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ORIGINAL ARTICLE

Removal of multi-metals from water using reusable pectin/cellulose microfibers composite beads

Emanuele F. Lessa [a], **Aline L. Medina** [b], **Anderson S. Ribeiro** [b], **André R. Fajardo** [a,*]

[a] *Laboratório de Tecnologia e Desenvolvimento de Compósitos e Materiais Poliméricos – LaCoPol, Centro de Ciências Químicas, Farmacêuticas e de Alimentos, Universidade Federal de Pelotas (UFPel), 96010-900 Pelotas, RS, Brazil*
[b] *Laboratório de Metrologia Química – LabMeQui, Centro de Ciências Químicas, Farmacêuticas e de Alimentos, Universidade Federal de Pelotas (UFPel), 96010-900 Pelotas, RS, Brazil*

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Abstract Pectin (Pec) and cellulose microfibers (CF) extracted from orange waste were combined to form composite beads with enhanced adsorption capacity. Such beads were extensively tested in the removal of multi-metal ions from water. A factorial design approach was conducted to establish the optimum conditions for adsorption of Cd(II), Cu(II), and Fe(II) on Pec-CF beads. Batch adsorption experiments revealed that removal efficiency of such metal ions falls in the range of 94–58% and it followed the order Fe(II) > Cu(II) > Cd(II). The maximum Cd(II), Cu(II) and Fe(II) adsorption capacities calculated from the Langmuir isotherm were 192.3, 88.5 and 98.0 mg/g, respectively. FTIR analysis suggests that the functional groups on Pec-CF beads (binding sites) favor the adsorption of such metal ions. Desorption and reuse experiments demonstrated the beads could be used for at least five consecutive adsorption/desorption cycles. Our finds suggest the Pec-CF beads can serve as an efficient adsorbent for the removal of multi-metal ions from wastewater.

1. Introduction

Composite materials based on polysaccharides and polysaccharides-derivatives have been extensively referred in the literature as efficient and low-cost adsorbents for wastewater treatment (Carpenter et al., 2015; Crini, 2005; de Azevedo et al., 2017). As demonstrated by several authors, the use of such composites enables the remediation of different aqueous effluents since they are able to adsorb metal ions, dyes, organic compounds, and other water contaminants (Barakat, 2011; Lin et al., 2005; Lu et al., 2015; Malik and Iyer, 2017). Moreover, the recycling and reuse capabilities exhibited by these materials and the eco-friendly aspects related to their designing are attractive from the practical, economic and environmental points of view (Li et al., 2016; Luo et al., 2015).

In this way, one of the most interesting polysaccharides utilized to prepare low-cost adsorbent materials is pectin (Pec), a

* Corresponding author.
E-mail address: andre.fajardo@pq.cnpq.br (A.R. Fajardo).
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naturally occurring biopolymer composed of *D*-galacturonic acid (GalA) units joined in chains by means of α-(1→4) glycosidic linkage (Sila et al., 2009). Commercially, Pec is isolated from different plant-based sources (*e.g.* fruit peels and pulp, sugar beet, sunflower heads, among others) and its utilization in diverse applications is encouraged because of their low-cost, renewable nature, and abundance. The pK_a of GalA units in pectin is 3.5 (Opanasopit et al., 2008), which means that at pH values above 3.5 the Pec carboxyl groups are ionized ($-COO^-$) facilitating the ionic crosslinking of Pec with divalent cations (usually Ca(II) ions). The formation of Pec-Ca (II) networks has been extensively studied for different applications (Mata et al., 2010; Nguyen et al., 2014; Zahran et al., 2014). Furthermore, the excessive free carboxyl groups of Pec may act as binding sites for cationic pollutants found in wastewater (Jakobik-Kolon et al., 2017; Khotimchenko et al., 2007; Mata et al., 2010).

Recently, we reported the development of composite beads based on Pec and cellulose microfibers (Lessa et al., 2016). Cellulose microfibers (CF) were incorporated into the Pec-Ca(II) network due to its reinforcing properties and its ability to fix different solutes by adsorption (Urruzola et al., 2013). Such features can be ascribed to the large surface area of CF and the numerous hydroxyl groups distributed along the CF molecules. Both Pec and CF were extracted from orange waste by using facile protocols resulting in low cost, renewable and biodegradable starting materials. Pec-CF beads were previously tested for the removal of methylene blue, an organic dye (Lessa et al., 2016). Herein, we investigated the adsorption capacity of pectin/cellulose microfibers (Pec-CF) beads towards the removal of multi-metals ions from water. For this, a series of experiments were performed and rationalized to establish the optimum conditions for the adsorption of copper (Cu), cadmium (Cd) and iron (Fe) on Pec-CF beads. The effects of selected experimental parameters on the adsorption capacities of such metals were examined by applying a factorial design approach. Factorial design results confer more precise chemical interpretation than univariate study results (Bera et al., 2015; Rodrigues et al., 2013). As demonstrated by Taleb et al., factorial design can be utilized as an efficient tool in optimizing the adsorbent, in particular for the content of CF (Taleb et al., 2016). Other relevant aspects (*e.g.* adsorption kinetics, metal-adsorbent mechanisms, metal distribution on beads surface, metal desorption, reuse, among others) regarding the adsorption process and the applicability of such system were studied in detail. To the best of our knowledge, this is the first study that demonstrates that pectin/cellulose microfibers beads can serve as an adsorbent for the removal of multi-metal ions from wastewater.

2. Materials and methods

2.1. Materials

Pectin (Pec) and cellulose microfibers (CF) were extracted from orange waste using protocols described previously (Lessa et al., 2016). Ethanol (P.A.), hydrochloric acid (HCl, 30–34 v/v-%) and calcium chloride ($CaCl_2$, P.A.) were purchased from LabSynth (Brazil). Sodium hydroxide (NaOH, P.A.) and nitric acid (HNO_3, 65–70 v/v-%) were purchased from Vetec (Brazil). Copper(II) chloride dihydrated ($CuCl_2 \cdot 2H_2O$), cadmium chloride ($CdCl_2$) and iron(II) chloride tetrahydrated ($FeCl_2 \cdot 4H_2O$) were purchased from Sigma-Aldrich (USA). All chemicals of analytical grade were used as received.

2.2. Preparation of Pec-CF beads

Pec aqueous solution (2 w/v-%, 50 mL) was stirred with adequate amounts of CF (the amount of CF varied from 1 to 10 wt-% according to the factorial design approach) for 30 min at room temperature. Next, the resulting solution containing Pec/CF was introduced into a plastic syringe equipped with a needle (inner diameter 1.2 mm) and then carefully poured dropwise into $CaCl_2$ solution (10 w/v-%, pH 5). Spherical beads were formed instantaneously due to ionic crosslinking of Pec with Ca(II) ions. The beads were kept in $CaCl_2$ solution for 4 h to ensure complete crosslinking. Pec-CF beads were recovered and thoroughly washed with distilled water to eliminate the excess of calcium. Finally, purified beads were dried under vacuum for 48 h at 35 °C.

2.3. Factorial design

The effect of some parameters on the adsorption of Cd(II), Cu (II), and Fe(II) ions on Pec-CF beads was investigated by using a central composite design (CCD), 2^3 with 3 central points and 6 axial points, totaling 17 experiments. Three independent variables were evaluated: the content of CF into the composite beads (1–10 wt-%), adsorbent dosage (50–250 mg), and pH of the medium (2 –5). The variables and levels used in the factorial design are presented in Table 1. The experiments were performed in triplicate according to the Statistica© software (StatSoft Inc., USA) at a 95% significance level. Other experimental parameters (contact time, temperature, solution volume, initial metal concentration, and stirring rate) were kept fixed. After each experiment run, the removal capacity for each metal was evaluated by microwave induced plasma optical emission spectrometry (MIP OES) using an Agilent spectrometer (model Agilent 4200, Australia) equipped with an inert nebulizer, a double-pass glass cyclonic spray chamber and a nitrogen generator (model Agilent 4107, Australia). Optimized instrumental parameters were: pump speed 15 rpm, uptake time 15 s, stabilization time 15 s, read time 3 s, 3 replicates, and automatic background correction. Moreover, instrumental parameters relative to each metal ion are described in Table S1 (Supporting information).

The amount of metal adsorbed per gram of beads (q_t) at a different time (t) and the removal efficiency for each metal were calculated per Eqs. (1) and (2):

$$q_t = \left[\frac{(C_o - C_e)}{m}\right] V \qquad (1)$$

$$removal\ (\%) = \left[\frac{(C_0 - C_e)}{(C_0)}\right] \times 100 \qquad (2)$$

where C_o (mg/L) is the initial metal concentration, C_e (mg/L) is the concentration of metal remaining in the stock solution after the adsorption process, m (g) is the weight of the beads, and V (L) is the solution volume.

Table 1 Variables and levels used in the factorial design to evaluate the adsorption of Cd(II), Cu(II), and Fe(II) ions onto the Pec-CF beads.

Independent variables	Level				
	−1.68	−1	0	+ 1	+ 1.68
Content of CF into the beads (wt.%)	1.0	2.8	5.5	8.2	10.0
Adsorbent dosage (mg)	50	90	150	210	250
pH of the medium	2.0	2.6	3.5	4.4	5.0

2.4. Effect of initial metal concentration

Batch adsorption experiments were performed to investigate the effect of the initial metal concentrations on the adsorption capacity of Pec-CF beads. For this, the optimum conditions revealed by the factorial design (content of CF into the beads, adsorbent dosage and pH of the medium) were utilized. The initial metal concentrations were ranged from 50 to 150 mg/L (solution volume – 100 mL) and the set (beads + solutions) was kept under stirring (100 rpm) for 2 h at room temperature. All runs had the same initial concentrations of Cd(II), Cu(II), and Fe(II). At predetermined time intervals, the metals concentrations were determined by MIP OES analysis. The q_e values and the removal efficiencies for each metal ion were calculated per Eqs. (1) and (2), respectively. Each experiment was performed in triplicate ($n = 3$).

2.5. Desorption and reuse experiments

The metals desorption and the adsorbent recycling were investigated to assure the reusability of Pec-CF beads in further applications. Briefly, 50 mg of Pec-CF beads were added to 100 mL of metals solution ($C_0 \approx 100$ mg/L) at optimum pH. The system was kept under stirring (100 rpm) for 2 h. Next, the metal-loaded beads were recovered by filtration and rinsed several times with distilled water to remove the unabsorbed metals ions. The amounts of Cd(II), Cu(II) and Fe(II) adsorbed on Pec-CF beads were determined by MIP OES analysis. The metal-loaded beads were placed in contact with the HNO_3 solution (50 mL, pH $\sim$ 1) and this set was kept under stirring (100 rpm) for 2 h at room temperature. The amount of each metal desorbed was determined by MIP OES analysis and desorption efficiencies were calculated per equation (3):

$$desorption\ (\%) = \left[\frac{Q_{des}}{Q_{ads}}\right] \times 100 \quad (3)$$

where Q_{des} (mg/g) and Q_{ads} (mg/g) are the amounts of metal ions desorbed and absorbed, respectively. The regenerated beads were washed with distilled water up to neutral pH and then reused in a new adsorption/desorption cycle. Five consecutive adsorption/desorption cycles were performed. This experiment was run in triplicate ($n = 3$).

2.6. Characterization techniques

Fourier transformed infra-red (FTIR) spectra were recorded in a Shimadzu (model Affinity, Japan) spectrometer operating in the region from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} and 64 scan acquisitions. The samples were smashed and pressed with KBr to form disks for FTIR analysis. SEM images were recorded using a JEOL (model JSM-6610LV, USA) microscope coupled with an energy-dispersive X-ray (EDX) analyzer. Before SEM visualization, the swollen samples were quickly frozen in liquid nitrogen and then freeze-dried (−55 °C for 48 h). Finally, the dried samples were gold-coated by sputtering.

3. Results and discussion

3.1. Factorial design

The adsorption of metal ions on solid adsorbents is controlled by thermodynamic and environmental factors as well as by the properties of the metal specimen and the chemical/physical properties of the adsorbent (Dabrowski, 2001; Myers, 2002). Taking into account this, a factorial design was performed to investigate the effect of three variables (adsorbent dosage, pH of the medium and content of CF into the Pec-CF beads) on the removal of multi-metal ions from water using Pec-CF beads. Table 2 shows the CCD matrix for the different experimental trial formulations and the results regarding the removal efficiency for Cd(II), Cu(II), and Fe(II) ions. As observed, the central point showed slight variation indicating good repeatability of the adsorption process.

Pareto charts (Fig. S1, Supporting information) show the relative importance of the individual and interaction effects on removal efficiency of each metal. As noticed, the pH of the medium is the only significant individual parameter on the adsorption of all metals ions (confidence level of 95%). In addition, individual parameters adsorbent dosage and content of CF also showed significant on the adsorption of Cd(II) ions (Fig. S1a). Taking into account the Cu(II) removal, it was observed a significant interaction effect between the pH of the medium and the content of CF (Fig. S1b). The equation models generated from the significant effects on the removal of Cd(II) (4), Cu(II) (5) and Fe (II) (6) are listed below:

$$Cd(II)removal = 53.16 - 1.53x_1^2 - 2.23x_2^2 - 1.22x_3^2 (R^2 = 0.832) \quad (4)$$

$$Cu(II)removal = 64.35 - 2.31x_2^2 - 2.66x_2x_3 (R^2 = 0.549) \quad (5)$$

$$Fe(II)removal = 53.16 - 1.12x_2 - 1.25x_2^2 (R^2 = 0.553) \quad (6)$$

where x_1, x_2, and x_3 are the coded variables (x_1 – adsorbent dosage, x_2 – pH of the medium and x_3 – content of CF). Considering only the significant terms, the ANOVA analysis (Tables S2–S4, Supporting information) shows the analysis of variance for the absorption of Cd(II), Cu(II) and Fe(II) ions on Pec-CF beads. The calculated F-values confirmed the models were significant and adequate to generate response surfaces (Figs. S2–S4, Supporting information). These response

Table 2 CCD matrix for the adsorption of Cd(II), Cu(II), and Fe(II) ions onto the Pec-CF beads.

Run	Independent variables			Dependent variable		
	Adsorbent dosage (mg)	pH	Content of CF (wt.%)	Removal (%)		
				Cd(II)	Cu(II)	Fe(II)
1	90	2.6	2.8	47.79	62.64	88.17
2	210	2.6	2.8	48.90	59.07	89.33
3	90	4.4	2.8	48.78	63.47	91.61
4	210	4.4	2.8	47.56	66.39	90.72
5	90	2.6	8.2	47.36	60.70	90.57
6	210	2.6	8.2	47.86	67.33	91.29
7	90	4.4	8.2	47.14	59.17	93.54
8	210	4.4	8.2	47.79	55.76	92.20
9	50	3.5	5.5	48.37	60.25	88.92
10	250	3.5	5.5	50.10	63.07	87.15
11	150	2.0	5.5	47.70	58.22	88.99
12	150	5.0	5.5	46.83	58.05	93.87
13	150	3.5	1.0	49.29	62.64	91.57
14	150	3.5	10.0	50.94	62.72	87.29
15	150	3.5	5.5	55.09	70.13	88.39
16	150	3.5	5.5	52.18	63.87	87.34
17	150	3.5	5.5	52.07	68.89	88.17

*Other experimental conditions: Initial metals concentration 100 mg/L; solution volume 100 mL; room temperature; contact time 2 h; stirring 100 rpm.

surfaces allow investigating the main effects of independent factors and their interaction on the removal of the metals (Fakhri, 2014). In this sense, the response surfaces demonstrated that the optimum pH for the removal of Cd(II) and Cu(II) is 3.5 while the optimum pH for the removal of Fe(II) is 5.0. This result can be associated with the ionization of the carboxyl groups of Pec under this pH condition. The carboxyl groups of Pec exhibit pK_a around 3.5 (Opanasopit et al., 2008). Thereby, above pH 3.5 the electrostatic interaction among the divalent ions and carboxylate groups of Pec increased favoring the adsorption process. Lessa et al. (2016) demonstrated that Pec-CF beads with 5 wt-% of CF exhibited a point of zero charge (PZC) at pH 3.7. Above such pH, these beads show a negatively charged surface improving the adsorbent-adsorbate interaction. For higher pHs (pH $\geq$ 5), the adsorption can be damaged due to precipitation of metal hydroxides (Lee and Saunders, 2003). In addition, the response surfaces (Fig. S2–S4) showed that the optimum content of CF into the beads for the Cd(II) and Cu(II) removal is 5.5 wt-% and the optimum adsorbent dosage for Cd(II) removal is 150 mg. Previously, we had observed that the Pec-CF beads with 5 wt-% of CF showed highly porous surface, which is an attractive aspect for promising adsorbent materials (Lessa et al., 2016). This systematic study complements and refines our previous work. Moreover, such data are important to design Pec-CF beads with superior properties. The optimized analytical conditions set for the further experiments were: adsorbent dosage – 150 mg; pH of the medium – 4; and content of CF – 5.5 wt-%. This pH (pH 4) was chosen because it is an intermediate value between the optimum pHs verified for the removal of Cd(II), Cu(II), and Fe(II) ions.

3.2. Adsorption of multi-metal ions on Pec-CF beads

Batch adsorption experiments were performed to investigate the adsorption of Cd(II), Cu(II), and Fe(II) ions on Pec-CF beads at three different initial concentrations (50, 100 and 150 mg/L) using the optimized conditions revealed by the CCD analysis. The calculated values of q_t and the removal efficiencies are shown in Fig. 1(a–d).

It can be seen from these results that the amount of metal adsorbed on beads increased with increasing initial metal concentration in the medium. For example, the amount of Cd(II) adsorbed per gram of Pec-CF at equilibrium (q_e) increases ca. 310% when the initial concentration of such ion in solution increases from 50 to 150 mg/L. For Cu(II) and Fe(II), the q_e values increased ca. 345% and 333% upon increasing the metals concentration from 50 to 150 mg/L. These results suggest the adsorption capacity of Pec-CF beads regarding these metals is affected by their initial concentration in solution. In addition, it is noticed the q_t values increased quickly for the first 10 min of contact for all tested metals in the three different initial concentrations. Above 20 min, the q_t values tend to level off and they showed slight variation up to the end of the experiment. Apparently, the adsorption rate of each metal is not affected by the presence of other metals or by its initial concentration in the medium. Fig. 1d shows the removal efficiency of the three applied metals as a function of their initial concentrations in solution. Overall, removal efficiencies were slightly affected by the initial metals concentration. The maximum removal of Cd(II), Cu(II), and Fe(II) ions was ca. 58%, 77%, and 94% when the initial concentration of such metals falls in the range of 50–150 mg/L. According to the experimental results, the adsorption capacities and removal efficiencies followed the order Fe(II) > Cu(II) > Cd(II). Anionic sites along the surface of the beads attract the metals ions and the metal binding to these sites depends on certain intrinsic metal properties (*e.g.* ionic radius, atomic weight, coordination geometry and electro-negativity) (Laus and de Favere, 2011; Petrovic and Simonic, 2016). Herein, the Fe(II) ions exhibit the smallest ionic radius and atomic weight followed by the Cu(II) and Cd(II) ions (Wells, 1984). Likely due to these fea-

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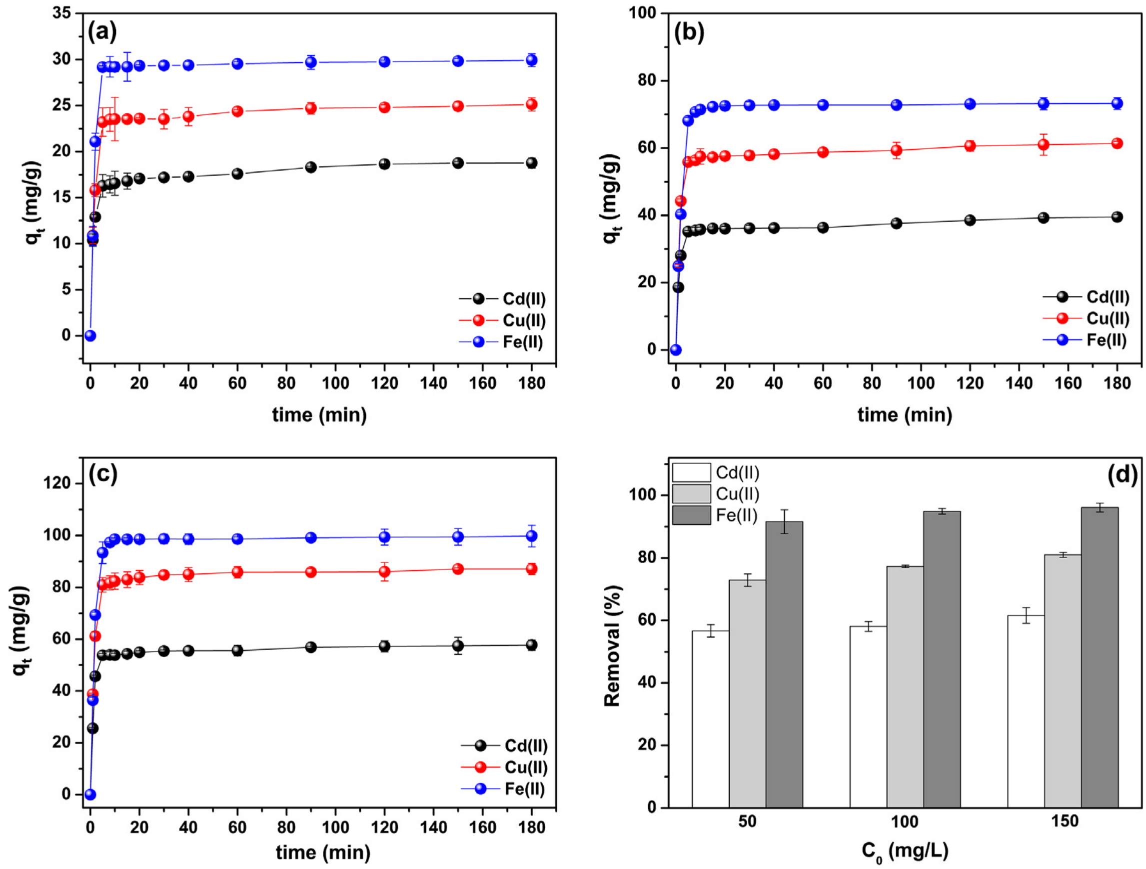

Fig. 1 Amount of adsorbed Cd(II), Cu(II) and Fe(II) ions on Pec-CF beads versus contact time for various initial concentration: (a) C_0 50 mg/L, (b) C_0 100 mg/L and (c) C_0 150 mg/L. (d) Removal of metals ions calculated for each experiment (Volume: 100 mL; adsorbent dosage: 150 mg; pH: 4; room temperature; stirring 100 rpm).

tures, the Fe(II) ions had been adsorbed easier than other metals ions. The smallest ionic radius and atomic weight of Fe(II) ions facilitate their interaction with the Pec-CF surface and aid its transport through the internal surface of the adsorbent (Zawierucha et al., 2016). Thus, the high adsorption of Fe(II) ions decreased the number of active sites on the Pec-CF surface for binding of Cu(II) and Cd(II) ions.

The adsorption kinetics of Cd(II), Cu(II), and Fe(II) ions on Pec-CF beads at the three different initial metal concentrations were examined using two simplified models: Pseudo-first order (Eq. (7)) and pseudo-second order (Eq. (8)) models. The robustness of such models was analyzed by using the non-linear Chi-square test (χ^2-test, Eq. (9)). This test allows evaluating the agreement among the experimental and the theoretical data (in terms of deviation) and then to determine which kinetic model describes properly the adsorption process. If theoretical data are similar to the experimental data, χ^2 will be a small value, while if they are discrepant, χ^2 will be a larger value.

$$\ln(q_e - q_t) = lnq_{e(th)} - k_1 t \quad (7)$$

$$t/qt = 1/k_{2q^2_{e(th)}} + t/q_{e(th)} \quad (8)$$

$$\chi^2 = \sum \frac{(q_{e(exp)} - q_{e(th)})^2}{q_{e(th)}} \quad (9)$$

where k_1 (1/min) and k_2 (g/mg min) are the rate constants of the pseudo-first-order and pseudo-second-order kinetic models. $q_{e(\exp)}$ (mg/g) is the amount of metal adsorbed per gram of adsorbent under the experimental conditions and $q_{e(th)}$ (mg/g) is the theoretical value calculated from the kinetic models. The kinetic parameters calculated from the pseudo-first order and pseudo-second order plots are listed in Table 3 (Fig. S5(a-c) and S6(a-c) in the Supplementary information present the linearized plots).

According to the data presented in Table 3, the determination coefficients (R^2) for the pseudo-second order model were higher than those calculated for the pseudo-first order. The high R^2 values presented by the pseudo-second order for all metals at different initial concentrations suggest that this kinetic model fits the experimental adsorption data. Furthermore, the small values calculated from the χ^2-test for the pseudo-second order kinetics confirmed that the experimental data (q_e) is in accordance with the theoretical data ($q_{e(th)}$). The rate constants for pseudo-second order (k_2) increased with increasing initial metal concentration. In general lines, the calculated values of k_2 for each initial metal concentration followed the order Fe(II) > Cu(II) > Cd(II), which may be assigned to the intrinsic features of each metal (*e.g.* ionic radius, atomic weight, etc.). These finds are in agreement with other studies reporting the adsorption of metals ions on bio-based adsorbents (Fares et al., 2011; Petrovic and Simonic, 2016; Zhou et al., 2009).

Table 3 Parameters of pseudo-first and pseudo-second order kinetics models for Cd(II), Cu(II) and Fe(II) ions onto Pec-CF beads.

Pseudo-first order

Metal	C_0 (mg/L)	q_e (mg/g)	$q_{e(th)}$ (mg/g)	k_1 (1/min)	R^2	χ^2
Cd(II)	50	18.76	4.53	0.033	0.908	44.70
	100	39.51	7.11	0.019	0.759	147.64
	150	57.76	6.79	0.022	0.764	382.61
Cu(II)	50	25.13	3.34	0.021	0.703	142.16
	100	61.41	8.64	0.020	0.728	332.30
	150	87.08	2.97	0.037	0.913	2464.98
Fe(II)	50	29.93	1.82	0.022	0.503	434.78
	100	73.27	4.66	0.032	0.601	1010.16
	150	99.82	5.19	0.022	0.431	1725.40

Pseudo-second order

Metal	C_0 (mg/L)	q_e (mg/g)	$q_{e(th)}$ (mg/g)	k_2 (g/mg min)	R^2	χ^2
Cd(II)	50	18.76	18.87	0.008	0.999	6.4×10^{-4}
	100	39.51	39.37	0.013	0.999	9.1×10^{-5}
	150	57.76	57.80	0.016	0.999	2.8×10^{-5}
Cu(II)	50	25.13	25.19	0.031	0.999	1.4×10^{-4}
	100	61.41	61.35	0.042	0.999	5.9×10^{-5}
	150	87.08	86.96	0.043	0.999	1.7×10^{-4}
Fe(II)	50	29.93	29.69	0.051	0.999	1.9×10^{-3}
	100	73.27	73.53	0.057	0.999	9.2×10^{-4}
	150	99.82	100.00	0.069	0.999	3.2×10^{-4}

The adsorption mechanism of Cd(II), Cu(II), and Fe(II) on Pec-CF beads was investigated using isotherm models. Such mathematical models allow correlating the q_e data and the metal residual concentration (C_e) in solution at a specific temperature (Kumar et al., 2010; Laus and de Favere, 2011). The parameters calculated from the adsorption isotherms express the surface properties of the adsorbent and the metal-adsorbent affinity, as well as the adsorption efficiency. Herein, the experimental adsorption data were analyzed by fitting them to linear forms of Langmuir (Eq. (10)), Freundlich (Eq. (11)), Temkin (Eq. (12)) and Dubinin-Raduskevich (Eq. (13)) isotherms (Gomes et al., 2015; Laus and de Favere, 2011).

$$1/qe = (1/K_L q_m)1/C_e + 1/q_m \quad (10)$$

$$log q_e = log K_F + 1/n \log C_e \quad (11)$$

$$q_e = (RT/b) ln K_T + (RT/b) ln C_e \quad (12)$$

$$ln q_e = ln q_s - K_D 2\varepsilon^2 \quad (13)$$

where q_m (mg/g) is the maximum theoretical adsorption capacity presented by the adsorbent under the tested experimental conditions and K_L (L/mg) is the Langmuir isotherm constant that correlates the affinity between the adsorbent and the adsorbate. K_F [(mg/g)(mg/L)$^{1/n}$] is the Freundlich isotherm constant, which is associated with the relative adsorption capacity, n (dimensionless) is the Freundlich model exponent related to the adsorption intensity (*i.e.* heterogeneity factor). K_T (L/mol) is the Temkin isotherm constant relative to the maximum binding energy, b (J/mol) is a constant related to the adsorption heat, R is the universal gas constant (8.314 J/K mol) and T (K) is the absolute temperature. K_D (mol^2/kJ^2) is the Dubinin-Radushkevich isotherm constant that is inversely related to the mean free energy of adsorption, q_s (mg/g) is the theoretical isotherm saturation capacity and ε is a Polanyi adsorption potential [$\varepsilon = RT log(1 + 1/C_e)$]. The calculated parameters from the isotherms are summarized in Table 4 (Fig. S7a-d in Supplementary information presents the linearized isotherms plots).

As observed in Table 4, the R^2 values calculated from the chosen isotherm models suggest that the experimental data relative to the adsorption of Cd(II), Cu(II), and Fe(II) ions on Pec-CF beads can be well fitted by Langmuir isotherm. The Langmuir isotherm designates the adsorption process is driven by the monolayer formation on the outer surface of the beads, which contain a limited number of binding sites (Petrovic and Simonic, 2016). The suitability demonstrated by the Langmuir isotherm for describing the adsorption of Cd(II), Cu(II) and Fe(II) ions on Pec-CF beads suggest that such monolayer formation occurred during the adsorption process. It is, moreover, worthy of note that, ion exchanging between the tested metal ions and the Ca(II) ions bound to the carboxylate groups on the surface of the beads also occur. This observation has been reported by other studies involving metal adsorption on ionically crosslinked materials (Feng and Guo, 2012; Jain et al., 2016; Laus and de Favere, 2011; Petrovic and Simonic, 2016). Therefore, it is expected that both adsorption and ion exchange processes take place for this system.

According to Langmuir isotherm, the maximum theoretical adsorption capacities (q_m) of Pec-CF for Cd(II), Cu(II), and Fe (II) ions adsorption were 192.30, 88.49 and 98.04 mg/g. From these data, it is possible to infer that the under these experimental conditions the maximum adsorption was achieved for Cu(II) and Fe(II) ions. Table 5 lists the q_m values presented by other adsorbents for Cd(II), Cu(II), and Fe(II) adsorption. As observed, the adsorption of such metals ions varies considerably as a function of the adsorbent nature. In spite of this, Pec-CF beads showed remarkable adsorption capacity in com-

Table 4 Parameters and correlation coefficients (R^2) calculated from Langmuir, Freundlich, Temkin and Dubinin-Raduskhevich and isotherm models for the adsorption of Cd(II), Cu(II) and Fe(II) onto Pec-CF beads.

Isotherm	Parameters	Cd	Cu	Fe
Langmuir	q_m (mg/g)	192.30	88.49	98.04
	K_L (L/mg)	0.004	0.016	0.127
	R^2	0.995	0.992	0.991
Freundlich	n	0.65	0.84	0.35
	K_F (mg/g)(mg/L)$^{1/n}$	0.447	0.483	0.539
	R^2	0.960	0.984	0.934
Temkin	b (J/mol)	18.40	34.57	44.36
	K_T (L/mol)	0.372	0.100	0.056
	R^2	0.838	0.836	0.963
Dubinin-Radushkevich	q_s (mg/g)	62.21	105.41	254.68
	K_D (mol^2/kJ^2)	5.03×10^{-4}	2.58×10^{-4}	3.86×10^{-5}
	E (kJ/mol)	0.030	0.044	0.114
	R^2	0.893	0.911	0.919

Table 5 Maximum adsorption capacity (q_m) of various polysaccharide-based adsorbents for Cd(II), Cu(II) and Fe(II) ions adsorption.

Adsorbent	pH	Contact time (h)	q_m (mg/g)			Reference
			Cd(II)	Cu(II)	Fe(II)	
Pectin-Guar gum beads	3.5	24	92.0	–	–	Jakobik-Kolon et al. (2014)
Pectin beads	6	24	16.9	–	–	Mata et al. (2010)
Pectin beads	5	24	–	22.8	–	Mata et al. (2010)
Pectin-*g*-poly(acrylate) gels	9.8	6	53.6	–	–	Fares et al. (2011)
Pectin/iron oxide gels	5	24	–	49.0	–	Gong et al. (2012)
Alginate/pectin beads	3	4	–	23.9	–	Tiwari et al. (2009)
Silver nanoparticles/alginate beads	2	2	–	–	236.4	Asthana et al. (2016)
Kondagogu gum	2	5	97.3	93.8	86.3	Vinod et al. (2010)
Pec-CF beads	4	2	192.3	88.4	98.0	Present study

parison to these adsorbents. Furthermore, beads prepared in this study achieved high q_m values more quickly than other adsorbents (only 2 h of contact time), which is a particular advantage for practical applications.

The K_L value, which denotes the affinity among the adsorption sites on the adsorbent surface and the metal ions, was higher for Fe(II) than those of other metals. This result suggests the affinity between Pec-CF and the Fe(II) ions is higher than those for Cd(II) and Cu(II) ions. Such behavior aids to explain the higher q_e values observed for Fe(II) adsorption as compared to the other two metals. The separation factor (R_L), a dimensionless constant derived of Langmuir isotherm that denotes the favorability and feasibility of the metal adsorption, was calculated for the metals at the three different initial metal concentrations (Gomes et al., 2015; Pandey et al., 2010). The calculated values of R_L (Table S3, Supporting information) for Cd(II), Cu(II), and Fe(II) ions at 50, 100 and 150 mg/L of initial metal concentration were within the range of 0–1 indicating the favorable nature of the adsorption of such metals on Pec-CF beads (Gomes et al., 2015; Pandey et al., 2010).

The interaction between the adsorbed metal ions and the Pec-CF beads was investigated by using FTIR spectroscopy technique, which has been successfully utilized for this purpose (Medina et al., 2016; Petrovic and Simonic, 2016). FTIR spectra were recorded for the Pec-CF beads unexposed to the metals solution and for the Pec-CF beads exposed to the single metal or to the multi-metal solutions ($C_0 \approx 100$ mg/L) (Fig. 2).

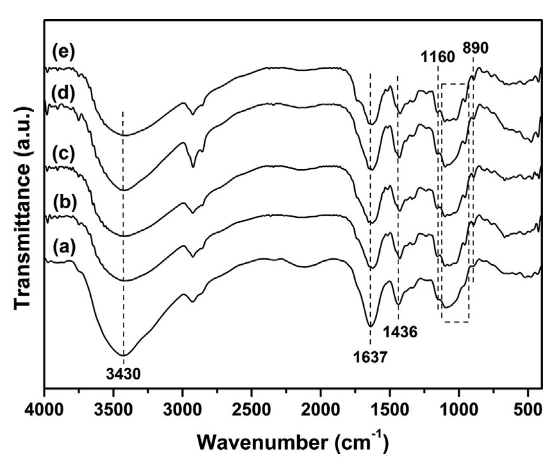

Fig. 2 FTIR spectra recorded for (a) unexposed Pec-CF beads, (b) Cd(II)-loaded beads, (c) Cu(II)-loaded beads, (d) Fe(II)-loaded beads and (e) multi-metal-loaded beads.

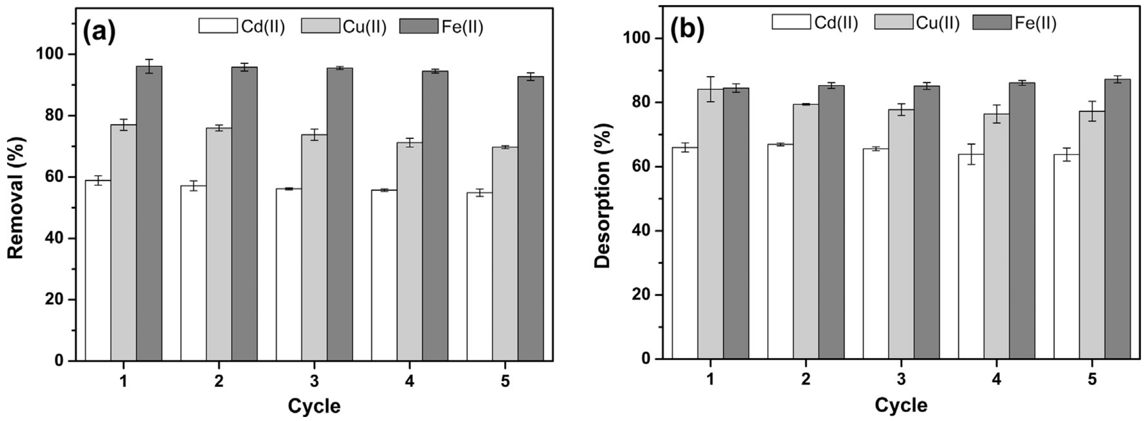

Fig. 3 (a) Removal and (b) desorption consecutive cycles (Adsorption – Volume: 100 mL, C_0: 100 mg/L, adsorbent dosage: 150 mg, pH: 4; room temperature; contact time: 2 h; stirring 100 rpm. Desorption – Volume: 50 mL of HNO_3 solution; pH ~ 1; room temperature; contact time: 2 h; stirring: 100 rpm).

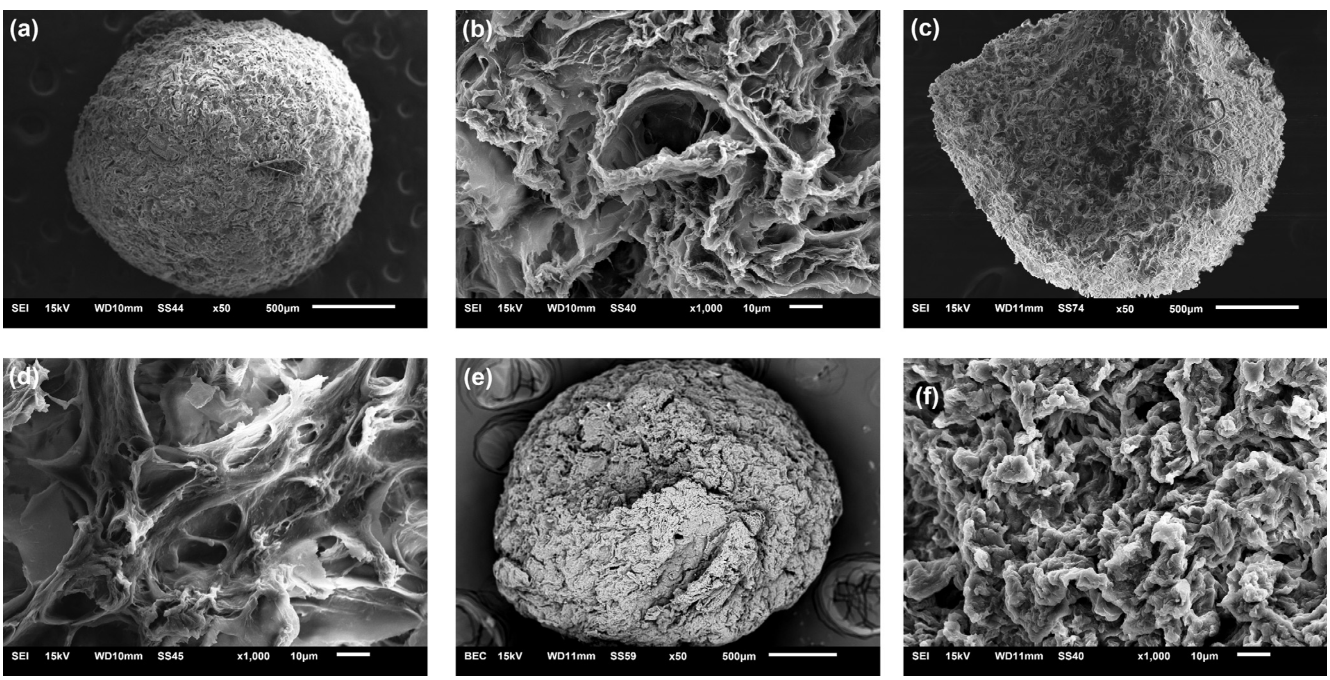

Fig. 4 SEM images of (a, b) Pec-CF beads; (c, d) metals-loaded Pec-CF beads and (e, f) regenerated Pec-CF beads (Images (a, c, d): Mag × 50; Images (b, d, f): Mag × 1000). (Adsorption – Volume: 100 mL, C_0: 100 mg/L, adsorbent dosage: 150 mg, pH: 4; room temperature; contact time: 2 h; stirring 100 rpm. Desorption – Volume: 50 mL of HNO_3 solution; pH ~ 1; room temperature; contact time: 2 h; stirring: 100 rpm).

The Pec-CF spectrum (Fig. 2a) exhibited great similarity to the spectrum described in our previous work (Lessa et al., 2016), whereby the broad band centered at 3430 cm^{-1} is assigned to the –OH stretching of hydroxyl groups of Pec and CF, while the band at 2923 cm^{-1} corresponds to the aliphatic C—H stretching. Bands assigned to C═O stretching of carboxyl groups of Pec are observed at 1637 and 1436 cm^{-1} (symmetrical and antisymmetric), respectively. It should be mentioned here, these groups are ionically bound with Ca (II) ions (Mata et al., 2009). Bands observed in the 1250–950 cm^{-1} region are assigned to the saccharide backbone (C—C, C—O—C, C—OH stretching) of Pec and CF (O'Connell et al., 2006; Urias-Orona et al., 2010). The FTIR spectra recorded for the beads exposed to the single metal solutions (Fig. 2(b-e)) showed the bands corresponding to the functional groups of Pec-CF shifted to lower wavenumber indicating the interaction among these groups and the metal ions. The decreasing in the intensities of such bands, as compared to other bands, reinforces this suggestion. The FTIR spectrum recorded for the beads exposed to the multi-metal solution (Fig. 2e) showed the highest differences in comparison to the spectrum recorded for the unexposed beads. The bands

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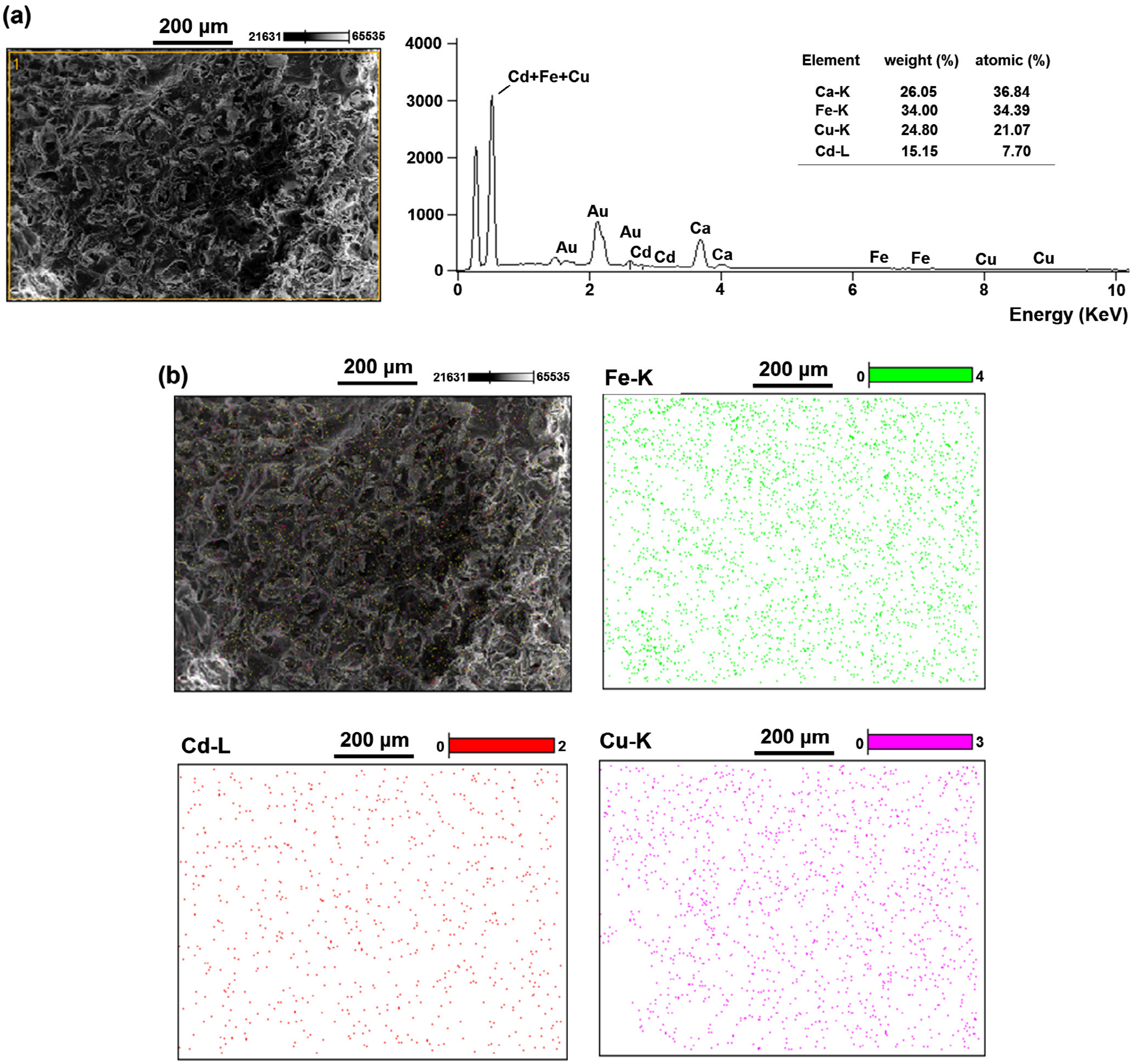

Fig. 5 (a) EDX analysis and (b) element mapping of metals-loaded Pec-CF beads.

assigned to —OH stretching broadened and shifted to lower wavenumber (ca. 3410 cm^{-1}), while the bands assigned to C=O stretching (symmetric and antisymmetric) shifted to 1621 and 1425 cm^{-1}. Furthermore, noticeable changes were observed in the bands in 1100–1050 cm^{-1} region indicating that the hydroxyl groups of saccharide structure of Pec and CF interacted with these metals. The sharp bands at 1160 and 890 cm^{-1} evidenced in the FTIR spectra of Pec-CF beads exposed to single metal and multi-metal solutions were attributed to the metal-oxygen vibration of bound hydroxylate and/or hydrated metal ions confirming the metal-beads interaction (Petrovic and Simonic, 2016; Senesi and Loffredo, 2008). In general lines, polysaccharide structures have previously been reported to be effective at attracting metal ions due to their functional groups (*e.g.* carboxyl, hydroxyl, amine, amide, among others) (Gerente et al., 2000; Skwarek et al., 2017).

3.3. Metal desorption and reuses experiments

Desorption experiments were performed in order to investigate the metal releasing capacity of metal-loaded Pec-CF beads and the further reusability of such beads in new adsorption/desorption cycles. The adsorbent reusability is paramount for practical applications. Herein, adsorption sites on beads surface were regenerated by using HNO_3 solution (pH ~ 1). The protonation of carboxyl and hydroxyl groups caused due to HNO_3 breaks off the interaction between these groups and the adsorbed metals, which are eluted to the solution. After the regeneration treatment, the Pec-CF beads were re-utilized in further adsorption/desorption experiments. Fig. 3(a and b) depicts the removal and desorption percentages for the metals in each adsorption/desorption cycle.

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As observed, removal profiles for each cycle followed the previously observed order (Fe(II) > Cu(II) > Cd(II)). Overall, there was a decreasing of 10% in the removal capacity of each metal from the first to the last cycle. It is worthy to note that even after the fifth cycle of use the removal (%) of Cu(II) remained close to 55%, while the removal of Cd(II) and Fe(II) remained close to 69% and 92%, respectively. The calculated values of q_e for the metals after each cycle (Fig. S8, Supporting information) showed similarity. Moreover, adsorption capacities regarding each metal showed slight variation from the first to the fifth cycle. These findings allow inferring the Pec-CF beads exhibited remarkable reuse capability encouraging their utilization as a low-cost adsorbent.

The desorption efficiency for Cd(II), Cu(II) and Fe(II) ions were ca. 65%, 79% and 86%, respectively (Fig.3b). As mentioned above, metal intrinsic features (*e.g.* ionic radius, atomic weight, coordination geometry and electro-negativity) have a clear effect on desorption process of such adsorbate. For example, small ionic radius and low atomic weight are features that facilitate the diffusion of the metal ion outward the adsorbent. Thereby, the differences on these intrinsic features affected the adsorption and desorption processes of each metal ion. Similar observations are reported in the literature (Laus and de Favere, 2011; Zhou et al., 2004).

The effects of the metal adsorption and desorption on the beads morphology were investigated by SEM (Fig. 4(a-f)).

As observed in Fig. 4(a and b), the Pec-CF beads showed a porous and irregular surface with high roughness. Moreover, the pores are distributed heterogeneously on the bead surface. Such kind of morphology is very attractive for adsorbent materials since the high surface area increases the adsorption sites on the beads surface (Barakat, 2011). A similar description was done by Lessa et al. (2016) regarding pectin beads filled with different amounts of CF. SEM images taken from the metals-loaded beads (Fig. 4(c and d)) revealed that after the adsorption process the surface of the beads becomes less rough. Furthermore, the empty spaces on the surface decreased in comparison to the unexposed beads. Such more compact and regular morphology resulted from the interaction between the functional groups of Pec-CF and the divalent metals. This additional interaction kept the polymeric chains closer to each other and increased the surface homogeneity. EDX analysis and element mapping (Fig. 5) confirmed the presence of the adsorbed metals as well as their good distribution along the surface of the beads. Moreover, the quantitative analysis showed that the presence of the metals on the surface of the beads followed the order Fe(II) > Cu(II) > Cd(II), which is in agreement with the adsorption data. The EDX analysis also demonstrated the presence of calcium on the beads surface confirming that both adsorption and ion exchange processes take place in this adsorption system. Fig. 4(e and f) show the SEM images taken from the regenerated Pec-CF bead. As observed, it is evident that the acidic treatment utilized in the metal desorption procedure has affected the bead morphology. The beads surface showed high roughness and irregular aspect similar to that observed for the unexposed beads. However, regenerated beads showed small pore size, which can explain the decreasing in the adsorption capacity after the acidic treatment. On the other hand, beads utilized in consecutive adsorption/desorption cycles did not show evidence of degradation (*i.e.* loss of shape, erosion, etc.) or changes in their chemical structure, as assessed by FTIR analysis (Fig. S9). These results encourage the use of Pec-CF beads as an adsorbent in the treatment of metal-contaminated wastewater.

Here we demonstrated that these optimized composite beads based on polysaccharides extracted from orange waste could be efficiently employed in the removal of multi-metal ions from the aqueous medium. This contribution complements our previous study and it suggests that Pec-CF beads are promising adsorbents for the removal of different pollutants from wastewater.

4. Conclusion

Pectin-cellulose microfibers (Pec-CF) composite beads were efficiently employed as adsorbents for the removal of multi-metal ions from water. A preliminary factorial design approach revealed the metals adsorption is enhanced for pH close to 4, using 150 mg of beads filled with 5.5 wt-% of CF. Batch adsorption experiments showed that the metal removal follows the order Fe(II) > Cu(II) > Cd(II). The theoretical maximum adsorption capacities (q_m) of Pec-CF beads for Cu(II), Cd(II) and Fe(II) ions were 192.30, 88.5 and 98.0 mg/g, respectively. Such results are comparable or are even superior to those reported previously in the literature. The experimental adsorption data were fitted closely by the Langmuir isotherm indicating monolayer formation and ion exchanging drive the adsorption process. As assessed by FTIR, the functional groups of Pec-CF interacted with the divalent ions making a significant contribution to the adsorption process. These observations strengthen the suggestion that the polysaccharide structure of Pec and CF is imperative for the adsorption process. Overall, Pec-CF composite beads can be employed in at least five consecutive adsorption/desorption cycles without demonstrating drastic loss of adsorption capacity. Furthermore, the post-treatment performed under acidic condition allowed the recovery of the adsorbed metals and also regenerated the adsorption sites on the surface of the beads. The results presented here confirm our hypothesis that the Pec-CF beads can be utilized as an efficient and reusable adsorbent material for removing of multi-contaminants from wastewater. The efforts and advances described here may be relevant to designing enhanced low-cost adsorbent materials based on polysaccharides and polysaccharides-derivatives for practical uses.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2017.07.011.

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