

Simultaneous adsorption of heavy metals from water by novel lemon-peel based biomaterial

Elma Šabanović, Mustafa Memić*, Jasmina Sulejmanović, Alisa Selović

University of Sarajevo, Faculty of Science, Department of Chemistry, Zmaja od Bosne 33-35, 71 000 Sarajevo, Bosnia and Herzegovina

*Corresponding authors: e-mail: m_memic@yahoo.com

Simultaneous adsorption of heavy metals in complex multi metal system is insufficiently explored. This research gives results of key process parameters optimization for simultaneous removal of Cd(II), Co(II), Cr(III), Cu(II), Mn(II), Ni(II) and Pb(II) from aqueous solution (*batch* system). New lemon peel-based biomaterial was prepared and characterized by infrared spectroscopy with Fourier transformation (FTIR), scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS), while the quantification of metals was made by atomic absorption spectrometry (AAS). Simultaneous removal of seven metals ions was favorable at pH 5 with 300 mg/50 mL solid-liquid phase ratio, within 60 min at room temperature with total obtained adsorption capacity of 46.77 mg g⁻¹. Kinetic modeling showed that pseudo-second order kinetic and Weber-Morris diffusion models best describe the adsorption mechanism of all seven heavy metals onto lemon peel.

Keywords: lemon peel, heavy metals, biosorption, FAAS

INTRODUCTION

Heavy metal ions are the most common pollutants found in water/wastewaters due to their high mobility and persistence in the environment, having serious environmental impacts worldwide¹. Traditional methods of industrial wastewater treatment, such as chemical precipitation, coagulation, the use of activated carbon or polymer resin etc. have several drawbacks, which include sludge formation and high cost². Therefore, the use of non-eatable agricultural parts that have no nutrition value, considered as green, non-toxic and biodegradable adsorbents, has becoming alternative to traditional treatment methods for heavy metal removal.

One group of such low-cost agricultural waste, generated in high quantities mostly by the juice producing industry, is citrus peels³. There is some indication that the carboxyl groups of pectic acid (a biopolymer known to be present in citrus peels) as well as functional groups of cellulose are acting as binding sites for positively charged metal resulting in good metal uptake. Several types of citrus peels, native or chemically modified, have been recently explored for the removal of various heavy metals from wastewaters^{4–11}.

Wastewaters contain more than one metal ion that could mutually interfere affecting each other's removal^{12–13}. Therefore, it is important to investigate and optimize insufficiently explored adsorption in multi-metal systems, which is the novelty of the present study. To the best of our knowledge, *Citrus limon* peel has never before been used as biosorbent for simultaneous removal of seven (Cd(II), Co(II), Cr(III), Cu(II), Mn(II), Ni(II) and Pb(II)) heavy metal ions from aqueous solutions.

Regarding this, used biosorbent was characterized and applied in batch experiments in order to optimize key process parameters (sample pH, biosorbent dose, sample volume, contact time, temperature and initial metal concentration).

The research has been carried out at the Faculty of Science University of Sarajevo, Bosnia and Herzegovina, in 2019.

MATERIALS AND METHODS

Chemicals and Instruments

All chemicals were of analytical grade. A multi element stock standard solution of Cd, Co, Cr, Cu, Mn, Ni, and Pb (5000 mg L⁻¹ of each ion) was prepared by weighing (Metler Toledo balance, ± 0.1 mg) and dissolving acquired mass of Cd(NO₃)₂ · 4H₂O, Co(NO₃)₂ · 6H₂O, Cr(NO₃)₃ · 9H₂O, Cu(NO₃)₂ · 3H₂O, Mn(NO₃)₂ · 4H₂O, Ni(NO₃)₂ · 6H₂O and Pb(NO₃)₂ salts supplied by Merck Darmstadt. A mixed working solution was daily prepared by diluting multi element stock standard solution.

Sodium hydroxide (Merck, Darmstadt), 65% nitric acid (Carlo Erba, Milano) and 96% sulphuric acid (Merck, Darmstadt) were used for different modification procedures of lemon peel applied in this study. pH adjustment (CG 841 SchottGERÄTE GmbH) was made by sodium hydroxide (Merck, Darmstadt). Varian SpectrAA model 240 FS flame atomic absorption spectrometer (FAAS) was used for carrying out all the measurements.

Infrared spectroscopy with Fourier transformation (FTIR) was used to identify the functional groups in native as well as modified lemon peel before and after adsorption. The spectra were recorded by PerkinElmer BX FT-IR spectrometer with the samples prepared as KBr pellets.

Surface morphology of used biomaterial was characterized by scanning electron microscopy (SEM) model JEOL JSM-6610LV, while electron dispersive spectroscopy (EDS) unit (model: X-Max Large Area Analytical Silicon) was used for the elemental analysis.

Other equipment used for the experimental part of this study included orbital shaker (BOECO PSU-10i, Germany), magnetic stirrer (MR Hei-Standard, Heidolph, Germany) and dryer (Bodalec & Havoic, Croatia).

Preparation and modification of biosorbent

In order to improve sorption properties, native lemon peel purchased at local supermarket was washed several times with distilled water, air-dried, cut into pieces of 0.5–1.0 cm, blended and sieved through a standard

steel sieve (\emptyset 0.25 mm). One part was used as native lemon peel in this form and the rest was subjected to six different modification processes.

Selection of modification processes was focused on two criteria: (i) avoidance of using hazardous reagents and/or their high amounts as well as any complicated procedures; (ii) removal of excess cations such as calcium or magnesium that could interfere with metal sorption and to creation of a more defined sorbent material.

Therefore, according to procedures described by Šabanović et al.¹⁴ native peel (A) and (B) peel treated with 0.25 mol L⁻¹ nitric acid followed by 0.1 mol L⁻¹ sodium hydroxide were prepared. Furthermore, (C) material was obtained following the treatment with 0.1 mol L⁻¹ HNO₃ described by Schiewer and Patil¹⁵, while (D) modification was same as (B) only applied to different starting size fraction (< 250 μ m instead to 0.5–1.0 cm pieces). Additionally, (E), (F) and (G) materials were obtained according to Mallampati and Valiyaveetil¹⁶, Memon et al.¹⁷ and Özer and Piringçi¹⁸, using 2-propanol, excess of 1 mol L⁻¹ NaOH and concentrated sulphuric acid, respectively. In the final stage these materials were dried, grounded and sieved (\emptyset 0.25 mm).

Methodology

Prepared lemon peel based biosorbent (50–300 mg) was added into a multi-element solution (50–100 mL) of a defined pH value (3–5) containing seven heavy metals (5–100 mg L⁻¹, each). The simultaneous removal of tested ions was carried out at 250 rpm and filtrates were collected at suitable time intervals (0–180 min) at four different temperatures (room, 30, 40 and 50°C). Adsorption capacity (Eq. 1) i.e. the adsorbed amount of each metal ion (q , mg g⁻¹) was calculated by subtracting initial and final ion concentration at the moment of measurement according to Vanderborgh and Van Grieken¹⁹:

$$q = (C_i - C_f) \cdot V / m \quad (1)$$

where C_i and C_f are initial and final concentrations of each metal ion at the filtrate (mg L⁻¹), V is the volume of solution (L) and m is the mass of the biosorbent (g). Heavy metal removal efficiency (Eq. 2) was expressed as:

$$\text{Removal efficiency (\%)} = (C_i - C_f) \cdot 100 / C_i \quad (2)$$

where Removal efficiency (%) is the amount of analyte retained on the biosorbent.

To ascertain whether there is a loss of analytes due to their possible adsorption on the walls of used glass flasks and/or other processes occurring within i.e. adjusting the pH value, etc., under identical conditions only without biosorbent, a control sample or a blank was subjected to all steps of the experiment. Concentration of each metal ion measured in the control sample was taken as the initial concentration (C_i).

All experiments were made in triplicates and the results were expressed as mean value \pm RSD.

Kinetic modeling

Pseudo-first (Eq. 3) and pseudo-second order model (Eq. 4) developed by Lagergren²⁰, Ho and McKay²¹, respectively, as well as intraparticle diffusion model (Eq. 5) developed by Weber and Morris²² were fitted to the obtained results. Based on the coefficient of correlation, as

a measure of experimental data matching the proposed model, the best model was chosen. The integrated forms of used models can be expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

$$q_t = k_{in} \cdot t^{0.5} + c \quad (5)$$

where q_e and q_t (mg g⁻¹) are the amounts adsorbed at equilibrium and at time, t , respectively; k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the rate constant of the pseudo-first and pseudo-second order adsorption, respectively; k_{in} represent the diffusion rate constants within the biosorbent particle (mg g⁻¹ min^{-1/2}) and c is the constant of the diffusion model in the function of the boundary layer thickness (mg g⁻¹).

Error analysis

The correlation coefficient (R^2) and statistical functions (Eqs. 6, 7 and 8): Chi square test (X^2), normalized deviation (ND) and normalized standard deviation (NSD) between experimental and calculated values were applied as suitable error tools to evaluate the significance of the kinetic models applicability as follows:

$$X^2 = \sum_{i=1}^n \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \quad (6)$$

$$ND = \frac{100}{N} \sum \left| \frac{(q_{e,exp} - q_{e,cal})}{q_{e,exp}} \right| \quad (7)$$

$$NSD = \left(\sqrt{\frac{\sum (q_{e,exp} - q_{e,cal} / q_{e,exp})^2}{N}} \right) \cdot 100 \quad (8)$$

where N is the number of data points.

RESULTS AND DISCUSSION

Lemon peel modification screening

In order to enhance the biosorption characteristics of native lemon peel, six different modifications were applied and the results are shown at Fig. 1. Shown values are given as average of all seven tested ions for each used material. A-G marks at x axis are clarified in *Preparation and modification of biosorbent* Section.

It can be assumed that acid treatments increased the number of positive acidic oxygen functional groups²³,

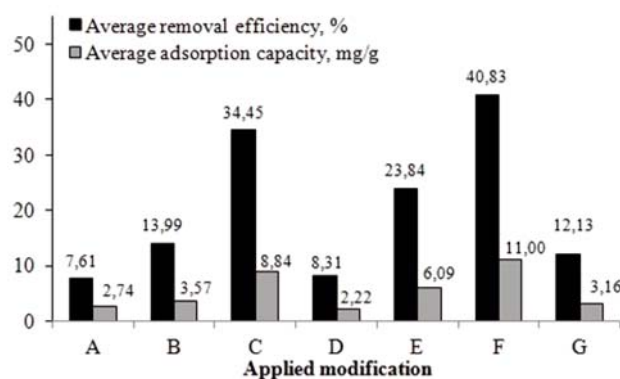


Figure 1. Lemon peel modification screening. Conditions: pH 5; total metal concentration 350 mg L⁻¹; amount of biomass 100 mg; volume of the solution 50 mL; room temperature; equilibrium time 60 min at 250 rpm

while NaOH cleaved ester bonds and generated more hydroxyl groups¹⁶. As can be seen, F material treated by 1 mol L⁻¹ NaOH had shown the best metal uptake ability both in Removal efficiency (%) and adsorption capacity (mg g⁻¹). Therefore, for all experiments within this study only this lemon peel-based sorbent was utilized.

Biomaterial characterization

Point of zero charge

According to Ghasemi et al.²⁴ the pH at the point zero charges (pH_{PZC}) indicate the net surface charge responsible for electrostatic repulsion or affinity for cations. The determination of this parameter has been made following the procedure described by Sulejmanović et al.²⁵ which included suspending 0.10 g of biosorbent into 30 mL of 0.1 mol L⁻¹ KNO₃ as electrolyte buffered to pH 2–10, stirred 24 h followed by filtration and pH measuring. As can be seen from Fig. 2, pH_{PZC} of modified lemon peel was 5.67, which means that at pH lower than 5.67 its surface is positively charged and at pH higher than this values it is negatively charged. The point of zero charge of native lemon peel was 3.95, meaning that the modification made the material more alkaline and negatively charged, resulting in better affinity to bind positively charged metal ions.

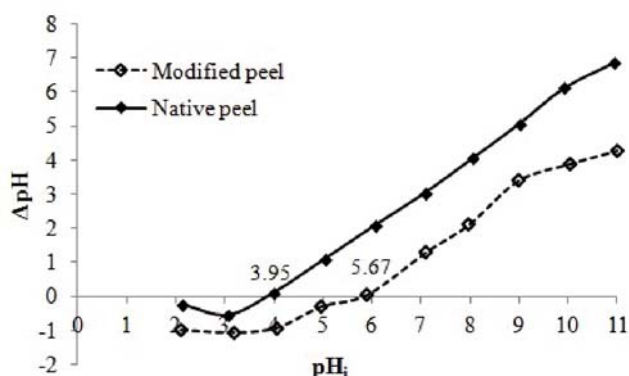


Figure 2. Point of zero charge

FTIR spectra

Since protein, pectin, cellulose, hemi cellulose, lignin and pigments are the most important components of lemon peel, FTIR spectra was used to detect reactive functional groups containing different donor atoms (i.e. oxygen, nitrogen, sulfur and phosphorus)²⁶. Fig. 3 shows the FTIR spectra of native lemon peel (a), modified lemon peel (b) and modified lemon peel with 7 heavy metals (c). The expectation was that saponification of protein and other organic substances of native lemon peel would result in higher quantity of carboxyl groups and reduced amount of phenolic and lactonic groups²⁷. As can be seen, the wide and intense peaks among 3200 and 3600 cm⁻¹ in both (a and b) spectra are due to the stretching vibrations of free or H-bonded hydroxyl groups of phenols, alcohols and carboxylic acids contained in cellulose, pectin and lignin²⁸. The peaks observed around 2926 cm⁻¹ were due to the stretching vibrations of the methylene, methoxy and methyl groups¹⁴. The characteristic peak at 1742 cm⁻¹ in case of native lemon peel could be assigned to stretching vibrations of ester carbonyl (C=O) group. After hydrolysis of carbonyl to

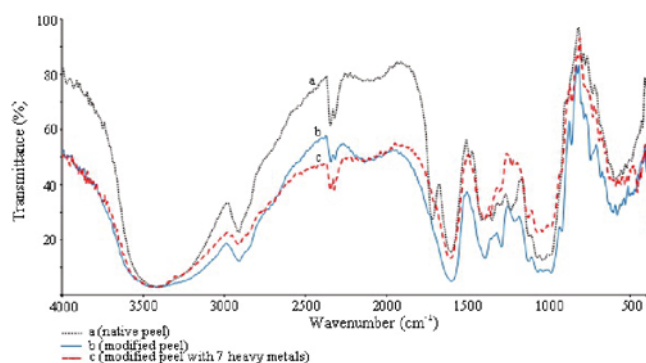


Figure 3. FTIR spectra of native lemon peel (a), modified lemon peel (b) and modified lemon peel with 7 heavy metals (c)

carboxyl group, this peak disappeared in case of modified lemon peel as a result of protein, pectin and some organic substances removal^{11, 26, 29}. This was additionally supported by disappearance of stretching vibration of C=C in aromatic rings of lignin which in native lemon peel spectrum was obtained at 1515 cm⁻¹³⁰. The peak around 1622 cm⁻¹ was indication for stretching vibration of carboxylate ions (COO⁻) and strengthening of this peak, in case of modified peel, was due to increased number of carboxyl group in cellulose or pectin²⁸. The peaks in the range of 1300–1020 cm⁻¹ could be attributed to the compounds containing a C-O group. Also, a new, less intense and sharp band at 894 cm⁻¹ in modified peel spectrum was characteristic α-glycoside bonds between anhydrous glucose units in celluloses structure after removal of hemi cellulose and lignin³¹. This was additionally supported by the increase of cellulose content according to the band intensity increase, due to HCH and OCH in plane bending vibration in cellulose around 1423 cm⁻¹³².

By peak position and peak intensity comparison within spectra before and after metal ion adsorption, FTIR technique is a very useful tool in the confirmation of removal of metal ions. FTIR spectrum of modified lemon peel (b) showed cellulose as main constituent, having functional groups such as carboxyl and hydroxyl, capable to bond metal ions in aqueous solutions^{26, 27}. Observed FTIR spectrum of modified lemon peel loaded with 7 metal ions (c) shows that all peaks regarding carboxyl and hydroxyl groups have shifted to higher wave numbers and their intensities were lower compared to spectrum of unloaded modified lemon peel (b). From this point of view it could be concluded that metal ions were incorporated within the modified lemon peel *via* interaction with COO⁻ and OH⁻ groups.

SEM-EDS analysis

In the present study SEM analysis was used for characterizing the morphology and structure of the chosen F material before and after metal ions sorption. SEM micrograph of native lemon peel, F modified peel within heavy metals as well as loaded with 7 heavy metals are shown at Fig. 4.

Comparing SEM images of native and modified lemon peel, there are evident structural differences within shape, distribution and size of the particles, which is at the same time an indicator of successful modification. Heterogeneous surface of native peels particles is noticeable (a1, a2), while modified particles are bigger, homogeneous,

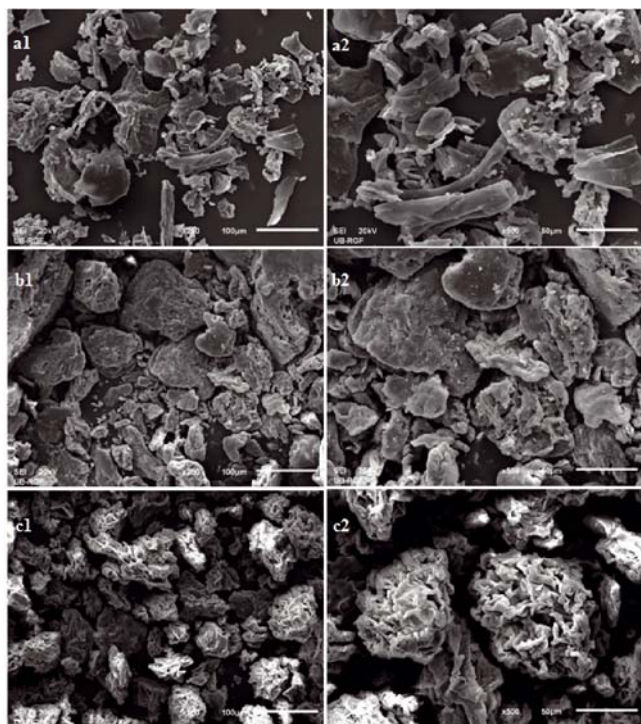


Figure 4. SEM images of the lemon peel based native (a), modified (b) and modified sorbent loaded with metals (c) amplified by 250x (a1, b1, c1) and 500x (a2, b2, c2), respectively

smooth and more compact (b1, b2). It can be seen that the modification resulted in the removal of smaller particles of native material and it can be assumed that the treatment of lemon peel resulted in the reduction of “inactive” parts of the biomass and other impurities, thereby making the “active” surface of the biosorbent (surface rich in functional groups) more accessible for binding of ions. The presence of impurities, waxes and greases can interfere with sorption by masking or blocking active sites on the material surface. Furthermore, after adsorbing/incorporating heavy metals, significant change in morphological structure of modified peel has been occurred. Instead of expectably layers, particles and/or “islands” as separate phase on the biomaterial surface, a “sponge” like porous structure was obtained after adsorption (c1, c2). This phenomenon indicates that the sorption took place on the biosorbent surface.

Additionally, EDS data confirmed the successful modification of native lemon peel (sodium was detected after modification) as well as successful metal ions sorption (all seven metals were detected). At Fig. 5, EDS spectrum with respectful surface mapping (inset) of analyzed surface has been presented.

Furthermore, element weights (%) are given in detail at Table 1. Based on weight percentage quantification of samples, it can be seen that the surface composition of the biosorbent is mostly carbon and oxygen. Also, the

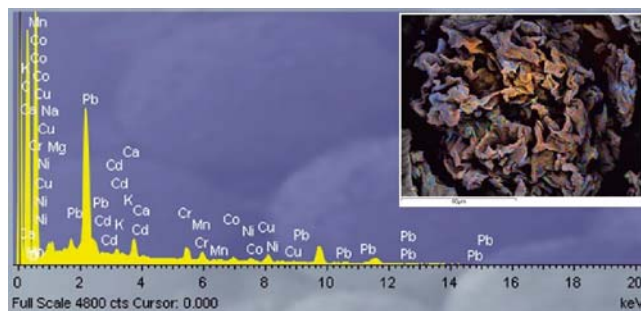


Figure 5. EDS spectrum of lemon peel loaded with 7 metals and surface mapping

presence of K, Ca, Mg and Cu was observed as they are mineral constituents of lemon peel³³.

The modification completely removed magnesium, while the potassium and copper content significantly decreased. Additionally, after simultaneous sorption of analytes, content of calcium ions becomes negligible, which could imply that ion exchange could be a kind of mechanism of interaction of this biomaterial with cationic species in general.

Optimization of process parameters

Solution pH

The effect of this parameter on metal Removal efficiency was investigated by varying the pH of multi metal solution from 3 to 5. Fig. 6 plots the Removal efficiency values of all seven tested ions for each tested pH.

As can be seen, this biomaterial can be efficiently applied in batch experiments at pH 5 because it showed the highest Removal efficiency values for all ions in general (36.40% Cd(II), 12.24% Co(II), 68.46% Cr(III), 81.73% Cu(II), 12.40% Mn(II), 17.35% Ni(II) and 87.84% Pb(II)). At pH below 5, the main groups responsible for metal sorption (which are seen from FTIR spectrum of lemon peel given at Fig. 3) are protonated due to the high concentration of H⁺ species. Regarding

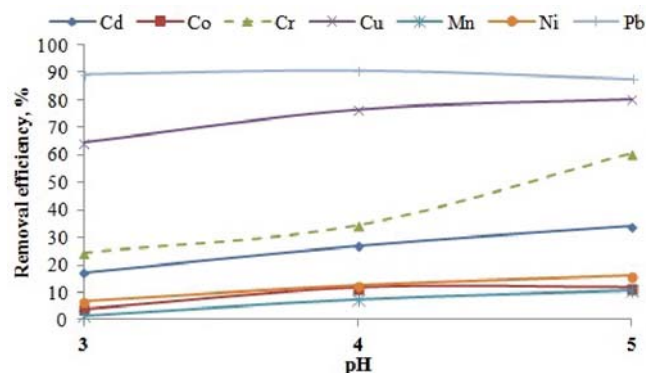


Figure 6. Effect of solution pH on the simultaneous removal of heavy metals. Conditions: total metal concentration 350 mg L⁻¹; amount of biomass 100 mg; volume of the solution 50 mL; room temperature; equilibrium time 60 min at 250 rpm

Table 1. EDS results of weight percentage quantification of samples

Sample	Element weight [%]							Total
	C	O	Ca	Mg	Na	K	Cu	
Native lemon peel	30.48	63.85	3.04	0.85	0.00	0.49	1.29	100.00
Modified lemon peel	24.44	67.89	3.52	0.00	3.42	0.16	0.56	100.00
Modified lemon peel with 7 metals adsorbed	24.35	67.15	0.80	0.00	0.63	0.00	1.74	100.00
	Cd	Co	Cr	Mn	Ni	Pb		
	0.83	0.59	1.21	0.68	0.60	1.41		

this, lower average values were obtained at pH 3 and 4. Furthermore, multi metal solutions with pH above 5 were not tested in view of the risk of hydrolysis and/or precipitation. Therefore, pH 5 was chosen as optimal value for further experiments.

Biomaterial dose

Biomaterial dose is an important parameter used to find out its adsorption capacity at particular initial concentration. The effect of this parameter was tested by dosing a different biosorbent mass (from 50 to 300 mg) in 50 mL of multi metal solution in which the initial concentration of each metal was 50 mg L⁻¹. The obtained results are presented in Table 2. The relative standard deviations for all obtained results were lower than 5.0%.

With the use of sorbent dose below 300 mg, a significantly lower Removal efficiency (R_{eff} , %) values were obtained, especially for Co, Mn and Ni. Therefore, 300 mg was selected for subsequent work because it represents an adequate compromise in the meaning of R_{eff} and q .

Sample volume

Sample volume, as well as sorbent dose, determines biosorbents capacity, so it is important to be optimized. To determine the best relation between the solid and liquid phase at which adsorption of investigated ions was most effective, sample volume varied from 50 to 100 mL (Table 3).

In general, a sample volume negatively correlated with R_{eff} in the case of 5 of 7 tested ions. Obtained relative standard deviations for all results were lower than 7.0%. However, at various tested solid-liquid phase ratios there was no significant difference in R_{eff} for Pb and Cu ions (> 90%) resulting in higher adsorption capacities. Based on this, it could be concluded that this biomaterial has stronger affinity toward Pb and Cu ions. Regarding simultaneous removal of heavy metal ions, for further testing 50 mL of multi metal solution was applied.

Contact time and biosorption kinetics

The contact time is one of the most important parameters for successful usage of the biosorption in practical and rapid adsorption application³⁴. At the previously determined optimal conditions (pH 5, sorbent dose 300 mg and sample volume 50 mL), contact time was varied in the range of 0–180 min, and the results are plotted at Fig. 7.

Fig. 7 shows a high Removal efficiency percentage in the initial minutes followed by a gradual stabilization. In order to assure enough time for establishing the dynamic equilibrium, all further experiments lasted 60 min.

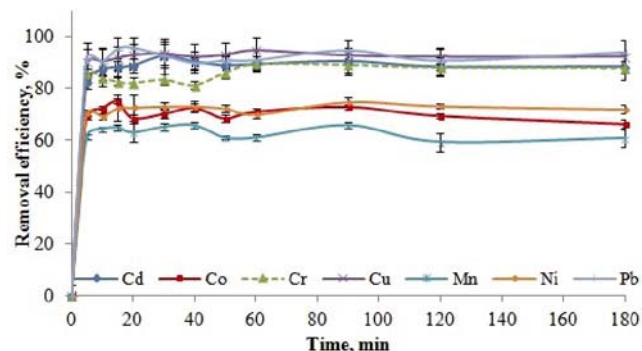


Figure 7. Effect of the contact time on simultaneous uptake of heavy metals by lemon peel-based biosorbent. Conditions: pH 5; total metal concentration 350 mg L⁻¹; biosorbent dose 300 mg; sample volume 50 mL; room temperature at 250 rpm

Pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models were used to simulate adsorption of metal ions onto modified lemon peel in order to examine the controlling mechanism of adsorption process. In Table 4, maximum adsorption capacities (q_{max}), kinetic constants (k) and correlation coefficients (R^2) used in the three named fittings, are listed. The calculated q_{max} of the pseudo-second-order model were

Table 2. Effect of sorbent dose on the simultaneous removal of heavy metals. Conditions: pH 5; total metal concentration 350 mg L⁻¹; sample volume 50 mL; room temperature; equilibrium time 60 min at 250 rpm

Dose	Parameter	Cd	Co	Cr	Cu	Mn	Ni	Pb
50 mg	R_{eff} , %	12.24	1.55	32.45	49.95	5.42	0.70	72.03
	q , mg g ⁻¹	6.17	0.77	19.88	23.88	2.78	0.35	36.63
100 mg	R_{eff} , %	36.40	12.24	68.46	81.73	12.40	17.35	87.84
	q , mg g ⁻¹	9.20	3.06	17.94	19.35	3.18	4.44	22.09
200 mg	R_{eff} , %	74.78	44.71	76.65	90.74	38.53	40.42	86.48
	q , mg g ⁻¹	9.39	5.59	11.74	10.84	4.93	5.09	10.99
300 mg	R_{eff} , %	89.10	70.98	89.59	94.77	60.79	69.91	90.66
	q , mg g ⁻¹	7.49	5.92	9.15	7.55	5.19	5.87	7.68

Table 3. Effect of sample volume on the simultaneous removal of heavy metals. Conditions: pH 5; total metal concentration 350 mg L⁻¹; biosorbent dose 300 mg; room temperature; equilibrium time 60 min at 250 rpm

Volume	Parameter	Cd	Co	Cr	Cu	Mn	Ni	Pb
50 mL	R_{eff} , %	89.10	70.98	89.59	94.77	60.79	69.91	90.66
	q , mg g ⁻¹	7.49	5.92	9.15	7.55	5.19	5.87	7.68
60 mL	R_{eff} , %	87.92	60.31	87.04	95.12	49.71	59.57	91.47
	q , mg g ⁻¹	7.89	6.32	10.68	8.96	5.22	5.79	9.87
70 mL	R_{eff} , %	75.69	51.62	86.31	95.01	44.00	55.25	88.54
	q , mg g ⁻¹	8.61	6.31	12.36	10.44	5.39	6.27	10.91
80 mL	R_{eff} , %	64.92	38.07	80.28	93.95	31.62	44.55	90.81
	q , mg g ⁻¹	8.44	5.32	13.13	11.80	4.43	5.77	12.79
90 mL	R_{eff} , %	57.54	34.35	75.14	91.40	30.67	36.32	91.81
	q , mg g ⁻¹	8.42	5.40	13.83	12.92	4.83	5.30	14.54
100 mL	R_{eff} , %	48.72	25.95	71.56	89.28	22.57	32.92	92.99
	q , mg g ⁻¹	7.92	4.53	14.63	14.02	3.95	5.33	16.37

Table 4. Kinetic parameters for Cd, Co, Cr, Cu, Mn, Ni and Pb ($q_{e,exp}$: 7.34; 5.63; 7.56; 7.17; 5.17; 5.73 and 8.17 mg g⁻¹, respectively)

Metal ion	Pseudo-first order			Pseudo-second order			Intraparticle diffusion					
	q_{max} [mg g ⁻¹]	k_1 [min ⁻¹]	R ²	q_{max} [mg g ⁻¹]	k_2 [g mg ⁻¹ min ⁻¹]	R ²	k_{i1}	R ₁ ²	k_{i2}	R ₂ ²	k_{i3}	R ₃ ²
Cd	1.10	-0.018	0.1525	7.34	0.243	0.9998	0.23	0.8695	-0.12	0.7585	-0.04	0.5720
Co	2.06	-0.001	0.0590	5.68	0.078	0.9976	0.03	0.0101	-0.47	0.7627	-0.14	0.9675
Cr	4.12	0.005	0.0199	7.54	0.066	0.9970	-0.20	0.4955	0.40	0.3893	-0.02	0.7576
Cu	7.10	0.019	0.1742	7.17	0.484	0.9997	0.10	0.9036	0.12	0.4312	-0.01	0.6135
Mn	1.42	-0.013	0.5138	5.12	0.103	0.9977	0.07	0.2696	-0.43	0.9339	-0.09	0.3967
Ni	5.24	0.014	0.3151	5.79	0.929	0.9993	0.09	0.4944	-0.10	0.1778	-0.06	0.9560
Pb	1.63	-0.002	0.0124	8.18	0.051	0.9979	0.18	0.5887	0.08	0.0606	-0.01	0.0011

closest to the experimental values with correlation coefficient (> 0.9970) higher than the pseudo-first-order (< 0.5138) and intraparticle diffusion kinetic model (< 0.9675).

Additionally, error analysis (the lowest X², ND and NSD values) supported the applicability of pseudo-second order model and chemisorption for each tested ion onto modified lemon peel.

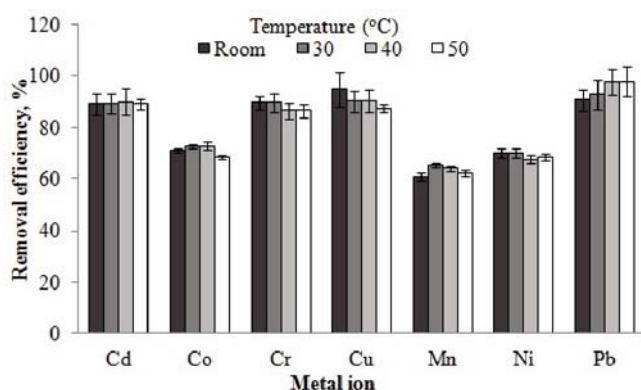
Diffusion of analyte toward the outer lemon peel surface as well as the ion exchange of the analyte with the weakest bonded and easily interchangeable ions on the biomaterial surface (first stage of Webber-Morris model) are also involved, especially in the case of Cd and Cu adsorption processes.

Furthermore, the combination of intraparticle diffusion of the analyte ions into the internal channels and the cavities of lemon peel, the ion exchange with the more difficult interchangeable ions as well as the binding of an analyte to active centers of biomass (second stage of Webber-Morris model) occurred, primarily for Mn. Attainment of equilibrium (third stage of Webber-Morris model) is important, mainly for the process of adsorption of Co and Ni ions.

Consequently, it can be concluded that the mechanism of Cd, Co, Cr, Cu, Mn, Ni and Pb adsorption onto lemon peel is mixed process of surface chemisorption, which takes place through the boundary layer of the biosorbent particles and intraparticle diffusion^{35, 36}.

Temperature

To establish the effect of temperature on the simultaneous heavy metal sorption onto used biomaterial, batch equilibrium studies at different temperatures (room, 30, 40 and 50°C) were carried out and the result were shown in Fig. 8.

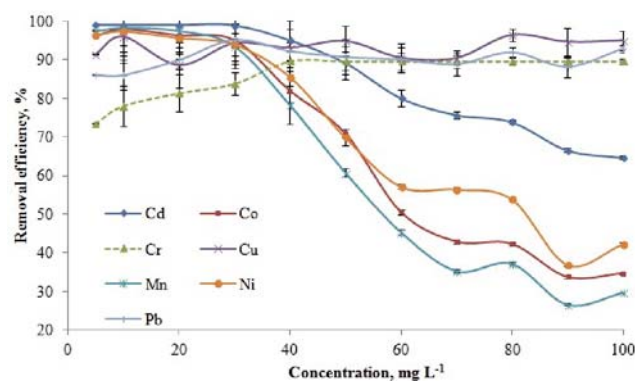
**Figure 8.** Simultaneous sorption of heavy metals at different temperatures. Conditions: pH 5; total metal concentration 350 mg L⁻¹; biosorbent dose 300 mg; sample volume 50 mL; equilibrium time 60 min at 250 rpm

Simultaneous heavy metal sorption was temperature independent, with slight fluctuations in removal efficiency. The fact that the proposed adsorption process does not require heating makes it very economic and could have industrial application in wastewater treatment. Therefore, the room temperature was the most suitable.

Initial metal concentration

Effect of initial multi metal concentration on the R_{eff} was investigated at the range from 5 to 100 mg L⁻¹ (Fig. 9).

In general, two different trends were obtained among tested metals. Copper, chromium and lead ions could be effectively adsorbed at all tested concentrations by used biosorbent. Obtained R_{eff} values were $>90\%$ for their initial concentrations above 40 mg L⁻¹. On the other side, R_{eff} sharply decreased after 30 mg L⁻¹ for cadmium, cobalt, manganese and nickel ions. This indicates that lemon peel has stronger affinity toward Cu, Cr and Pb ions showing that their adsorption is not influenced by matrix effect or ionic strength.

**Figure 9.** Effect of initial multi metal concentrations on the simultaneous biosorption. Conditions: pH 5; biosorbent dose 300 mg; sample volume 50 mL; room temperature; equilibrium time 60 min at 250 rpm

Comparison of adsorption capacity

The biosorption capacities for heavy metal ions of used lemon peel and other adsorption materials^{11, 37-41} were compared (Table 5). Used peel exhibited better adsorption capacity for Cd, Co, Cr, Cu, Mn and Ni than other listed biosorbents. Additionally, obtained adsorption capacity values were similar to Fe₂O₃-SiO₂-PAN nanocomposite material, which is less economical, high cost and more difficult to prepare. Despite lower achieved lead adsorption by used lemon peel, total capacity for heavy metals was better compared to all listed materials. It is important to highlight that lemon peel is applicable for simultaneous removal of seven metal ions, which is

Table 5. Comparison of various sorption capacities (mg g⁻¹) with the results of this study

Adsorption material	Cd	Co	Cr	Cu	Mn	Ni	Pb	Total ads. capacity	Ref.
Sunflower head carbon	0.20	–	0.18	–	–	0.26	–	0.64	37.
Banana peel	3.66	–	6.85	–	–	–	20.90	31.41	38.
Non activated peanut hull AHC	~0.45	–	–	~1.40	–	–	~10.36	47.39 (including methylene blue)	39.
Rice husk	5.54	–	3.00	–	–	–	4.10	12.64	40.
Tangerine peel	0.65	1.58	1.48	1.63	1.53	1.56	1.55	10.62 (including Zn)	11.
Fe ₂ O ₃ –SiO ₂ –PAN nanocomposite	–	6.65	4.36	7.20	6.79	2.60	–	44.49 (including Al, Ba, Zn and Ti)	41.
Modified lemon peel	7.34	5.63	7.56	7.17	5.17	5.73	8.17	46.77	This study

more than the average number of metals for which the other materials were used.

Therefore, this biomass may be considered as an excellent adsorbent with promising potential applications for the treatment of waters polluted with listed heavy metals due to its numerous advantages i.e. it is inexpensive biocompatible and readily available, biodegradable a nontoxic material with minimum effort in its preparation and minimum chemical consumption for its surface modification.

CONCLUSIONS

Biosorption using *Citrus limon* peel could make simultaneous metal removal economically feasible in situation where pollution control is otherwise insufficient due to prohibitively high costs. Kinetic modeling showed that pseudo-second order kinetic and Weber-Morris diffusion models best describe the adsorption mechanism of all seven heavy metals onto lemon peel with total obtained adsorption capacity of 46.77 mg g⁻¹.

This low-cost, easily available, eco-friendly and highly efficient biomass can be exploited for simultaneous removal of Cd(II), Co(II), Cr(III), Cu(II), Mn(II), Ni(II) and Pb(II) ions from polluted water.

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Disclosure statement

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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