

Use of Ponkan mandarin peels as biosorbent for toxic metals uptake from aqueous solutions

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Abstract

Waste Ponkan mandarin (*Citrus reticulata*) peel was used as biosorbent to extract Ni(II), Co(II) and Cu(II) from aqueous solutions at room temperature. To achieve the best adsorption conditions the influence of pH and contact time were investigated. The isotherms of adsorption were fitted to the Langmuir equation. Based on the capacity of adsorption of the natural biosorbent to interact with the metallic ions, the following results were obtained 1.92, 1.37 and 1.31 mmol g⁻¹ for Ni(II), Co(II) and Cu(II), respectively, reflecting a maximum adsorption order of Ni(II) > Co(II) > Cu(II). The quick adsorption process reached the equilibrium before 5, 10 and 15 min for Ni(II), Co(II) and Cu(II), respectively, with maximum adsorptions at pH 4.8. In order to evaluate the Ponkan mandarin peel a biosorbent in dynamic system, a glass column was fulfilled with 1.00 g of this natural adsorbent, and it was feed with 5.00×10^{-4} mol l⁻¹ of Ni(II) or Co(II) or Cu(II) at pH 4.8 and 3.5 ml min⁻¹. The lower breakpoints (BP₁) were attained at concentrations of effluent of the column attained the maximum limit allowed of these elements in waters (>0.1 mg l⁻¹) which were: 110, 100 and 130 bed volumes ($V_{\text{effluent}}/V_{\text{adsorbent}}$), for Ni(II), Co(II) and Cu(II), respectively. The higher breakpoints (BP₂) were attained when the complete saturation of the natural adsorbent occurred, and the values obtained were: 740, 540 and 520 bed volumes for Ni(II), Co(II) and Cu(II), respectively.

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1. Introduction

The presence of the metals in quantities above their natural abundances in the lithosphere, even as trace amounts in the environment, is normally associated with local problems and affects the human activity in a given ecosystem. The principal concerns relate to toxicity and also to their persistence [1–3].

When toxic metals are present in the aquatic system, the abatement of the pollutant to an acceptable level is necessary [4]. Adsorption and ion exchange processes are the most useful methods to removal them, by exploring the availability of different kinds of adsorbents associated with convenient procedures for obtaining high efficiency [5,6]. A large number of different adsorbent materials containing a variety of attached chemical functional groups has been reported for this purpose, with acti-

vated carbon being the most popular [6–10], however, the high cost of this material restricts its use on large scale [9,10].

In recent years, special attention has been focused on the use of natural adsorbents as an alternative to replace the conventional adsorbents, based on both the environmental and the economical points of view [9,10]. In order to overcome high cost problems, an increasing interest in producing new alternative adsorbent materials to replace activated carbon has been explored, taking also into account the local availability, since frequently these new materials are constituted of residues from agricultural activity or sea food processing [9–19].

A potential cheap natural source is the abundant waste from the non-profitable part of fruits that might be useful for such procedure. One of these materials is derived from mandarin (*Citrus reticulata*), that is cultivated and well-adapted in several countries, mainly in those where a high temperature predominates in summer, followed by a mild winter. This fruit is very common cultivated in Brazil, which results in a large quantity of waste residues [20]. These wastes, give rise to serious environ-

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mental pollution, although a portion of the Ponkan mandarin peels is used as animal food. Another use of citrus peel wastes is the production of flavonoids and other organic compounds [21]. This investigation reports the use of Ponkan mandarin peel waste as an alternative natural adsorbent for extraction of toxic metals, which are commonly present in waters from a variety of sources and industrial effluents. For this propose, the adsorption isotherms of divalent nickel, cobalt and copper from aqueous solution at room temperature were explored, bearing in mind the influence of different parameters such as solution pH and contact time. The performance in adsorbing cations from natural water under dynamic flow (column) conditions was also studied and the results confirmed the batch experiments.

2. Experimental

2.1. Ponkan mandarin peel

For the series of experiments the Ponkan mandarin fruits were purchased from a local market. The waste white peel was removed from coat by rejecting the covering yellow part. The crude material obtained was dried at room temperature and ground in a knife-mill. The resulting powder was washed with doubly distilled water and then dried in an oven at 333 K for 24 h. Powdered material containing particle sizes ≤ 0.6 nm was used for the adsorption studies.

2.2. Characterization of the biosorbent

2.2.1. Infrared measurements

Ponkan mandarin peel was characterized by FTIR using a Shimadzu FTIR, model 8300 (Kyoto, Japan). The spectra were obtained with a resolution of 4 cm^{-1} , with 100 cumulative scans.

2.2.2. Pore size distribution

The pore size distribution was obtained by the N_2 adsorption–desorption isotherm, determined at liquid nitrogen boiling point, using a homemade volumetric apparatus, connected to turbo molecular Edwards vacuum line system, employing a Hg capillary barometer and also an active Pirani gauge [22]. The apparatus is frequently checked with alumina standard reference. The biosorbent material was previously degassed at 150°C , in vacuum, for 2 h. The data analysis was made using the Barret, Joyner and Halenda (BJH) method [22].

2.2.3. Surface area

The specific surface area of the previous degassed solid at 150°C , under vacuum, was determined by the Brunauer, Emmett and Teller (BET) [22] multipoint technique in the volumetric apparatus, cited above, using nitrogen as probe.

2.3. Reagents and solutions

The solutions of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were prepared from reagent grade salts (Merck). The desired pH

was adjusted with 0.10 mol l^{-1} sodium hydroxide or hydrochloric acid solution. Deionised water was used throughout the experiments.

2.4. Adsorption studies

2.4.1. pH variation

The maximum adsorption capacity was determined by the batch method at pH values varying between 2 and 6, by shaking the suspension for 1 h at a temperature of $298 \pm 1\text{ K}$. The desired pH was adjusted with 0.10 mol l^{-1} sodium hydroxide or hydrochloric acid solutions using a Digimed Model DM 20 pH meter. In a typical experiment 100 mg of the adsorbent was suspended in 25.0 ml of $1.00 \times 10^{-2}\text{ mol l}^{-1}$ of the cation solution at the desired pH and the mixtures were orbitally stirred at $298 \pm 1\text{ K}$ for 2 h. The solid was filtered from the solution phase and the metal remaining in solution was analyzed. The amount of the metal adsorbed on the adsorbent surface (N_f) was calculated by applying the equation $N_f = (N_i - N_s)/m$, where N_i and N_s are the initial and the amount (mmol) of the metal ion which remained in solution after adsorption procedure, respectively, and m is the mass (g) of the solid in each flask. The metal ions were analyzed by complexometric EDTA titration using an appropriate indicator [23].

2.4.2. Contact time

The main purpose in this study is to establish the ideal conditions of the adsorbent capacity, by considering the contact time of the solution at the solid/liquid interface. The capacity of the sieved adsorbent in extracting cations from aqueous solutions was determined through a batch method. For such determinations, to a series of polyethylene flasks, containing metal solutions with concentrations on the order of $1.00 \times 10^{-2}\text{ mol l}^{-1}$, about 100 mg of the adsorbent was added and the suspensions were orbitally shaken at $298 \pm 1\text{ K}$ at the optimum pH 4.8. At determined intervals of the time each solution was filtered and the supernatant metal ions were analyzed as before.

2.4.3. Batch adsorption

The mandarin peel adsorption capacity for individual metals was studied at the optimum pH 4.8 using the batch procedure. For this determination, about 100 mg of the adsorbent was immersed in 50.0 ml of the metal solutions, whose concentrations varied between 1.0×10^{-4} and $1.0 \times 10^{-2}\text{ mol l}^{-1}$. The mixtures were orbitally shaken in a thermostated water bath with constant speed for 1 h. After the prescribed contact time, the solutions were filtered and the metallic ions were analyzed as stated before.

2.4.4. Column adsorption study

A glass column of 15 cm length and 0.5 cm internal diameter containing a porous sintered glass disk at the bottom and a Teflon stopcock was packed with 1.00 g of Ponkan mandarin peels, which occupied 5 ml of these column. Above the packing material, the column was fulfilled individually with $5.00 \times 10^{-4}\text{ mol l}^{-1}$ of the Ni(II) or Co(II) or Cu(II) at pH 4.8. The effluent column flow-rate was adjusted to 3.5 ml min^{-1} and

the height of the metallic ions above the biosorbent, was kept constant by feeding the column with a peristaltic pump (Milan, Colombo-PR, Brazil). The column effluents were collected at each 50.0 ml and metallic ions contents were determined using a Flame Atomic Absorption Spectrometry (Analyst 200, Perkin-Elmer).

3. Results and discussion

3.1. Characterization of the biosorbent

The Ponkan mandarin peel is constituted basically by polysaccharide pectin, containing hydroxyl and acidic organic functions which are promptly available to interact with cations, by firstly exchanging with protons and subsequently by chelating with the metallic ion. Therefore, Ponkan mandarin peel can be used as a low-cost natural adsorbent for removal of metallic ions from aqueous solutions [24,25].

The pore size distribution curve, obtained by using BJH calculus [22], is presented in Fig. 1. As can be seen, the Ponkan mandarin peel presents two maxima regions of pore size distribution. The major region presents porosity of the biosorbent with an average pore diameter of 5 nm and a lower percent of biosorbent with average pore of 7.6 nm. Based on these results, it can be inferred that Ponkan mandarin peel presents a mesoporous structure [22]. The surface area and pore volume for Ponkan mandarin peel obtained were $119.3 \text{ m}^2 \text{ g}^{-1}$ and $0.38 \text{ cm}^3 \text{ g}^{-1}$, respectively.

Fig. 2 shows the FTIR absorption spectra of Ponkan mandarin peel. The absorption bands at 3400 and 2930 cm^{-1} are assigned to O–H bonds of macromolecular association, and $-\text{CH}_2-$ bonds, respectively [25]. The sharp peak observed at 1745 cm^{-1} for is considered to be due to a CO bond of a carboxylic acid or its ester. The strong peak that appears at 1645 cm^{-1} is CO stretching vibration of a carboxylic acid that exists in an intermolecular hydrogen bond. From these results, it can be inferred that the metallic ions would bond to Ponkan mandarin peel natural adsorbent through interaction with the active groups OH, COOH [25].

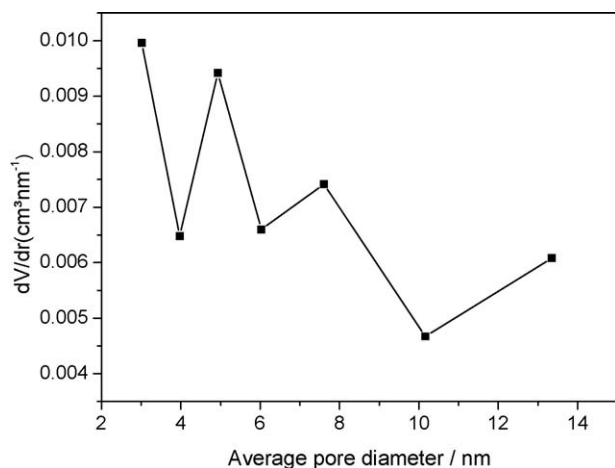


Fig. 1. Pore size distribution of Ponkan mandarin peel obtained by BJH method.

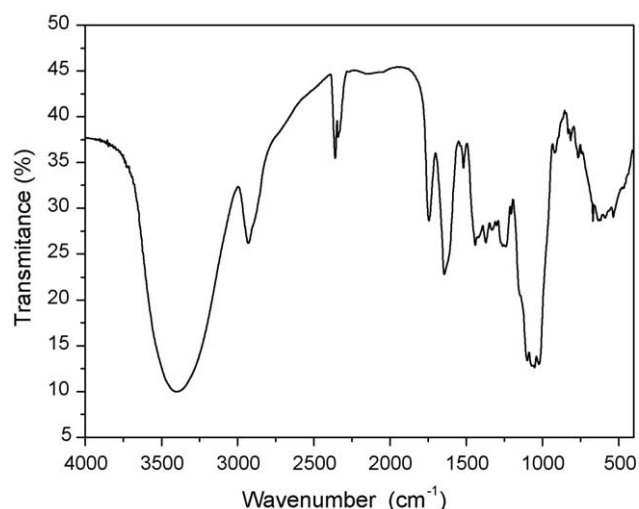


Fig. 2. FTIR spectra of Ponkan mandarin peel.

3.2. Effects of pH

The extractability of the cations from the solution phase is pH dependent. The effectiveness of the process can be expressed by the number of moles adsorbed (mmol g^{-1}) versus pH plot for the cations involved, as represented in Fig. 3 for divalent nickel, cobalt and copper. From the corresponding data for each metal, an increase in pH was followed by an increase in adsorption, reaching the maximum capacity at pH 4.8. For higher pH values it was observed a slightly decrease of adsorption for Co(II) and nickel(II) and for Cu(II), this diminution was more remarkable. The metallic ions could be suffering hydrolysis, starting at pH higher than 5, forming $\text{Ni}(\text{OH})^+$, $\text{Co}(\text{OH})^+$ and $\text{Cu}(\text{OH})^+$ species, which promotes a diminution of the adsorption capacity, because the diminution of the formal charge of the metallic ion. Besides that, at pH around 7.0, a slight decomposition of the natural adsorbent could takes place.

Based on the results a mechanism is proposed for metallic ion uptake by Ponkan mandarin peel is depicted on the Scheme 1.

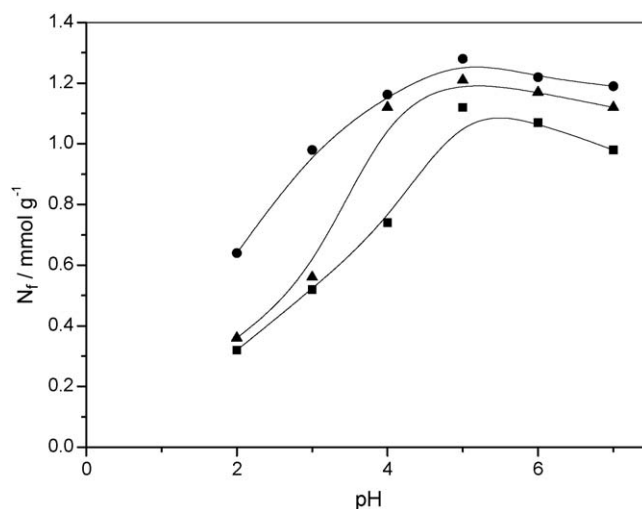
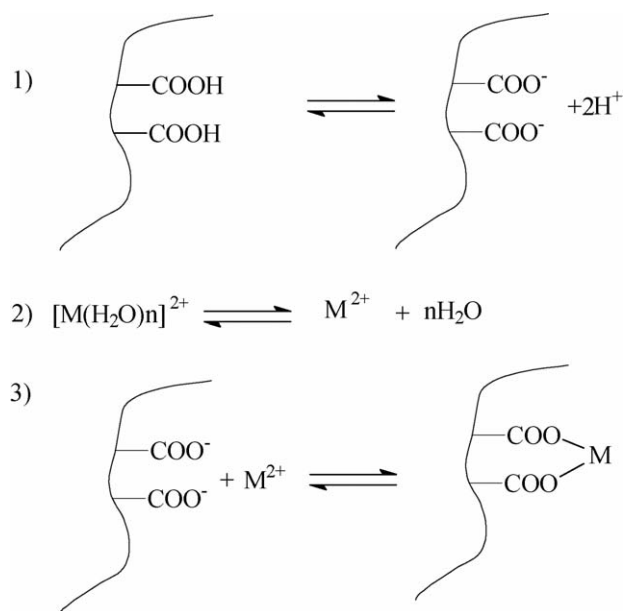


Fig. 3. Effect of pH on $1.00 \times 10^{-3} \text{ mol l}^{-1}$ of nickel (●), cobalt (▲) and copper (■) chloride adsorptions from aqueous solution at $298 \pm 1 \text{ K}$.



Scheme 1. Reactions that take place for divalent ion uptake by natural adsorbent.

As can be seen, the fibrous Ponkan mandarin peel containing pectin (carboxylic groups) loses two protons per each mol of divalent cation (the fibrous materials contains several carboxylic group which were withdrawn from the scheme for simplicity) at the first step. In the second step the hydrated metallic ion loses its hydration waters. In the third step the fibrous material uptakes the non-solvated metallic ion. At pH lower than 4.8, the first step of the adsorption procedure is hindered, diminishing the adsorption of the divalent metallic ions.

It should be stressed that, the maximum metal uptake at pH around 5 allows this low-cost natural adsorbent be used for metallic ion removal from natural waters without requiring pH adjustments [26].

3.3. Effects of contact time

The adsorption data for metal uptake versus contact time for a fixed adsorbent amount is shown in the Fig. 4, giving identical abrupt increases in adsorption at low times before reaching the plateaus. According to these data, equilibrium is achieved at around 5, 10 and 15 min for divalent nickel, cobalt and copper, respectively, at $1.00 \times 10^{-3} \text{ mol l}^{-1}$. However, to be sure of the best adsorption conditions at higher concentrations levels, to obtain equilibrium at the solid/liquid interface, all the experiments were carried out with 1 h of contact time. This short time period required to attain equilibrium suggests an excellent affinity of the adsorbent for these metals from aqueous solution. A more detailed kinetics studies for determining the rate constants of adsorption are out of the scope of this paper.

3.4. Adsorption data

The isotherms of adsorption for these three divalent cations, as represented by number of moles per gram of the adsorbent

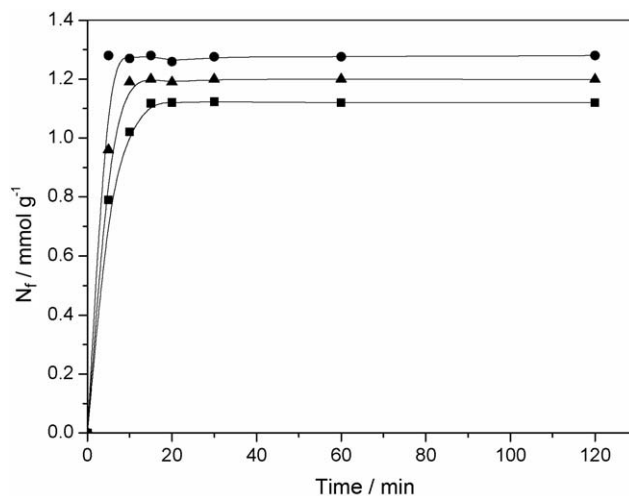


Fig. 4. Contact time for $1.00 \times 10^{-3} \text{ mol l}^{-1}$ of nickel (●), cobalt (▲) and copper (■) chloride adsorptions from aqueous solution at $298 \pm 1 \text{ K}$.

at $298 \pm 1 \text{ K}$, under optimum contact times and pH values, are shown in Fig. 5. Taking into account the experimental data to adjust to an adsorption model, the results from these isotherms conform to that proposed by Langmuir, showing that this equation is adequate for fitting the metal ion adsorption to Eq. (1), as observed for a series of systems [27–29].

$$\frac{C_s}{N_f} = \frac{1}{KN^s} + \frac{C_s}{N^s} \quad (1)$$

where C_s is the supernatant concentration after the equilibrium of the system (mmol l^{-1}), K the Langmuir affinity constant (l mmol^{-1}) and N^s is the maximum adsorption capacity of the material (mmol g^{-1}). Fig. 6 shows the linearization of the isotherm behavior by plotting C_s/N_f against C_s .

Based on the N^s values obtained from Fig. 6 for this linearized equation form, then the maximum adsorption capacities of adsorbent were 1.92, 1.37 and 1.31 mmol g^{-1} for Ni(II), Co(II) and Cu(II), respectively, as shown in Table 1. Thus, these

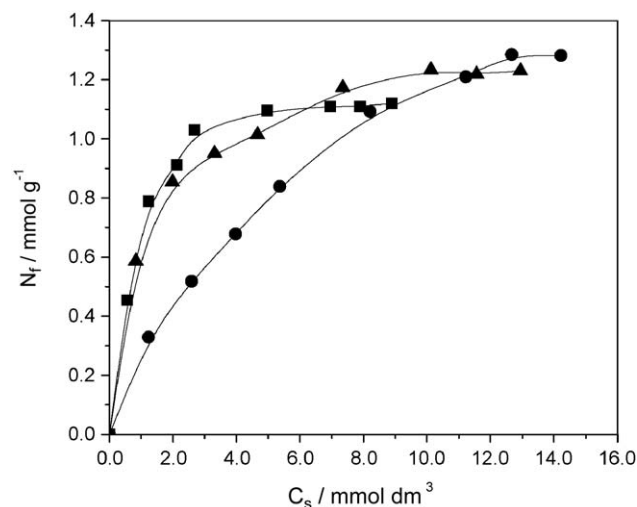


Fig. 5. Isotherms of adsorption of nickel (●), cobalt (▲) and copper (■) chlorides at $298 \pm 1 \text{ K}$.

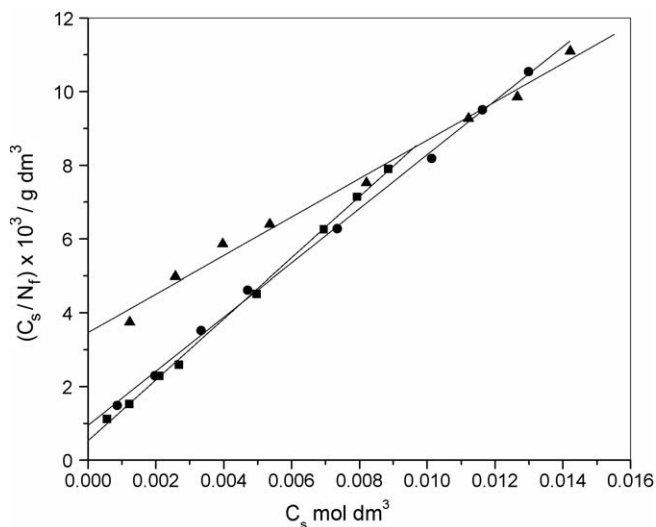


Fig. 6. Linearization of adsorption data for nickel (●), cobalt (▲) and copper (■) chlorides.

values means that the Ponkan mandarin peel natural adsorbent will uptake these metallic ions from aqueous solution in the order $Ni > Co > Cu$.

The higher maximum adsorption capacity acquired for nickel compared with other metals can be explained by the difference in affinity of the metallic ions when bonding to the available basic centers attached to the natural adsorbent on the peel structure [24,25].

Some examples of different adsorbents focusing on the available metallic ion extraction data from aqueous solutions are listed in Table 2. As observed the present series of results obtained from Ponkan mandarin peel presents the same order of magnitude as those obtained with a chemically modified surface on inorganic silica [41]. The maximum adsorption capacity for natural or synthetic adsorbents showed a tendency to increase the extracting ability of the natural material for these three cations, in particular, natural adsorbents coming from fruits, as represented by mandarin, orange and mango. Another extracting material source is the polysaccharide chitosan [37] that employs the basic nitrogen atom to extract cations. However, the results in Table 2 showed an effectiveness of less than one-third when compared with the present fruit peel adsorbent. This behavior should be expected because the isolated macromolecules from Ponkan peel fruit present a series of basic oxygen centers, including hydroxyl and carboxylic functions that are potentially available to extract cations [24].

Table 1

Adsorption capacity of divalent cations (M^{2+}), indicating the number of adsorbed moles (N_f), maximum adsorption capacity of the material (N^s) and the equilibrium constant (K) at 298 ± 1 K

M^{2+}	N_f (mmol g ⁻¹)	N^s (mmol g ⁻¹)	K (l mmol ⁻¹)
Ni	1.22 ± 0.01	1.92 ± 0.02	149 ± 2
Co	1.18 ± 0.03	1.37 ± 0.01	768 ± 3
Cu	1.11 ± 0.02	1.31 ± 0.02	1106 ± 3

Table 2

Comparison of the maximum adsorption capacity (N^s) of some divalent cations (M^{2+}) on some natural and synthetic adsorbents from aqueous solution at 298 ± 1 K

Adsorbents	N^s (mmol g ⁻¹)			Reference
	Ni ²⁺	Cu ²⁺	Co ²⁺	
Pyrolyzed coffee residue		0.28		[30]
Graphe stalks waste	0.18	0.15	–	[31]
Cation exchange resin	1.0		1.2	[32]
Orange peel	2.6			[33]
Eutrophic peat	0.19		0.18	[34]
Clinoptilolite		0.024	0.026	[35]
Wheat bran	0.20	0.23	–	[36]
Chitosan	0.37	0.38	0.27	[37]
Aniline/silica xerogel	0.45			[38]
Mango tree sawdust	1.41		1.35	[39]
Carbonaceous materials	0.57	0.53	0.81	[40]
Silica modified with ethylenimine	1.20	1.70	1.08	[41]
Ponkan peel	1.92	1.31	1.37	This work

3.5. Adsorption study in dynamic conditions

In order to evaluate Ponkan mandarin peel as a biosorbent for wastewater treatment of Ni(II), Co(II) and Cu(II) containing effluents, breakthrough curves of these individual metallic ions using Ponkan mandarin peel as biosorbent were obtained (Fig. 7). In Table 3 were presented the lower (BP₁) and higher breakpoints (BP₂) of the breakthrough curves depicted on Fig. 7. As can be seen, the lower breakthrough points (BP₁), determined when the metallic ion effluents from column attained the concentration higher than 0.10 mg l^{-1} (which corresponds to the maximum allowed metallic ions concentration in natural waters). The BP₁ value is related with the capacity of the natural adsorbent in retaining metallic ions from aqueous solution. The higher breakpoints (BP₂) are related with the complete saturation of the biomaterial with the metallic ions. The values of BP₁ indicates that the Ponkan mandarin peel is a good natural adsorbent for decontaminating Ni(II), Co(II) and Cu(II) from

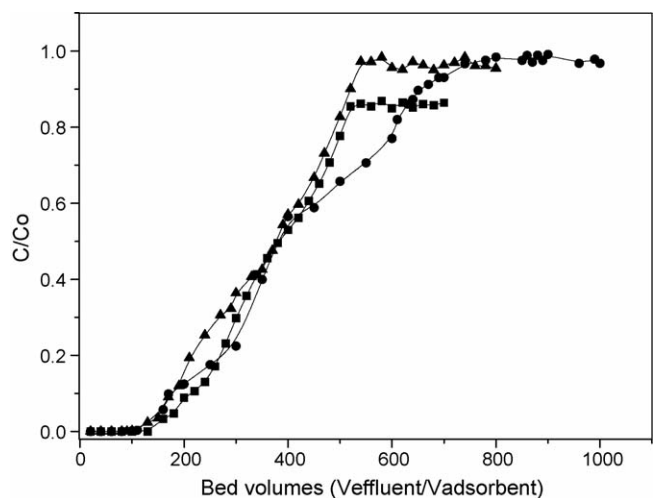


Fig. 7. Breakthrough curves for $5.00 \times 10^{-4} \text{ mol l}^{-1}$ of nickel (●), cobalt (▲) and copper (■) chlorides.

Table 3

Dynamic breakpoints for $5.00 \times 10^{-4} \text{ mol l}^{-1}$ of Ni(II), Co(II) and Cu(II) at pH 4.8 percolating an amount of 1.00 g Ponkan mandarin peel packed into a glass column at 3.5 ml min^{-1}

Breakpoint (BP)	Bed volumes ($V_{\text{effluent}}/V_{\text{adsorbent}}$)		
	Ni(II)	Co(II)	Cu(II)
BP ₁	110	100	130
BP ₂	740	540	520

Volume of adsorbent 5.0 ml. BP₁—lower breakpoint obtained after passing an effluent volume of $5.00 \times 10^{-4} \text{ mol l}^{-1}$ of the metallic ion by the adsorbent column, the maximum amount allowed of the metallic ion is surpassed. BP₂—higher breakpoint obtained after passing an effluent volume of $5.00 \times 10^{-4} \text{ mol l}^{-1}$ of the metallic ion by the adsorbent column, the saturation of the adsorbent occurs.

Table 4

Comparison of higher breakpoints (BP₂) saturation using dynamic adsorption with the maximum amount adsorbed (mmol g^{-1}) using batch conditions

Ni(II)	Co(II)	Cu(II)
1.85	1.35	1.30

Volume of adsorbent 5.0 ml, aqueous solutions containing $5.00 \times 10^{-4} \text{ mol l}^{-1}$ of Ni(II), Co(II) and Cu(II).

industrial effluents, using a dynamic system, since one volume of the biosorbent is able to remove completely at least 100 volumes of contaminated metallic ion from aqueous solution.

The higher breakpoints (BP₂) values are related with the saturation of the biosorbent by uptaking the metallic ion. Considering a biosorbent volume of 5.00 ml (bed volume) and a $5.00 \times 10^{-4} \text{ mol l}^{-1}$ concentration of individually metallic aqueous solution, the saturation of the biosorbent by metallic ions in dynamic conditions are depicted on Table 4. As can be seen, the maximum saturation of the natural adsorbent by Ni(II), Co(II) and Cu(II) using a dynamic adsorption system is very close to the values obtained in the batch adsorption experiments.

4. Conclusion

Mandarin peel is very efficient adsorbent for divalent Ni(II), Co(II) and Cu(II) removal from aqueous solutions in a very rapid adsorption process. The maximum adsorption capacities vary with pH values, being higher at pH 4.8, which was experimentally fixed at $298 \pm 1 \text{ K}$ for all adsorptions, and the values obtained were 1.92, 1.37 and 1.31 mmol g^{-1} for Ni(II), Co(II) and Cu(II), respectively, using batch adsorption system. Under dynamic adsorption conditions the mandarin peel saturation was 1.85, 1.35 and 1.30 mmol g^{-1} for Ni(II), Co(II) and Cu(II), respectively.

The mandarin peel demonstrates a great ability for extracting metallic ions from simulated industrial effluent contaminated individually with Ni(II) or Co(II) or Cu(II) solutions. The Ponkan mandarin peel is a natural adsorbent available from fruit plantations and, consequently, without prior treatment before use, gives a low cost natural material, with great potential in ecosystem clean-up.

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References

- [1] S.E. Manaham, Environmental Chemistry, seventh ed., CRC Press, Boca Raton, 2000.
- [2] M.H. Yu, Environmental Toxicology—Biological and Health Effects of Pollutants, second ed., CRC Press, Boca Raton, 2005.
- [3] K.A. Matis, A.I. Zouboulis, N.K. Lazaridis, Heavy metals removal by biosorption and flotation, Water Air Soil Pollut. 3 (2003) 143–151.
- [4] V.K. Gupta, C.K. Jain, I. Ali, M. Sharma, V.K. Saini, Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste, Water Res. 37 (2003) 4038–4044.
- [5] C.E. Harland, Ion Exchange Theory and Practice, second ed., Royal Society of Chemistry, Cambridge, United Kingdom, 1994, p. 285.
- [6] D.O. Cooney, Adsorption Design for Wastewater Treatment, Lewis Publishers, Boca Raton, 1999, p. 189.
- [7] N. Kannan, S.J.S. Malar, Removal of mercury(II) ions by adsorption onto dates nut and commercial activated carbons: a comparative study, Indian J. Chem. Technol. 12 (2005) 522–527.
- [8] S. Babel, T.A. Kurniawan, Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan, Chemosphere 54 (2004) 951–967.
- [9] S.E. Bailey, T.J. Olin, M. Bricka, D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.
- [10] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. 97 (2003) 219–243.
- [11] J.L. Brasil, R.R. Ev, C.D. Milcharek, L.C. Martins, F.A. Pavan, A. A. dos Santos Jr., S.L.P. Dias, J. Dupont, C.P. Zapata Noreña, E.C. Lima, Statistical design of experiments as a tool for optimizing the batch conditions to Cr(VI) biosorption on Araucaria angustifolia wastes, J. Hazard. Mater., in press.
- [12] J.S. Melo, S.F. DiSouza, Removal of chromium by mucilaginous seeds of *Ocimum basilicum*, Bioresour. Technol. 92 (2004) 151–155.
- [13] F. Pagnanelli, S. Mainelli, F. Véglid, L. Toro, Heavy metal removal by olive pomace: biosorbent characterisation and equilibrium modelling, Chem. Eng. Sci. 58 (2003) 4709–4717.
- [14] A.A.M. Daifullah, B.S. Girgis, H.M.H. Gad, Utilization of agro-residues (rice husk) in small wastewater treatment plans, Mater. Lett. 57 (2003) 1723–1731.
- [15] M.A. Farajzadeh, A.B. Monji, Adsorption characteristics of wheat bran towards heavy metal cations, Sep. Purif. Technol. 38 (2004) 197–207.
- [16] M.A. Hashim, K.H. Chu, Biosorption of cadmium by brown, green and red seaweeds, Chem. Eng. J. 97 (2004) 249–255.
- [17] M. Minamisawa, H. Minamisawa, S. Yoshida, N. Takai, Adsorption behavior of heavy metals on biomaterials, J. Agric. Food Chem. 52 (2004) 5606–5611.
- [18] A. Moret, J. Rubio, Sulphate and molybdate ions uptake by chitin-based shrimp shells, Miner. Eng. 16 (2003) 715–722.
- [19] M.L. Arrascue, H.M. Garcia, O. Horna, E. Guilbal, Gold sorption on chitosan derivatives, Hydrometallurgy 71 (2003) 191–200.
- [20] G. Mazza, Gas-chromatography and mass-spectrometry study of the aromatic composition of mandarine essential oil, Sci. Aliments 7 (1987) 459–479.
- [21] Y. Nogata, K. Sekija, H. Ohta, K.I. Kusumoto, T. Ishizu, Inhibitors of platelet lipoxigenase from Ponkan fruit, Phytochemistry 56 (2001) 729–732.

- [22] J.C.P. Vaghetti, M. Zat, K.R.S. Bentes, L.S. Ferreira, E.V. Benvenuti, E.C. Lima, 4-Phenylenediaminepropylsilica xerogel as a sorbent for copper determination in waters by slurry-sampling ETAAS, *J. Anal. At. Spectrom.* 18 (2003) 376–380.
- [23] H.A. Flaschka, EDTA Titration, An Introduction to Theory and Practice, second ed., Pergamon Press, London, 1959.
- [24] M.L. Lota, D.R. Serra, F. Tomi, J. Casanova, Chemical variability of peel and leaf essential oils of mandarins from *Citrus reticulata* Blanco, *Biochem. Syst. Ecol.* 28 (2000) 61–78.
- [25] M. Minamisawa, H. Minamisawa, S. Yoshida, N. Takai, Adsorption behavior of heavy metals in biomaterials, *J. Agric. Food Chem.* 52 (2004) 5606–5611.
- [26] S. Karabulut, A. Karabakan, A. Denizli, Y. Yürüm, Batch removal of copper(II) and zinc(II) from aqueous solutions with low-rank Turkish coals, *Sep. Purif. Techn.* 18 (2000) 177–184.
- [27] C. Airoidi, L.N.H. Arakaki, Two independent routes to synthesize identical silicas by grafting ethylenimine or 2-aminoethanethiol, their cation adsorbing abilities, and thermodynamic data, *J. Colloid Interface Sci.* 249 (2002) 1–7.
- [28] J.A.A. Sales, A.G.S. Prado, C. Airoidi, Interaction of divalent copper with two diaminealkyl hexagonal mesoporous silicas evaluated by adsorption and thermochemical data, *Surf. Sci.* 590 (2005) 51–62.
- [29] E.F.S. Vieira, A.R. Cestari, E.B. Bastos, F. Dias, Interaction of Ag(I), Hg(II), and Cu(II) with 1,2-ethanedithiol immobilized on chitosan: Thermochemical data from isothermal calorimetry, *J. Colloid Interface Sci.* 289 (2005) 42–47.
- [30] V. Boonamnuyvitaya, C. Chaiya, W. Tanthapanichakoon, S. Janrudilokkul, Removal of heavy metals by adsorbent prepared from pyrolyzed coffee residues and clay, *Sep. Purif. Technol.* 35 (2004) 11–22.
- [31] I. Villaescusa, N. Fiol, M. Martínez, N. Miralles, I. Poch, J. Serrols, Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, *Water Res.* 38 (2004) 992–1002.
- [32] S.Y. Kang, J.U. Lee, S.-H. Moon, K.-W. Kim, Competitive adsorption characteristics of Co^{2+} , Ni^{2+} , and Cr^{3+} by IRN-77 cation exchange resin in synthesized wastewater, *Chemosphere* 56 (2004) 141–147.
- [33] M. Ajmal, R.A.K. Rao, J. Ahmad, Adsorption studies on *Citrus reticulata* (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater, *J. Hazard. Mater.* 79 (2000) 117–131.
- [34] T. Gosset, J.L. Trancat, D.R. Thevenot, Batch metal removal by peat—kinetics and thermodynamics, *Water Res.* 24 (1986) 21–26.
- [35] M.J. Zamzow, B.R. Eichbaum, K.R. Sandgren, D.E. Shanks, Removal of heavy-metals and other cations from waste-water using zeolites, *Sep. Sci. Technol.* 25 (1990) 1555–1569.
- [36] M.A. Farajzadeh, A.B. Monji, Adsorption characteristics of wheat bran towards heavy metal cations, *Sep. Purif. Technol.* 38 (2004) 197–207.
- [37] I.S. Lima, C. Airoidi, A thermodynamic investigation on chitosan-divalent cation interactions, *Thermochim. Acta* 421 (2004) 133–139.
- [38] F.A. Pavan, I.S. Lima, E.V. Benvenuti, Y. Gushikem, C. Airoidi, Hybrid aniline/silica xerogel cation adsorption and thermodynamics of interaction, *J. Colloid Interface Sci.* 275 (2004) 386–391.
- [39] M. Ajmal, R.A.K. Rao, B.A. Siddiqui, Studies on removal and recovery of Cr(VI) from electroplating wastes, *Water Res.* 30 (1996) 1478–1492.
- [40] E. El-Shafey, M. Cox, A.A. Pichugin, Q. Appleton, Application of a carbon sorbent for the removal of cadmium and other heavy metal ions from aqueous solution, *J. Chem. Technol. Biotechnol.* 77 (2002) 429–436.
- [41] A.G.S. Prado, L.N.H. Arakaki, C. Airoidi, Adsorption and separation of cations on silica gel chemically modified by homogeneous and heterogeneous routes with the ethylenimine anchored on thiol modified silica gel, *Green Chem.* 4 (2002) 42–46.