical for an existence of intramolecular H-bridge between the OH groups. In both spectra bands at  $2921\text{ cm}^{-1}$  were observed that was due to C–H stretching vibrations. The band at  $1713\text{ cm}^{-1}$  that was assigned with C=O disappeared in biosorbent spectra. Moreover, the band at  $1735\text{ cm}^{-1}$  increased in the EOPW biosorbent spectrum (Figure 1b) that was due to the formation of carboxylic acid salt. The asymmetric stretching vibration of the carboxylate group appears at  $1620\text{--}1598\text{ cm}^{-1}$ . Band at  $1335.73\text{ cm}^{-1}$  corresponded to the C–N stretching of the aromatic amine group and was in accordance with observation for onion peel extract [29]. In EOPW biosorbent spectra (Figure 1b) was observed a new strong band at  $1239\text{ cm}^{-1}$  that was associated with the vibrations (C–H) of pectic acid salt. The band at  $1067$  and  $1323\text{ cm}^{-1}$  corresponding to  $\nu(\text{C–O–C})$  and  $\nu_s(\text{C–OH})$ . Moreover, some bands were observed that approved presence of quercetin in complex matrices. The data coincided with reports for its typical bands  $1622.20\text{ cm}^{-1}$  and  $1438.96\text{ cm}^{-1}$  are due to the C–C stretch of aromatic rings in onion peel [30]. In addition, bands at  $814, 706, 594\text{ cm}^{-1}$  are C–H bending of aromatic hydrocarbons. Savic-Gajic et al. (2018) mentioned additional characteristic bands of quercetin from onion peel at  $3434\text{ cm}^{-1}$  of  $\nu(\text{O–H})$ , at  $1656\text{ cm}^{-1}$  of free ketone group,  $1608\text{ cm}^{-1}$  of  $\nu(\text{C=O})$ ,  $1382\text{ cm}^{-1}$  and  $1295\text{ cm}^{-1}$  of  $\nu(\text{C–O})$  and  $\delta(\text{C–OH})$  [31]. Further analysis of the spectrum in the  $1200\text{--}1000\text{ cm}^{-1}$  region showed specific bands typical for a pyranose ring vibration. In a fingerprint region band at  $925\text{--}930\text{ cm}^{-1}$  assigned with pyran ring stretch vibrations, as a band at  $926\text{ cm}^{-1}$  was assigned with  $\alpha\text{-D-Glcp}$  residue in the carbohydrate chain [32]. Band at  $893\text{ cm}^{-1}$  was in the range of  $892\text{--}895\text{ cm}^{-1}$  that was considered as typical for C-anomeric groups stretch, C<sub>1</sub>–H-deformation; ring stretch and presence of  $\beta$ -mannose in pyranose form [33]. Typical band for  $\beta$ -glucopyranosyl residue was observed at  $897\text{ cm}^{-1}$  in both spectra. These bands together with others at  $1158\text{ cm}^{-1}, 1316\text{ cm}^{-1}, 1374\text{ cm}^{-1}, 1429\text{--}1422\text{ cm}^{-1}$  were typical for cellulose [34]. Our observations coincide with other authors who demonstrated that bands at  $1426\text{ cm}^{-1}$  and  $1422\text{ cm}^{-1}$  suggesting the C–H bending present in cellulose, while peaks at  $896\text{ cm}^{-1}$  reflected  $\beta$ -glycosidic linkages among sugar units [35]. In addition, a band at  $863\text{ cm}^{-1}$  was assigned with ring methylene rocking and was also characteristic for galactopyranose derivatives (pectin) [33]. Bands at  $832\text{ cm}^{-1}$  and  $817\text{ cm}^{-1}$  are typical for the inulin structure [32] and were assigned to the presence of 2-ketofuranose joined to pyranosyl or furanoside residues and presence of 2-ketose in type IIA bands [33]. Moreover, the absorption bands at  $781, 666$  and  $598\text{ cm}^{-1}$  showed the presence of ketopyranose and pyranose rings in the polymer chain [33, 37]. In fingerprint region bands  $833\text{--}810\text{ cm}^{-1}$  was also due to out of plane p-substituted phenyl and C–H bending of aromatic hydrocarbons [33]. Most of the bands in IR-FT spectra of EOPW biosorbent and OPW raw material (Table 1) were in accordance with reports of Chowdhury et al. (2012) [17] and Waweru et al. (2016) [19]. Similar observations for presence of carbohydrates in onion peels and skins were reported by other authors with characteristic bands (O–H stretch:  $3400\text{ cm}^{-1}$ , C–H stretch:  $2925\text{ cm}^{-1}$ , C–O, C–C stretch, C–OH, and C–O–C:  $1200\text{--}950\text{ cm}^{-1}$ ) [17, 38]. The FT-IR spectra of OPW raw material contained typical bands for carboxyl, carbonyl, and hydroxyl groups that were the dominating functional groups that may play a major

role in Cr (VI) ion biosorption, similar to reported results for Cd<sup>2+</sup> biosorption and other heavy metals [18, 39].

**Table 1.** FT-IR infrared absorption bands of OWP raw material and EOPW biosorbent

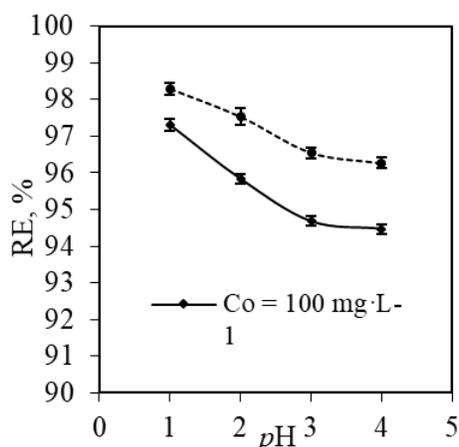
Wavelength [cm <sup>-1</sup> ]	OWP raw material	EOPW biosorbent	Assignments [17, 33, 35, 36]
3450 – 3570	-	3435	OH stretch, intramolecular H-bridge between the OH groups
3200 – 3400	3340	-	OH stretch, intermolecular H-bridge between the OH groups
3000 - 2800	2921	2921	CH <sub>2</sub> asymmetric stretching, Ar-CH <sub>3</sub>
2900 - 2800	2852	2852	CH <sub>2</sub> symmetric stretch
1745 - 1735	1735	1735	C=O stretching vibration from ester group or salt ester
1720 - 1700	1713	-	C=O symmetrical stretching, vibration from COOH, aliphatic carboxylic acid
1650 - 1630	1640	-	N-H primary amide
1670 - 1620	1632	1636	C=O primary amide, H-bonding
1620 - 1590	1617	-	N-H deformation, primary amide
1517	1517	-	C=O aromatic stretch, C=C aromatic skeletal vibration
1450 - 1300	1423	1430	C=C aromatic stretch; C=O stretching vibration
1385 - 1375	1374	1384	C-H bending of CH <sub>3</sub>
1320 - 1290	1328	1334	C-H; bend in alkane
	1248	1239	C-O stretch of Aryl ether, C=C stretching vibration of aromatic ring
1125 - 1162	1157	1158	asymmetric stretching of C-O-C
1105	-	1105	C-F monofluoro derivatives
1015 - 1060	1065	1062	C-O stretching (C-O)
1029	1029	1029	C-O stretching

Many studies demonstrated the potential of onion as biosorbent of heavy metal ions, as Pb<sup>2+</sup>, Sn<sup>2+</sup>, Fe<sup>2+</sup>, Hg<sup>2+</sup>, As<sup>3+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup> [18, 20, 39]. In obtained EOPW biosorbent spectra (Figure 1b) the new bands at 535 and 414 cm<sup>-1</sup> appeared that could be explained by the presence of bond with metal ion [18]. Some authors [18, 40] explained that the presence of carbohydrates and inulin (non-digestible oligosaccharides) in onion theoretically make them good biosorbents. In EOPW biosorbent spectra the conversion of secondary amide to primary amide and –CH to C=C, lowering the free COOH and transformation ester salt were evident of formation and dissociation of bonds and groups through ion exchange or some other mechanisms. Similar to the observation of Kim et al. (2015) [41] was found in our case.

### Impact of pH on Cr (VI) removal efficiency

Among process factors, the pH value of the solution plays a significant role in controlling the adsorption of heavy metals, because the pH can affect the surface charge of the adsorbents, the degree of ionization and speciation of heavy metals [2, 10]. Determination of the optimal pH value at which the maximum metal removal efficiency

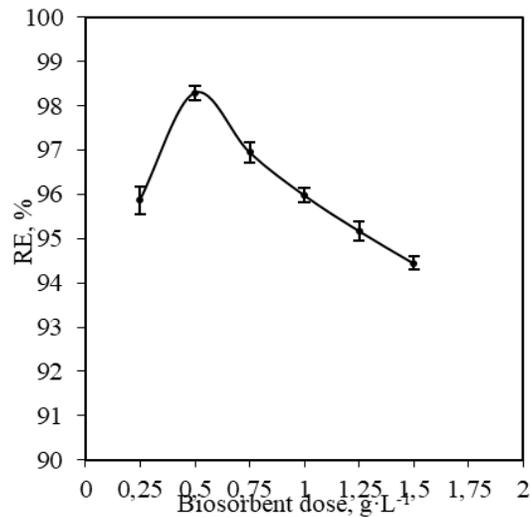
could achieve is very important from the practical point of view [42]. Impact of  $pH$  on Cr (VI) removal efficiency from the aqueous solution by EOPW biosorbent is presented in Figure 2. Maximum removal efficiency was found at  $pH = 1.0$  for the both initial metal concentrations of 50 and 100  $mg \cdot L^{-1}$ , respectively  $98.29 \pm 0.17 \%$  and  $97.31 \pm 0.15 \%$ . Wang et al. (2009) also reported that optimum Cr (VI) uptake by walnut hull occurred at  $pH = 1.0$  [43]. Most of the studies indicated that at low  $pH$ , chromium exists predominantly as negatively charged  $HCrO_4^-$  form and the positively charged surface of the adsorbent enhancing the sorbent-sorbate interaction resulting in high Cr (VI) removal [3 – 5, 7, 8, 14 – 16].



**Figure 2.** Impact of  $pH$  on the removal efficiency of Cr (VI) from aqueous solution by EOPW biosorbent (initial metal concentration 100 and 50  $mg \cdot L^{-1}$ , biosorbent dose 0.5  $g \cdot L^{-1}$ , 25 °C, 30 min, agitation speed 200 rpm)

### Impact of adsorbent dose on Cr (VI) removal efficiency

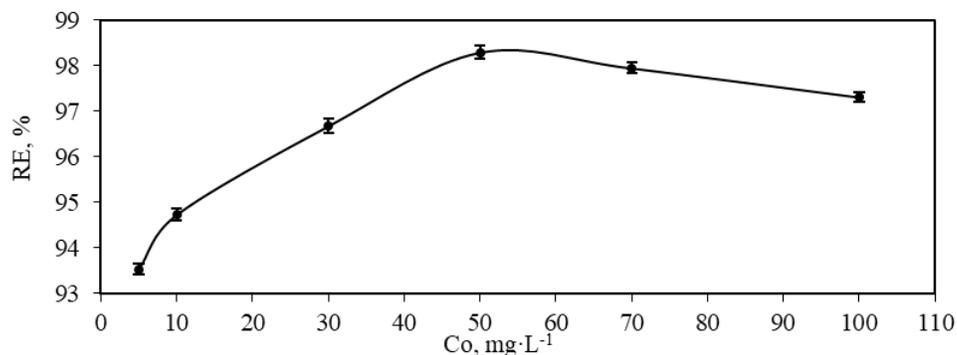
The removal of Cr (VI) from aqueous solutions by using of EOPW as a function of biosorbent dose is presented in Figure 3. The Cr (VI) removal efficiency was observed to increase with the increase in the biosorbent dosage up to 0.5  $g \cdot L^{-1}$ , but it then decreased. Nguyen et al. (2013) also reported that the removal of metal ions increases with increasing of biosorption dose because of the higher number of available adsorption active sites than decreased due to overlapping of adsorption sites leading to a decrease of total surface area [10].



**Figure 3.** Impact of biosorbent dose on the removal efficiency of Cr (VI) from aqueous solutions by EOPW biosorbent (initial metal concentration  $50 \text{ mg}\cdot\text{L}^{-1}$ , pH 1.0,  $25^\circ\text{C}$ , 30 min, agitation speed 200 rpm)

#### Impact of initial metal concentration on Cr (VI) removal efficiency

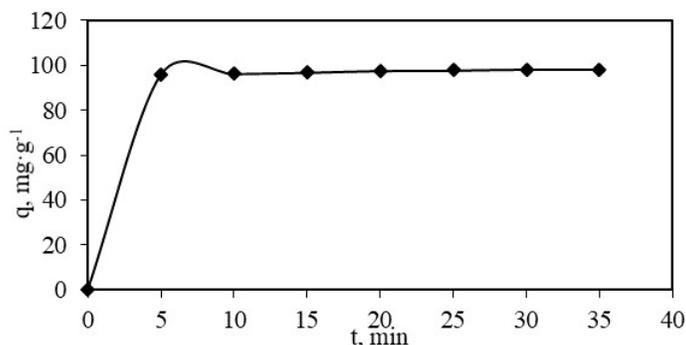
Figure 4 represents the results on the influence of the initial Cr (VI) concentration on metal removal efficiency. The maximum removal efficiency of  $98.29 \pm 0.17 \%$ , was found at an initial metal concentration of  $50 \text{ mg}\cdot\text{L}^{-1}$ . The removal efficiency of Cr (VI) ions from aqueous solutions by the EOPW was established to increase with the increase in the initial metal concentration up to  $50 \text{ mg}\cdot\text{L}^{-1}$ , probably due to at low concentration of metal ion solution the sorbent surface area is high as compared to the total metal ions available and there are more active sites on the biosorbent surface to be accessible by metal ions [15]. When the metal concentration increases above  $50 \text{ mg}\cdot\text{L}^{-1}$  the removal efficiency decreased because of overlapping of adsorption sites leading to decrease of total biosorbent surface area [10].



**Figure 4.** Impact of initial metal concentration ( $C_0$ ,  $\text{mg}\cdot\text{L}^{-1}$ ) on the removal efficiency of Cr (VI) from aqueous solutions by EOPW biosorbent (biosorbent dose  $0.5 \text{ g}\cdot\text{L}^{-1}$ , pH 1.0,  $25^\circ\text{C}$ , 30 min, agitation speed 200 rpm)

### Adsorption kinetics data

The contact time of the EOPW biosorbent and sorbate also has a significant impact on the biosorption efficiency [2]. The adsorption kinetics of Cr (VI) ions onto EOPW biosorbent is presented at Figure 5.



**Figure 5.** Adsorption kinetics of Cr (VI) ions onto EOPW biosorbent (biosorbent dose  $0.5 \text{ g}\cdot\text{L}^{-1}$ , pH 1.0,  $25^\circ\text{C}$ , agitation speed 200 rpm)

The results indicated that adsorption process is going on with rapid initial stage within the first 5 min and second slow stage with gradual adsorption until the system reached equilibrium. The established equilibrium time was 30 min. Such phenomenon was reported by others as well [3, 5, 8, 15, 43]. Kinetic data were fitted to two kinetic models and the obtained parameters are presented in Table 2.

**Table 2.** Kinetic parameters for the adsorption of Cr (VI) ions onto EOPW biosorbent

Experimental metal uptake ( $q_e^{\text{exp}}$ ) [ $\text{mg}\cdot\text{g}^{-1}$ ]	Pseudo-first order model			Pseudo-second order model		
	$q_e^{\text{cal}}$ [ $\text{mg}\cdot\text{g}^{-1}$ ]	$K_{1ads}$ [ $\text{min}^{-1}$ ]	$R^2$	$q_e^{\text{cal}}$ [ $\text{mg}\cdot\text{g}^{-1}$ ]	$K_{2ads}$ [ $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ ]	$R^2$
98.29	4.08	0.083	0.878	99.01	0.041	1.000

The results showed that pseudo-second order model gives better representation of the experimental kinetic data and the calculated value of equilibrium metal uptake ( $q_e^{\text{cal}}$ ) agree quite well with the experimental value ( $q_e^{\text{exp}}$ ). Most of the studies also reported that adsorption of Cr (VI) by different biosorbents follows the pseudo-second order kinetics an indication of chemisorption mechanism [3, 5, 8, 13 – 15, 44, 45].

### Equilibrium isotherms data

Equilibrium adsorption isotherms study is of fundamental importance in the design of adsorption systems. An adequate mathematical modelling of the experimentally obtained isotherm is essential for the efficient design of the system [2 – 5, 13, 26]. In the present work, the isotherm models of Langmuir and Freundlich, as two of the most frequently used models [3, 4, 44], were tested and the determined isotherm parameters by applying linear regression are summarized in Table 3.

**Table 3.** Isotherm parameters of Langmuir and Freundlich models for biosorption of Cr (VI) ions onto EOPW biosorbent

Langmuir isotherm model			Freundlich isotherm model		
$q_{max}$ [mg·g <sup>-1</sup> ]	$K_L$ , [L·mg <sup>-1</sup> ]	R <sup>2</sup>	1/n	$K_F$ [mg·g <sup>-1</sup> ]	R <sup>2</sup>
47.17	0.534	0.951	1.508	63.36	0.893

The obtained coefficients of determination (R<sup>2</sup>) indicate that the Langmuir model corresponded better to the experimental data within the concentration range studied compared to Freundlich model. Similar results were reported by other studies [7, 8, 14, 16]. The Langmuir separation factor (R<sub>L</sub>) values were found to be between 0.018 and 0.272, which indicated that the biosorption of Cr (VI) ions from aqueous solutions is favourable under conditions of this study [3 – 5, 46]. Based on the values of the maximum adsorption capacity (q<sub>max</sub>), the EOPW biosorbent was found to have good affinity for Cr (VI) ions compared to other biosorbents reported in the literature [3, 4, 14, 15, 47 - 50].

Further research is needed concerning regeneration of EOPW, determination of the reused biosorbent cycles and adsorption thermodynamics.

## CONCLUSIONS

The results from the present study indicated that EOPW could be applied as a cheap biosorbent for the removal of Cr (VI) ions from aqueous solutions. Adsorption batch experiments showed that maximum removal efficiencies of 98.29 ± 0.17 %, were obtained at pH = 1.0, adsorbent dose 0.5 g·L<sup>-1</sup>, initial Cr (VI) concentration 50 mg·L<sup>-1</sup>, temperature 25.0 ± 0.5 °C, agitation speed 200 rpm and contact time of 30 min. The pseudo-second order kinetic model was found to give a better representation of the experimental data with R<sup>2</sup> = 1.000. The results indicated that the adsorption isotherms followed the Langmuir model (R<sup>2</sup> = 0.951). Finally, the EOPW biosorbent was found to have good affinity for Cr (VI) ions with maximum adsorption capacity of 47.17 mg·g<sup>-1</sup>. The present study provides practical information for application of biosorbent obtained as waste material from the canning industry for removal of Cr(IV) ions from aqueous solution.

## ACKNOWLEDGMENTS

The manuscript is dedicated to the memory of Prof. Tsvetko V. Prokopov.

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