



Adsorptive removal of eight heavy metals from aqueous solution by unmodified and modified agricultural waste: tangerine peel

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Abstract

Analysis was carried out using tangerine peel aiming its use as a potential adsorbent of eight heavy metal ions (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) from aqueous solution. This agricultural waste was tested both in its untreated and also chemically modified form. Based on Fourier transformation infrared spectra, a comparison of biosorbent structure before and after chemical treatment was made. Batch adsorption tests were conducted at different pH and mass of sorbent to examine the influence on the effectiveness of simultaneous removal of tested ions. Kinetic studies were conducted at optimum pH 5.0 and sorbent dosage 300 mg. The pseudo-second-order kinetic model best fit the experimental data with high correlation coefficients ($r^2 > 0.9997$). By optimizing listed parameters, high removal efficiencies ($> 89\%$) were achieved. According to the results obtained in this study, the remediation of water polluted with heavy metals could be done using modified tangerine peel as an agricultural waste material.

Keywords Batch · Biosorbent · Kinetic studies · Sorption · Spectroscopy

Introduction

The discharge of untreated effluent containing toxic metals into aquatic ecosystems has been an outcome of the rapid increase in population coupled with high industrial-scale operations. On account of their toxicity, continuous accumulation of non-degradable toxic elements and persistency in the environment is a specific concern (Benhima et al. 2008). Therefore, one of the research focuses in environment science becomes the methods and technologies to treat this harmful effluent (Gardea-Torresdey et al. 1996).

Traditionally, waste has been considered as something that is not useful and has been often neglected over the years. Considering the potential of waste/wastewater, research is progressing toward developing a closed loop approach for valorization of waste. Development of environmental methods definitely plays a prominent role in maintaining the ecological footprint. Adsorption is an excellent way to

treat contaminated water, offering advantages such as low-cost, greater availability, profitability, ease of operation and effectiveness in reducing the concentration of heavy metal ions to very low levels (Demirbas 2008). The biosorption process showed many desirable features including its rapid kinetics of adsorption and desorption, the selective removal of metals over a wide range of pH and temperatures in addition to the low capital and operation cost (Migahed et al. 2017). Biosorbents are prepared from naturally waste biomass (i.e., tangerine peel) which have abundant amount of, i.e., hydroxyl (around 3400 cm^{-1}) and carboxyl (around 1740 cm^{-1}) groups, responsible for metal ion sorption. But it has been reported that the sorption capacities of native biosorbents are quite low (Ngah and Hanafiah 2008). The surface modifications of biomass by acid or alkali remove most of the non-cellulosic components in order to increase the efficiency of the metal biosorption (Ghimire et al. 2007; Biswas et al. 2008; Mahmood-ul-Hassan et al. 2015; Šabanović et al. 2016). In that way, it is important to design the adsorption processes correctly and to determine how external factors, i.e., type of used sorption material as well as contact time, concentration of the impurities, pH and liquid-to-solid ratio, effect the adsorption efficiency (Wu et al. 2007; Sadeghi and Sheikhzadeh 2009; Yu et al. 2011; Gupta et al. 2012a, b, c; Šabanović et al. 2015). Adsorption kinetics

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also significantly contributes to the improvement of the process (Ho and McKay 1999; Plazinski et al. 2009; Souag et al. 2009; Debnath and Ghosh 2011; Moreno-Pirajan et al. 2011; Okasha et al. 2012).

For the present study, a batch contact time method was used and the equilibrium of eight heavy metals (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) adsorption onto unmodified and chemically modified tangerine peels was investigated. Kinetic data of the biomaterial were analyzed. The uptake of tested heavy metals on used adsorbents was examined as a function of pH, adsorbent dosage and contact time. The research has been carried out at the Faculty of Science University of Sarajevo, Bosnia and Herzegovina, in 2015.

Materials and methods

Adsorbent, chemicals, reagents and instrumentation

Tangerine acquired from a supermarket was hand-peeled and the peel was shredded with plastic scissors into pieces of less than 1 cm and then washed with tap and distilled water for several times. After thorough washing, peel was dried at room temperature and milled to 250 μm . The milled material was divided into two parts. One part was kept without further treatment while the second part was treated with 0.25 M nitric acid (HNO_3) for 24 h at room temperature occasionally stirring. Subsequently, the sorbent was rinsed with distilled water several times to neutral pH of the filtrate and air-dried for additional 24 h. Further, this tangerine peel was placed in a solution of NaOH (0.1 M) for 3–4 h and washed again with distilled water till neutrality. Biosorbent dried at ambient temperature was powdered and sieved to pass through the 250 μm sieve.

All chemicals used in the experiments were of analytical grade. A mixed working solution of Cr, Cu, Mn, Co, Ni, Pb, Cd and Zn was prepared by diluting respective single-element atomic absorption Stock solution (1000 mg L^{-1} , Certipur grade, Merck, Germany). In all the experimental works, pH of the solutions was maintained by using 0.1 M HNO_3 and 0.1 M NaOH (Semikem, Sarajevo) and measured by CG 841 Schott–GERATE GmbH. During the experiments, the concentration of metal ions was analyzed using Atomic Absorption Spectroscopy (Varian Model AA 240 FS). The infrared spectra were obtained as KBr pellets on a PerkinElmer BX FT-IR Fourier transform spectrophotometer.

Adsorption experiments

The batch contact adsorption was used for the evaluation of the adsorption studies of tangerine peel adsorbents for the removal of eight heavy metal ions from aqueous solutions. For these experiments, 200 mg of each unmodified

and modified adsorbent was placed in a Erlenmeyer flasks containing 5 ppm (Cr, Cu, Mn, Co, Ni, Pb) and 2 ppm (Cd and Zn) solutions in a volume of 100 mL. The suspension was shaken constantly on a mechanical shaker at 95–100 movements at room temperature for period of 30 min. All the biosorption experiments were repeated three times to confirm the results. Also, blank experiments were conducted to ensure that no adsorption had taken place on the walls of the apparatus used. The equilibrated suspensions were filtered, and the filtrates were collected separately. The filtrates were analyzed for Cr, Cu, Mn, Co, Ni, Pb, Cd and Zn concentrations using FAAS. The percentage of heavy metal removal was calculated by using the relation

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \cdot 100$$

while the amount of metal ion uptake (biosorption capacity) per gram of the biomass q_t (mg g^{-1}) in t (min) was calculated as follows:

$$q_t = \frac{(C_0 - C_t)}{m} \cdot V$$

where C_0 and C_t are the concentrations of each metal ions in the solution before and after sorption, respectively (mg L^{-1}), V is the volume of the solution (L), and m is the mass of adsorbent (g).

Effect of pH, biosorbent amount and contact time

To determine the effect of pH, biosorbent amount and contact time different sets of experiments were carried out. The removal efficiency of the adsorbent was studied as the function of pH keeping the concentration of metal ions constant by using batch experiment. Hundred milliliters of mixture solution of eight metals with adjusted/tested pH was added to 500 mL Erlenmeyer flask with 200 mg of each unmodified or modified adsorbent. The flasks were shaken 30 min in a mechanical shaker at 95–100 movements per minute at room temperature. After shaking, the suspension was filtered. The remained concentrations of metal ions were determined using FAAS.

In other batch experiments, the influence of the mass of adsorbent was studied in the range between 1 and 4 g L^{-1} under the previously determined optimal pH value. An important factor for quantitative removal of heavy metal ions is the amount of solid phase material. Tested amount of modified biosorbent material was equilibrated with 100 mL of aqueous solution (5 ppm: Cr, Cu, Mn, Co, Ni and Pb; 2 ppm: Cd and Zn) by shaking at 95–100 movements per minute at room temperature 30 min. As described above, the suspensions were filtered, and filtrates were analyzed for Cr, Cu, Mn, Co, Ni, Pb, Cd and Zn concentrations using atomic absorption spectrometry.

The effect of contact time and determination of kinetic parameters was carried out by adsorption kinetic experiments. For these tests, 300 mg of modified tangerine peel was added to 100 mL multi-element solution (pH 5) with different initial concentrations of tested metals (5 ppm for Cr, Cu, Mn, Co, Ni, Pb; and 2 ppm for Cd and Zn). The mixture was shaken on a mechanical shaker at 95–100 movements at room temperature. At predetermined time intervals (0–120 min), 10 mL samples were taken out and filtered and filtrates were analyzed for Cr, Cu, Mn, Co, Ni, Pb, Cd and Zn concentrations using atomic absorption spectrometry.

Error analyses

For each kinetic model as suitable error tools to evaluate the significance of the kinetic models fitness (Pillai et al. 2014) were applied the correlation coefficient of determination (r^2) and three statistical functions: Chi-square test (χ^2), normalized deviation (ND) and normalized standard deviation (NSD) between experimental and calculated values. The mathematical formulations are represented in equations below:

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

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

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

where N is the number of data points, q_{exp} and q_{cal} (mg g^{-1}) are the experimental and calculated adsorption capacities.

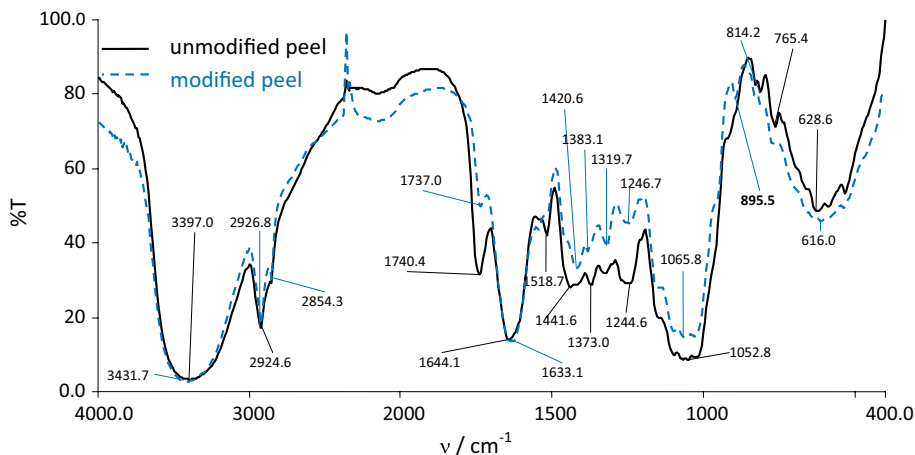
Results and discussion

Adsorbent characterization

Infrared spectra of the Fourier transform (FT-IR) biosorbent were recorded on a PerkinElmer BX FT-IR in a region from 4000 to 400 cm^{-1} using KBr pellet technique. Obtained spectra are shown in Fig. 1.

As can be seen for untreated tangerine peel, a broad absorption peak around 3400 cm^{-1} indicates the existence of free and intermolecular bonded hydroxyl groups. The O–H stretching vibrations occur within a broad range of frequencies indicating the presence of “free” hydroxyl groups and bonded O–H bands of carboxylic acids (Ribeiro et al. 2013; Torab-Mostaedi 2013; Ferraz et al. 2015; Nnaji et al. 2016). Chemical treatment resulted in shifting of this peak toward higher value of wave numbers (around 3430 cm^{-1}) which corresponds to polymorphic form of cellulose (Sokrates 2001). Also, for untreated peel, peak of medium intensity in the area of carbonyl group, around 1740 cm^{-1} , can be attributed to acetylene and uronic ester groups of pectin, lignin and hemicelluloses or to ester bonding of carboxyl groups from ferulic and coumaric acid of lignin and hemicelluloses. After chemical treatment of biosorbent, significant decrease in peak intensity and slight shifting toward lower value of wave numbers (1737 cm^{-1}) was obtained. This trend could be explained by the fact that chemical treatment of biosorbent has removed large amounts of hemicellulose and lignin. Intensive peak around 1630 cm^{-1} can be attributed to absorbed water molecules associated with cellulose fibers (Sain and Panthapulakkal 2006). Peak at 1519 cm^{-1} could be result of stretching vibrations of C=C in lignin’s aromatic rings. Significant intensity decrease in this peak was obtained after chemical treatment which can be explained by partial removal of lignin (Elanthikka et al. 2010). Additionally, 1373 cm^{-1} peak can be attributed to C–H bending vibrations in cellulose and 2930 cm^{-1} peak to the stretching vibrations of C–H bond of CH_3 and CH_2 groups in hemicellulose, cellulose and lignin

Fig. 1 Comparative IR spectra of modified (dash line) and unmodified (straight line) tangerine peels



(Pavan et al. 2008; Marino et al. 2015). Broad peak of lower intensity centered around 1245 cm^{-1} can be attached to C–O stretching vibrations in hemicellulose as well as C–O stretching vibration of acetyl group in lignin. Observed significant decrease in peak intensity, as a result of chemical treatment, pointed to a partial removal of hemicellulose and lignin (Sgriccia et al. 2008; Marino et al. 2015). Peak around 1060 cm^{-1} can be attributed to the stretching vibrations of lignin's $-\text{OCH}_3$ group or C–O and C–H stretching vibrations appearing in cellulose (Minamisawa et al. 2004; Torab-Mostaedi 2013). Increased intensity and shifting of these peaks toward higher wave number values could be result of a greater cellulose content obtained after chemical treatment (Elanthikka et al. 2010). An appearance of lower intensity sharp strip around 896 cm^{-1} on modified biosorbent spectrum, pointed at typical cellulose structure, i.e., after chemical treatment partial removal of hemicellulose and lignin was obtained (Alemdar and Sain 2008; Marino et al. 2015). This peak is characteristic of α -glycoside bonds between anhydrous glucose units in cellulose's structure. Peak around 630 cm^{-1} can be attributed to bending vibrations of aromatic compounds (Torab-Mostaedi 2013).

Effect of pH on the removal of heavy metals

Variations in pH could change the characteristics and availability of metal ions in solution as well as the chemical status of the functional groups responsible for sorption. Therefore, experiments were performed with multi-element solutions to study the Cr, Cu, Mn, Co, Ni, Pb, Cd and Zn adsorption on unmodified and modified tangerine peel as a function of solution pH. The results are shown in Fig. 2a, b. Influence of pH (range 3.0–5.0) on sorption of Cr, Cu, Mn, Co, Ni, Pb (concentration 5 mg L^{-1}) and Cd and Zn (concentration 2 mg L^{-1}) on tangerine peels (2 g L^{-1}) was very significant. By using unmodified sorbent, a very low sorption for most of the tested metals was obtained at pH 3 increasing up at pH 5. It can be explained that at low pH the H^+ ion concentration is high and occupies most of the active sites of the adsorbent decreasing the % removal efficiency of tested ions. Above pH 5, metal hydroxide formation and possible phenolic polymerization take place resulting in decrease in the % removal efficiency of tested ions. It is necessary to achieve such conditions in which the reduction in the concentration of metal would be caused only by the retention on the sorbent and not in a form of metal precipitate. Due to that fact higher pH values were not tested. For removing and determining eight heavy metals at the same time, it can be concluded that, in the case of both biosorbents the optimal pH value was 5.

The only difference between unmodified and modified peels was higher removal efficiencies at all tested pH values when modified peel was used. Thus, at the pH 5, where the maximum uptake was attained, removal of Cr, Cu, Mn, Co, Ni, Cd, Pb and Zn was higher for about 37.79, 1.85, 30.05, 23.56, 26.17, 27.48, 7.68 and 24.81%, respectively, for modified peel than

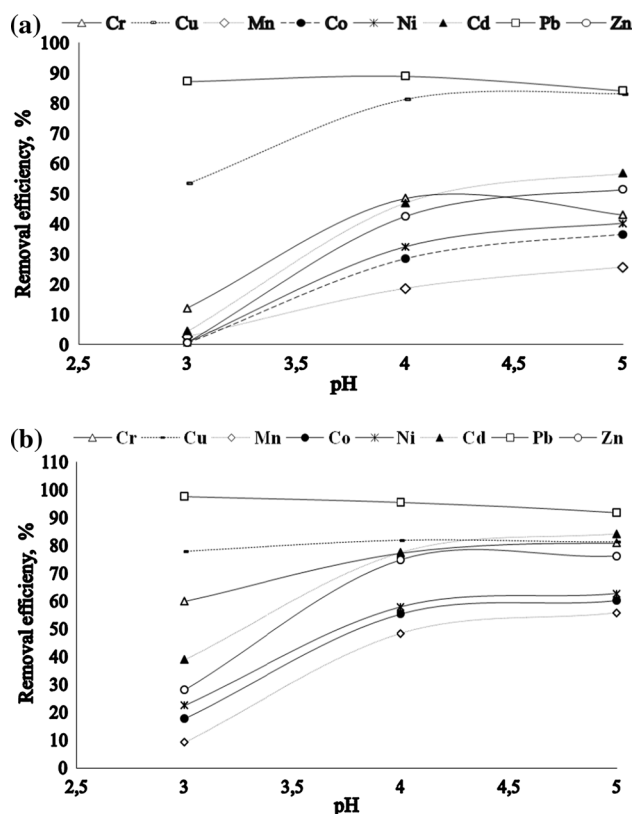


Fig. 2 Effect of pH variation on Cr, Cu, Mn, Co, Ni, Pb, Cd and Zn removal from solution through adsorption on unmodified (a) and modified (b) tangerine peel

unmodified. At $\text{pH} > 4$, functional groups are deprotonated and negatively charged and in that way they bind/attract positively charged metal ions. This confirms that the sorption of Cd(II), Co(II), Cr(III), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) is an ion exchange mechanism between the negatively charged groups present in the cell wall of tangerine peel and the cationic metal ions (Torab-Mostaedi 2013; Laidani et al. 2016).

Generally, adsorption of some metals was better due to different affinity of used biosorbent for different ions (affected by, i.e., electronegativity of different ions (Pauling); their covalent index (pm) or hydrated radius (pm)) as well as possible competition for adsorption sites between tested metal ions, because of the present of other metals in multi-component water solution.

Effect of adsorbent amount

As the fact that all eight metals were more effectively removed by using modified tangerine peel, for further analysis only results obtained by the use of this sorbent were presented. As can be seen from Fig. 3 with the increase in adsorbent mass, until the amount of 300 mg, an increase in tested metals removal efficiencies occurred. Larger amount means more contact surface between sorbent and metal ion, in the meaning

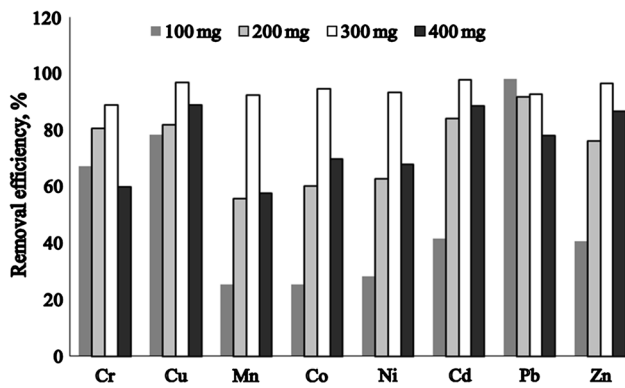


Fig. 3 Effect of the mass of the modified tangerine peel adsorbent on the adsorption of 5 ppm of each Cr, Cu, Mn, Co, Ni, Pb, and 2 ppm of Cd and Zn

of higher number of active sites for binding metals, resulting with more quantitative metal removal. Decrease in removal efficiency (%) by using dosage of sorbent > 300 mg could be result of aggregation phenomena, which cause decrease in active biosorbent surface and the number of available centers for binding ions. Additionally, large biosorbent mass also makes more difficult mixing of the suspension, resulting in low exchange gain. The similar phenomena were also observed in adsorption of metal ions reported in the study of Chand and Yogesh (2012). In accordance with the obtained results, 300 mg of sorbent was employed in further analysis.

Comparison of tested sorbents

The results obtained concerning the adsorption of eight metals from aqueous solution (pH 5) during 30 min by the usage of unmodified and modified tangerine peel are presented at Fig. 4.

Higher removal efficiency values (%) were obtained using modified sorbent as follows: 41.81% for Cr; 11.14% Cu; 65.38% Mn; 52.50% Co; 46.72% Ni; 34.76% Cd; 11.30% Pb and 37.10% Zn. These results are consistent with theoretical data according to which chemical modification generally improves the sorption capacity of sorbents. This could be probably due to larger number of active sites after modification, better ion exchange and the formation of new functional group responsible for metal binding (Wan Ngah and Hanafiah 2008). Thus, i.e., Tarley et al. (2004) recorded that the sorption of cadmium was approximately twice as higher in case of using rice crust treated with sodium hydroxide than the untreated biosorbent. Using sugarcane waste treated with indicated reagent resulted in much better adsorption capacity for cadmium and lead compared to the same untreated material (Šćiban et al. 2006). The similar phenomena was also observed in the study of Chubar et al. (2004) for the adsorption of copper, zinc and nickel by treated (NaCl and CaCl₂) cork biomass.

Additionally, a comparison of sorption capacities from the literature with the results of the present study ($\mu\text{mol g}^{-1}$)

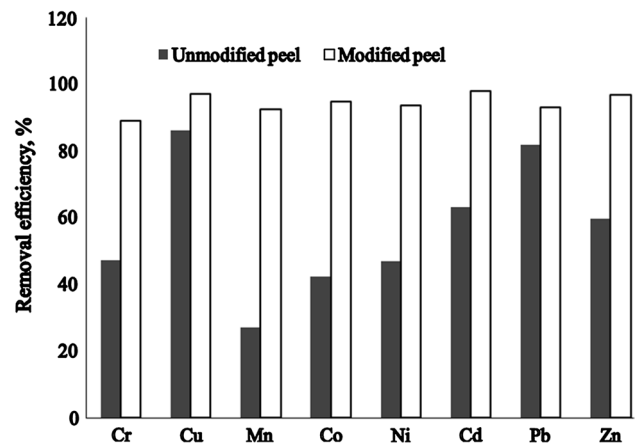


Fig. 4 Comparison of unmodified and modified tangerine peels under optimum conditions

was made. As can be seen from results (Table 1), sorption capacities of modified tangerine peel are lower than wheat straw (Ali et al. 2011) for Cu, Cd and Pb; orange peel (Annadurai et al. 2003) for Co, Ni and Pb; but some comparable values were obtained in the case of compost of aquatic weed *Myriophyllum spicatum* (Milojković et al. 2014) and banana peel (Šabanović et al. 2015). Nevertheless, tangerine peel exhibited a better capacity for most of tested metal ions compared to less economical sorbents, i.e., non-modified silica gel (Svraka et al. 2014) and acid red 88 (Kocjan 1999).

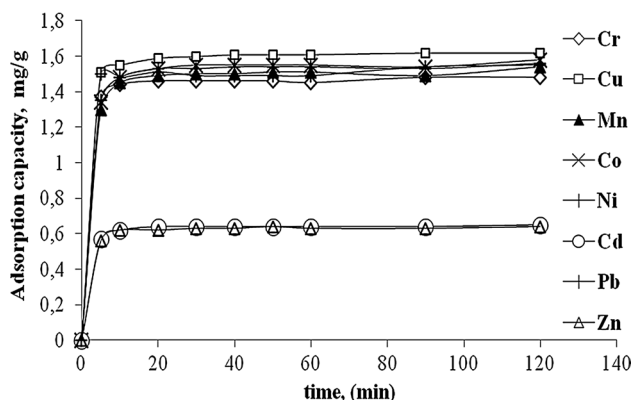
Effect of contact time

The minimum contact time in which the tested metal ions in solution reached the kinetic adsorption equilibrium onto the surface of the sorbent was obtained from the adsorption experiment in function of time. The modified tangerine peel presented a relatively rapid adsorption process, as can be seen from Fig. 5, reaching kinetic equilibrium in less than 20 min. This relatively short time to reach equilibrium indicated that the structure of the material provides high accessibility to its adsorption sites, so that tested metal ions could coordinate to them (Jorgetto et al. 2013).

The plot reveals that, probably due to larger surface area of the tangerine peel being available for the adsorption of ions, the amount of metals removal was higher at the beginning. As the surface adsorption sites become exhausted, the uptake was controlled by the rate at which the adsorbate was transported from the exterior to the interior sites of the adsorbent particles (Laidani et al. 2016). For all of the tested metals, after about 20 min of shaking, the maximum amount of metal removal was nearly attained.

Table 1 Comparison of sorption capacities from the literature with the results of this study ($\mu\text{mol g}^{-1}$)

Sorbent	Metal ion							
	Cr	Cu	Mn	Co	Ni	Cd	Pb	Zn
Wheat straw (Ali et al. 2011)		72.15				42.22	18.65	
Orange peel (Annadurai et al. 2003)				30.9	102.4		37.40	
Compost of aquatic weed <i>Myriophyllum spicatum</i> (Milojković et al. 2014)		70.34			9.88	10.14	80.07	7.64
Banana peel (Šabanović et al. 2015)	32.7		30.9	28.9	29.0	15.1	8.2	
Non-modified silica gel (Svraka et al. 2014)	13.08	10.70	12.38	11.54	11.59	6.05	3.28	
Acid red 88 (Kocjan 1999)		12.10	7.60	15.10	11.30	11.70	12.10	16.20
This study	28.46	25.65	27.85	26.81	26.58	5.78	7.48	9.78

**Fig. 5** Effect of contact time on metal ions removal onto modified tangerine peel

Kinetic studies

To describe the kinetics of adsorption of Cr, Cu, Mn, Co, Ni, Pb, Cd and Zn ions onto chemically modified tangerine peel pseudo-first- and pseudo-second-order kinetic models were applied. A linear model of the pseudo-first-order adsorption kinetics is defined by Lagergren's equation. The integrated form of the equation is given by:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t$$

where q_e and q_t are the amounts adsorbed at equilibrium and at time, t (mg g^{-1}), and k_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}) which can be obtained from the slope of the linear plot of $\ln(q_e - q_t)$ versus t . The kinetic parameters are given in Table 2.

The pseudo-second-order kinetic assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites, represented in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \cdot t$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of pseudo-second-order kinetics of adsorption. The plot of t/q_t versus t had given a linear relationship with a slope $1/q_e$ and an intercept of $1/(k_2 q_e^2)$.

Obtained k_1 values were in a range of 1.51×10^{-2} and 4.53×10^{-2} indicating a fast sorption process of tested metal ions on modified tangerine peel in accordance with the experimental observations. However, between the experimentally measured q_e values and those calculated from the plots, large deviations were obtained. Also, the obtained r^2 values were relatively low, ranging from 0.5934 to 0.7087 (except for Cu: 0.9409). That indicates that this kinetic model was not sufficient to describe the mechanism.

Table 2 Pseudo-first-order and pseudo-second-order kinetic parameters for the adsorption of Cr, Cu, Mn, Co, Ni, Pb, Cd and Zn onto tangerine skin

	Parameter	Cr	Cu	Mn	Co	Ni	Cd	Pb	Zn
Pseudo-first-order	C_0 (ppm)	5	5	5	5	5	2	5	2
	$q_{e,\text{exp}}$ (mg/g)	1.48	1.62	1.54	1.58	1.56	0.65	1.55	0.64
	$q_{e,\text{cal}}$ (mg/g)	0.05	0.10	0.10	0.10	0.08	0.03	0.09	0.03
	k_1 (min^{-1})	0.0184	0.0453	0.0151	0.0173	0.019	0.0178	0.0161	0.018
	r^2	0.5934	0.9409	0.6142	0.6461	0.6446	0.6455	0.7087	0.6937
Pseudo-second-order	$q_{e,\text{cal}}$ (mg/g)	1.48	1.62	1.54	1.58	1.56	0.65	1.55	0.64
	k_2 (g/mg min)	1.2467	1.3215	0.7732	0.7841	1.0199	2.5131	0.6166	2.7315
	r^2	0.9999	1	0.9998	0.9998	0.9999	0.9999	0.9997	0.9999

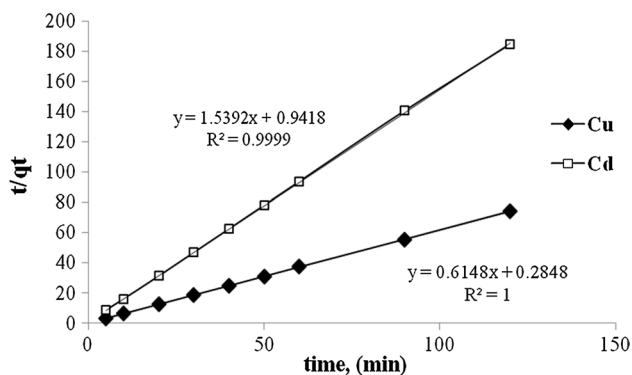


Fig. 6 Examples of pseudo-second-order kinetic model for adsorption of Cu and Cd ($C_0 = 5$ and 2 ppm, respectively) onto modified tangerine peel

The pseudo-second-order plots have high linearity, between 0.9997 and 1 (examples depicted in Fig. 6). Moreover, close agreement between experimental and calculated q_e values was obtained for pseudo-second-order model. That is supported by low values obtained for χ^2 , ND and NSD statistical analyses validated this kinetic model to best describe the adsorption process of tested ions onto the used sorbent compared to the pseudo-first-order kinetic model. Thus, the second-order kinetic model provides a better explanation of the kinetics of the biosorption of Cr, Cu, Mn, Co, Ni, Pb, Cd and Zn on modified tangerine peel indicating the applicability of pseudo-second-order model and chemisorptions for adsorption of all tested metal ions.

The similar phenomena was also observed for, i.e., adsorption of cadmium onto green coconut shell powder; uptake of chromium and lead by agro based waste materials; removal of Ni (II) ions by using biosorbent prepared from jackfruit; or adsorption of heavy metals on exhausted tea leaves (Pino et al. 2006; Qaiser et al. 2007; Boruah et al. 2015; Shrestha et al. 2016).

Conclusion

Based on the results obtained in this study, tangerine peel was confirmed as a very interesting material for removal of Cr, Cu, Mn, Co, Ni, Pb, Cd and Zn. FT-IR spectra of this peel have shown numerous functional groups in its structure that can easily adsorb positively charged metal ions. Analyzed natural sorbent exhibits relatively low sorption ability as compared to its modified form. Chemical treatment of tangerine peel has enhanced the adsorption process for an average of about 40% for all eight metals. By controlling physicochemical parameters such as pH of the reaction system, mass of sorbent and contact time, high

removal efficiencies (Cr: 88.92%; Cu: 97.04%; Mn: 92.48%; Co: 94.70%; Ni: 93.50%; Pb: 93.00%; Cd: 97.90% and Zn: 96.80%) can be achieved by modified peel. High correlation coefficients ($r^2 > 0.9997$) and low error analyses values for all studied metals confirmed that the metal adsorption process follows pseudo-second-order kinetic model. A follow-up study will be directed toward examination of possible interferences between tested metals as well as matrix influences (i.e., Na^+ , Al^{3+} , Mg^{2+} , Ca^{2+} , K^+ , or anions, i.e., nitrates, sulfates).

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