

## New, hybrid pectin-based biosorbents

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### ABSTRACT

In this work hybrid pectin-based biosorbents with secondary polysaccharide additives (gellan, carob and xanthan gum, ratio to pectin 1:1, 1:1 and 1:3, respectively) were obtained at two temperatures. The presence of these additives in prepared beads was confirmed by Raman spectra. The SEM micrographs show better homogeneity of blends and greater differences between structures of beads with various additives obtained at higher temperature. The sorption capacity of our hybrid biosorbents as well as sole pectin sorbent is rather the same, and equals 0.85 and 0.70 mmol/g for lead and cadmium, respectively, in pH 4–6.

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## Introduction

Heavy metals are currently one of the major threats to the ecosystem and human health. They are incessantly introduced to the environment from a variety of sources, e.g. industrial and agricultural waste. Two of the most widespread harmful metals are lead and cadmium. Both these elements have a toxic effect on the human body even at low exposure,<sup>[1–3]</sup> therefore purification of waste water and sewage polluted by these metals still raise universal interest. Chemical precipitation, carbon adsorption, membrane separation, ion exchange and biosorption have been proposed so far. Among all these suggested methods biosorption seems to be an interesting, economical alternative method, which allows rapid and selective removal of metals in a wide pH range even from diluted waste water or sewage.<sup>[1]</sup> Various materials of natural origin can be used for cadmium and lead removal: sawdust,<sup>[2–4]</sup> pine bark,<sup>[5]</sup> fruit, nut shells,<sup>[6–8]</sup> native grapefruit biomass,<sup>[9]</sup> water hyacinth,<sup>[10]</sup> mandarin, potato peel,<sup>[11, 12]</sup> mistletoe leaves,<sup>[13]</sup> Nordmann fir leaves,<sup>[14]</sup> algae,<sup>[15–17]</sup> lichen,<sup>[18,19]</sup> wheat straw<sup>[20]</sup> and various microorganisms.<sup>[21–27]</sup> Unfortunately, raw biosorbents usually consist of very fine particles and their separation from purified water constitutes the most problematic step in the whole purification process. Moreover, application of such biosorbents in column process is limited – fine particles of sorbent can make a dense cake, which inhibits the flow of liquid through the column.<sup>[28]</sup> Therefore, biosorbents

formed into beads, which are easy to separate from solution and which may be used in the column process, are demanded. Pectin-based biosorbents, which are known for their ability to remove heavy metals, are suitable for this purpose.<sup>[28–31]</sup>

Pectin belongs to the group of polysaccharides and consists mainly of galacturonic acid, which is easy to methylation or amidation.<sup>[32]</sup> Commercially available pectin is derived from vegetable or fruit by-product, e.g. sugar beet pulp, apple peel and citrus peel. Pectin-based biosorbents are mostly obtained as round beads using calcium ions as a crosslinking agent. Properties of such pectin-based biosorbents may be changed by addition of other polysaccharides, e.g. guar gum.<sup>[33]</sup> The addition may alter the swelling of material, improve sorption capacity or sorption kinetics, e.g. by extending the sorption area. Moreover, addition of such polysaccharides can decrease the final cost of prepared biosorbents, which is important for economic reasons. Therefore, there are some other polysaccharides that could be interesting for this purpose. Gellan gum is a linear tetrasaccharide obtained in the fermentation process with *Sphingomonas elodea* and, like pectin, is capable of forming gels in the presence of Ca<sup>2+</sup>.<sup>[34]</sup> Gellan gum also shows good sorption properties for heavy metals, e.g. maximum sorption capacity for Pb<sup>2+</sup> and Cd<sup>2+</sup> was 0.85 and 0.62 mmol/g, respectively.<sup>[35]</sup> Xanthan gum is also a polysaccharide obtained from

the fermentation of carbohydrates by the bacteria *Xanthomonas campestris*. It is composed mainly of glucose, mannose and glucuronic acid.<sup>[34, 36]</sup> There is only a little information available about sorption capacities of xanthan biosorbent for various heavy metals. The highest uptake has been achieved for  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  (57.22, 41.66 and 44.56 mg/g, respectively).<sup>[37]</sup> Carob gum is mainly secreted from the carob seeds or tree. It consists of mannose and galactose units joined in glycosidic linkages.<sup>[38]</sup> To the best of our knowledge, there are not any reports about the usage of carob gum in the studies of heavy metal sorption. Taking into account the above, in this work hybrid biosorbents being a blend of pectin with carob gum, gellan gum or xanthan gum were prepared and examined for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  removal.

## Experimental details

### Reagents and solutions

Amide pectin (NECJ A2) was purchased from C&G Spółka z o.o. (Jasło, Poland). Xanthan and carob gum were supplied by Agnex (Poland) and gellan gum by Biozoon (Germany). Reagent grade nitric acid ("Suprapur" from Merck) as well as lead nitrate, cadmium nitrate, calcium chloride, sodium hydroxide (Avantor, Gliwice, Poland) were used. Separate cadmium and lead standard solutions of 1 mg/mL were supplied by Merck. Water was purified using a Millipore Elix 10 system.

### Apparatus

Cadmium and lead were determined using ICP atomic emission spectrometer Varian 710-ES. The following parameters were used: RF power 1.0 kW, plasma flow 15 L/min, auxiliary flow 1.5 L/min, nebulizer pressure 200 kPa, pump rate 15 rpm, emission lines:  $\lambda_{\text{Cd}} = 508.582 \text{ nm}$ ,  $\lambda_{\text{Pb}} = 283.305 \text{ nm}$ .

The Raman spectra of hybrid biosorbents as well as raw substances were registered on Renishaw inVia Raman Microscope using 830 nm, max 500 mW laser source.

The SEM micrographs of lyophilized beads were made by Scanning Electron Microscope – Phenom Pro Desktop SEM. The biosorbents were lyophilized using Christ Alpha 1-2 LD plus apparatus.

### Preparation of pectin-based biosorbents

To check the effect of temperature, in which polysaccharide solution is prepared, on hybrid biosorbents

structure and properties, two various temperatures of solution preparation were applied. Additionally, the maximal possible amount of other polysaccharide added to pectin (started from ratio 1:1) was studied. Pectin (P) or xanthan gum (X) or carob gum (C) or gellan gum (G) solutions were prepared as follows: 6 g of raw substance and 94 g of water was shaken using Incu-Shaker at 22°C or 70°C for 2 h. The solutions of pectin and other polysaccharide (additive) were then mixed in proper proportions (started from 1:1) to obtain solution with appropriate P and additives (X, C or G) concentration and shaken for 4 h at 22°C or 70°C.

The beads of biosorbents were formed by slow drop-wise addition of a suitable solution with peristaltic pump into cold 1 M calcium chloride solution, in result the beads of ca. 4 mm diameter were received. Our previous studies<sup>[33]</sup> showed that for each 200 g of polysaccharide solution at least 1 L of cold 1 M  $\text{CaCl}_2$  solution should be used.

The pectin beads were left in the mother solution at about 4°C for at least 24 h and next they were filtered and washed from chloride ions. After drying them at 35°C for 24 h, the amber (dark brown in the case of carob gum addition) beads of xerogel (diameter ca. 1 mm) with moisture content ca. 10% (determined at 105°C) were obtained. The beads were then examined visually to be not flat and stuck together and manually for mechanical strength by circular rubbing of a few beads in the coupled palm with finger (they could be easily crushed, so moderate pressure should be applied). If the obtained biosorbent had improper properties, the pectin-to-additive ratio was changed till obtaining desirable biosorbent.

### Swelling index

The swelling index of the studied pectin-based biosorbents in the presence of cadmium and lead at various pH was determined during sorption studies. After adsorption procedure the beads were filtered, dried with paper towel and then weighed. The swelling index was calculated using the formula:

$$S = \frac{m_s}{m_d} \quad (1)$$

where  $S$  is swelling index;  $m_s$  is the mass of swollen sorbent (after 24 h in  $\text{Cd}^{2+}$  or  $\text{Pb}^{2+}$  solution of given pH value) (g); and  $m_d$  is the mass of dry sorbent (g).

### Adsorption procedure – the effect of pH value

Cadmium and lead ion adsorption was investigated as follows:

The 1.2 mmol/L  $\text{Cd}^{2+}$  or  $\text{Pb}^{2+}$  solution was prepared using stock solution of cadmium and lead nitrates. Next, the pH of the solutions was adjusted to 1, 2, 3, 4, 5 and 6 with nitric acid and sodium hydroxide solution. 20 mL of each solution was introduced into a plastic vessel with 0.02 g of proper biosorbent (dry form). The samples were then shaken using Incu-Shaker for 24 h at room temperature ( $22 \pm 1^\circ\text{C}$ ). The concentration of metal ions that remained in the solution after sorption was determined using ICP-AES spectrometer. The sorption capacity of studied hybrid biosorbents for cadmium and lead ions ( $q$ ) [mmol/g] was calculated using the formula:

$$q = \frac{(c_0 - c) \cdot V}{m} \quad (2)$$

where  $c_0$  is the initial concentration of metal ions ( $\text{Cd}^{2+}$  or  $\text{Pb}^{2+}$ ) in the solution (mmol/L);  $c$  is the final concentration of metal ions ( $\text{Cd}^{2+}$  or  $\text{Pb}^{2+}$ ) in the solution (mmol/L);  $V$  is the volume of the solution (L);  $m$  is the mass of the dry biosorbent (g). Each experiment was performed three times.

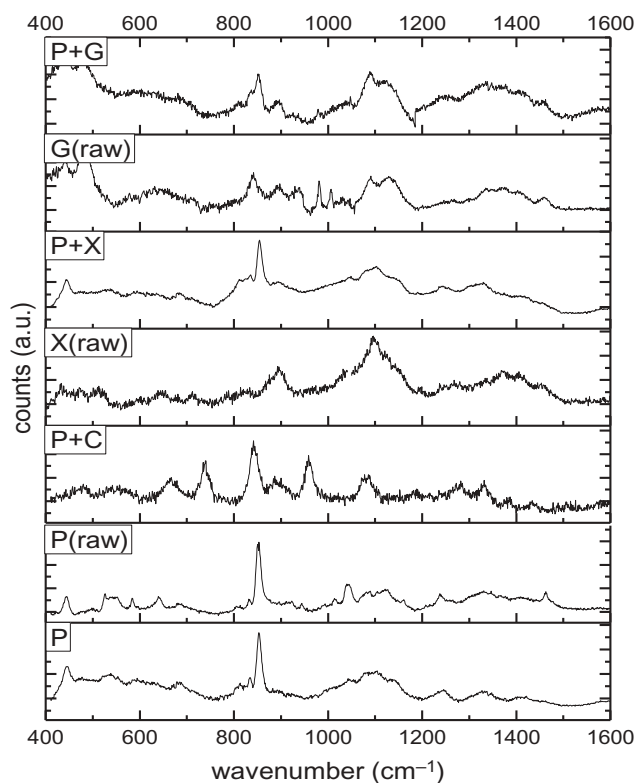
## Results and discussion

### Preparation and characterization of hybrid pectin-based biosorbents

Based on visual observation the maximal possible amount of modifying polysaccharide added to pectin (started from ratio 1:1) was established. Desirable biosorbents, of proper mechanical properties, were obtained if the compositions of mixed polysaccharide solutions were as follows: 3%P, 3.6%P + 1.2%X, 3%P + 3%C, 3%P + 3%G. Only xanthan gum cannot be introduced in maximal studied amount, so the final ratio of this polysaccharide to pectin in the hybrid beads was 1:3.

In order to confirm the presence of secondary additives in pectin-based beads, Raman spectra of the obtained materials (P + G, P + X and P + C), respective raw materials (G, X raw) and spectrum of sole pectin-based beads (P) or raw pectin (P(raw)) were registered – see Fig. 1. It can be seen that the characteristic bands present in raw substance are also present in the hybrid biosorbent. In the case of carob gum, the Raman spectrum could not be registered due to the effect of fluorescence. The P + C spectrum, which differs significantly from the raw P can be a proof that P + C contains both – pectin and carob gum.

Taking into account the complicated physicochemistry of polysaccharide solutions,<sup>[39]</sup> obtaining a homogenous blend of polysaccharides seems to be the crucial

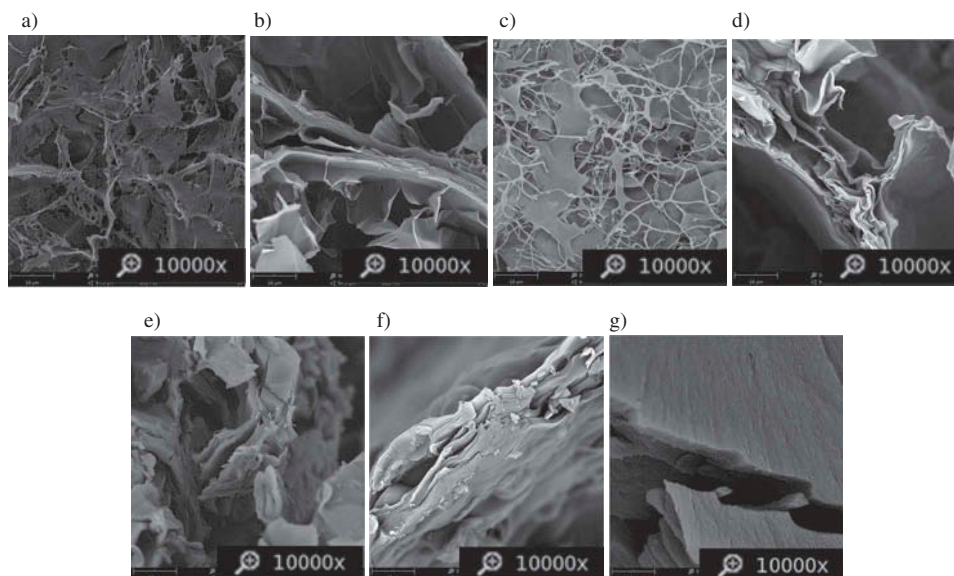


**Figure 1.** The Raman spectra of pectin-based biosorbents and respective raw materials.

step in preparation of pectin-based hybrid materials. Therefore, two various temperatures of solutions preparation were applied to check its influence on homogeneity of obtained blends. The solutions were prepared using shaker instead of mechanical stirrer to avoid mechanical degradation of polysaccharides.

In order to know the real structure of working biosorbents, beads were lyophilized in the swollen form and then analysed under scanning electron microscope. The SEM micrographs shown in Fig. 2 represents the influence of composition and preparation condition on the structure of received sorbent. Generally, all materials prepared at higher temperature ( $70^\circ\text{C}$ ) are more homogenous (Fig. 2a, c, e, and g) and, in the case of gellan and xanthan gum, more porous (Fig. 2a and c) than if they are prepared at room temperature (Fig. 2b, d, and f).

Great differences may also be observed between materials obtained at  $70^\circ\text{C}$  but containing various additives. The materials with gellan gum (Fig. 2a) or xanthan gum (Fig. 2c) are of network-like structure in opposite to beads with carob gum (Fig. 2e), which are definitely the most dense among the obtained mixed sorbents. Also, sole pectin beads differ significantly from other materials (Fig. 2g); their structure resemble hard and quite dense sponge. This is an evidence that



**Figure 2.** The SEM micrographs of hybrid pectin-based biosorbents in swollen form: (a and b) pectin–gellan gum; (c and d) pectin–xanthan gum; (e and f) pectin–carob gum; (g) sole pectin. During materials preparation, solutions of polysaccharides were shaken for 4 hours at  $22 \pm 1^\circ\text{C}$  (b, d, and f) or  $70 \pm 1^\circ\text{C}$  (a, c, e, and g).

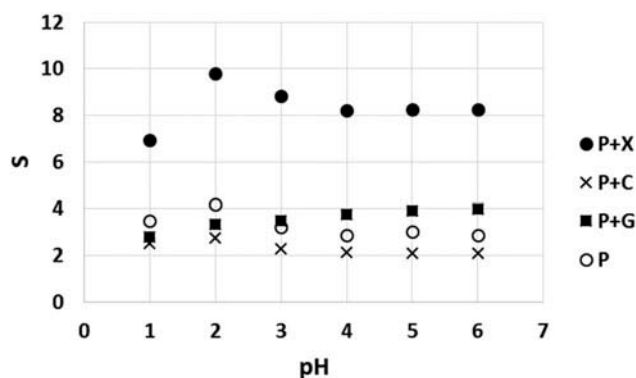
introduction of additives modify the structure of pectin-based biosorbents.

The sorbents prepared at lower temperature did not differ rather as significantly from each other; they consisted mainly of tightly packed laminar part – probably pectin and some paper-like structure – probably polysaccharide additive (Fig. 2b, d and f).

### Biosorbent swelling

The swelling index of the studied pectin-based biosorbents (prepared at  $70^\circ\text{C}$ ) in the presence of cadmium and lead at various pH was determined during sorption studies (Figs. 3 and 4).

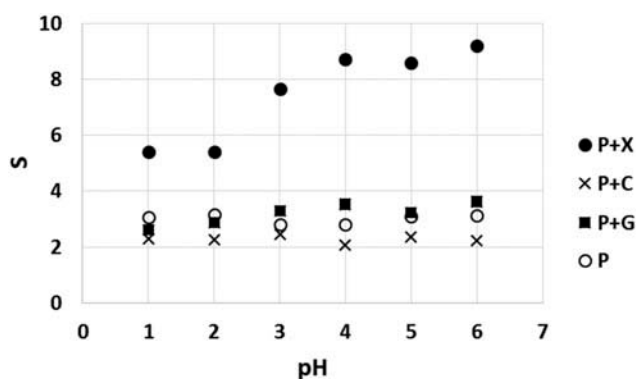
It can be observed that independently from the kind of metal ion studied, the swelling indexes of the three biosorbents (P + G, P + C, P), regardless of their great differences in structure (Fig. 2a, e, and g), are rather similar and equaled from 2 to 4 (Figs. 3 and 4). The explanation may be that the employed polysaccharides have similar branching factor as well as contain similar functional groups, which are responsible for gel-forming strength and hence the swelling properties. Significantly higher swelling index is achieved for pectin–xanthan gum beads. Moreover, its value differs for solutions with cadmium and lead, especially in lower pH region (Figs. 3 and 4). With lowering pH, at pH = 2 the swelling index of P + X sorbent in the presence of lead drops significantly while in the case of cadmium the presence of S increases with pH decrease from 3 to 2.



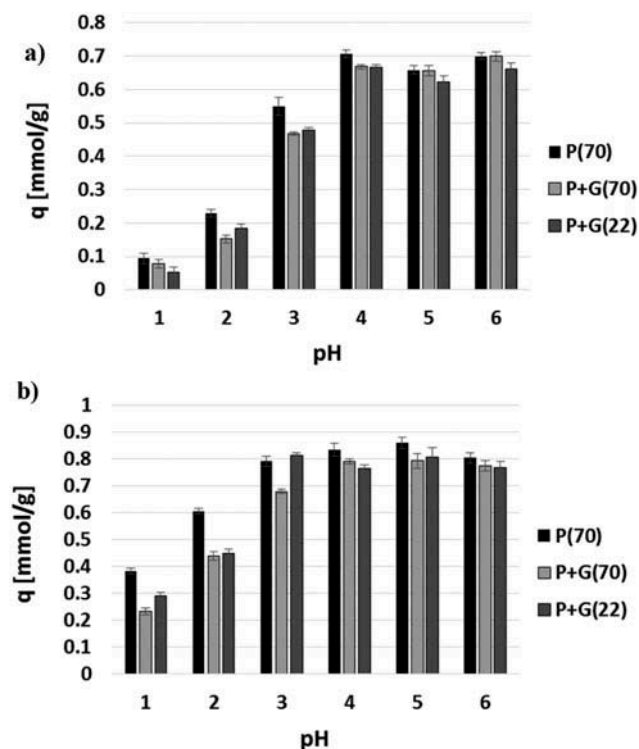
**Figure 3.** The swelling index (S) of hybrid pectin-based biosorbents in contact with cadmium solution of various pH (volume of solution: 20 mL, metal ion initial concentration: 1.2 mmol/L, mass of dry sorbent: 0.02 g, contact time: 24 h, temperature:  $(22 \pm 1^\circ\text{C})$  and  $n = 3$ ).

### The effect of pH value on adsorption of $\text{Cd}^{2+}$ and $\text{Pb}^{2+}$ on studied biosorbents – batch studies

The batch studies of cadmium and lead adsorption on pectin-based biosorbents at various pH have also been performed (Figs. 5–7). Generally, as reported previously, the affinity of lead ions to the studied sorbents is greater than cadmium ions. Sorption capacity (q) of lead is higher (up to 0.85 mmol/g at pH 4–6) in comparison to q for cadmium (up to 0.70 mmol/g at pH 4–6) and does not drop as strongly with pH decreasing – even in pH = 1 sorption capacity for Pb is quite high and equals about 0.4 mmol/g. The explanation of such behaviour may be based on Pearson acid–base theory (HSAB).

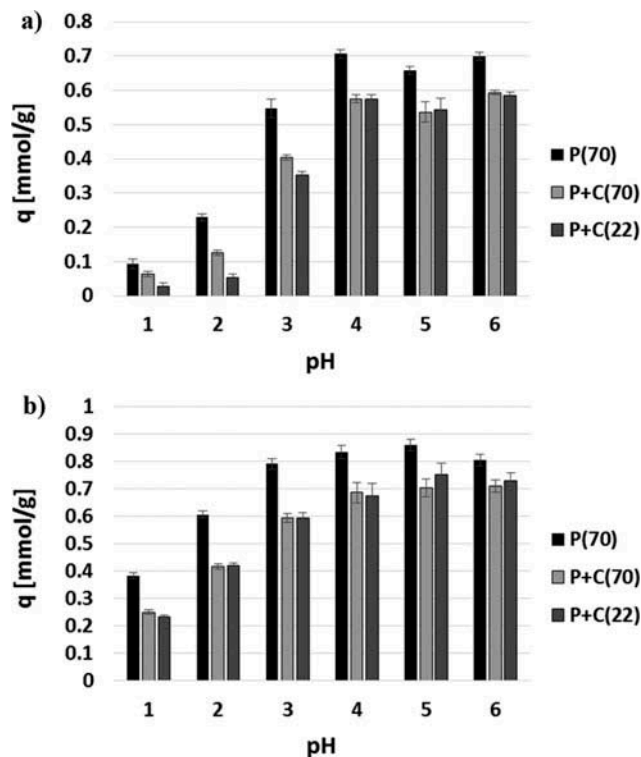


**Figure 4.** The swelling index ( $S$ ) of hybrid pectin-based biosorbents in contact with lead solution of various pH (volume of solution: 20 mL, metal ion initial concentration: 1.2 mmol/L, mass of dry sorbent: 0.02 g, contact time: 24 h, temperature:  $(22 \pm 1^\circ\text{C})$  and  $n = 3$ ).



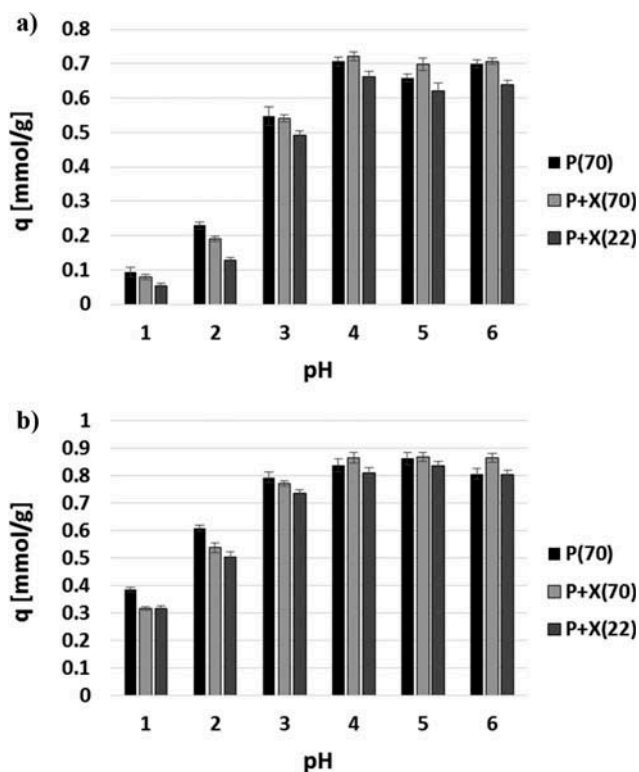
**Figure 5.** The comparison of (a) cadmium (b) lead sorption capacity at various pH values of sole pectin biosorbent ( $P(70)$ ) and hybrid pectin–gellan gum biosorbent prepared at  $22^\circ\text{C}$  and  $70^\circ\text{C}$  (volume of solution: 20 mL, metal ion initial concentration: 1.2 mmol/L, mass of dry sorbent: 0.02 g, contact time: 24 h, temperature:  $(22 \pm 1^\circ\text{C})$  and  $n = 3$ ).

Following this theory we can conclude that carboxyl and amide groups from polysaccharides acting as hard bases prefer binding the lead ions (borderline Pearson acids), over soft acids (cadmium ions).



**Figure 6.** The comparison of (a) cadmium (b) lead sorption capacity at various pH values of sole pectin biosorbent ( $P(70)$ ) and hybrid pectin–carob gum biosorbent prepared at  $22^\circ\text{C}$  and  $70^\circ\text{C}$  (volume of solution: 20 mL, metal ion initial concentration: 1.2 mmol/L, mass of dry sorbent: 0.02 g, contact time: 24 h, temperature:  $(22 \pm 1^\circ\text{C})$  and  $n = 3$ ).

Surprisingly, regardless of great differences in structure between the studied biosorbents, no significant differences may be noticed between sorption capacities of sorbents with various additives and prepared at various temperatures, nor sole pectin sorbent. Only in the case of sorbent with carob gum addition, the sorption capacity decreases by about 10–20%, similarly for cadmium and lead (Fig. 6). However, the carob gum cannot be considered an inert addition. Its ratio to pectin in hybrid sorbent was 1:1, so if it was an inert component the sorption capacity should decrease to half value of  $q$  for sole pectin beads. As mentioned above, there is no information in the literature about sorption properties of carob gum, so any synergism or opposite effect cannot be considered. However, a synergistic effect may be noticed in the case of xanthan gum addition (Fig. 7). According to literature, the  $q$  of xanthan gum sorbent for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions equals 41.66 mg/g (0.37 mmol/g) and 44.56 mg/g (0.21 mmol/g), respectively,<sup>[37]</sup> so it is significantly lower than sorption capacity of pectin biosorbent (0.70 and 0.85 mmol/g for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions, respectively). The



**Figure 7.** The comparison of (a) cadmium (b) lead sorption capacity at various pH value of sole pectin biosorbent (P(70)) and hybrid pectin-xanthan gum biosorbent prepared at 22°C and 70°C (volume of solution: 20 mL, metal ion initial concentration: 1.2 mmol/L, mass of dry sorbent: 0.02 g, contact time: 24 h, temperature: (22 ± 1°C) and  $n = 3$ ).

obtained hybrid P + X biosorbents have even slightly higher  $q$  than sole pectin beads, which is a proof of synergistic effect of this polysaccharide mixture.

In the case of gellan gum, it has been reported in literature that the sorption capacities for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ <sup>[35]</sup> are very close to those obtained for the studied P biosorbent. Therefore, it is not surprising that the same results for P + G biosorbent are obtained (Fig. 5).

The sorption capacities of our biosorbents are generally higher than reported in the literature for various biosorbents, e.g. sawdust ( $\text{Cd}^{2+}$ : 0.27 mmol/g)<sup>[3]</sup> sawdust of *Pinus sylvestris* ( $\text{Cd}^{2+}$ : 0.17 mmol/g,  $\text{Pb}^{2+}$ : 0.11 mmol/g)<sup>[4]</sup> pine bark ( $\text{Pb}^{2+}$ : 0.38 mmol/g)<sup>[5]</sup> custard apple fruit shell ( $\text{Cd}^{2+}$ : 0.63 mmol/g,  $\text{Pb}^{2+}$ : 0.44 mmol/g)<sup>[6]</sup> hazelnut shell ( $\text{Pb}^{2+}$ : 0.14 mmol/g)<sup>[7]</sup> mistletoe ( $\text{Cd}^{2+}$ : 0.45 mmol/g,  $\text{Pb}^{2+}$ : 0.33 mmol/g)<sup>[13]</sup> macrofungus (*Amanita rubescens*) ( $\text{Cd}^{2+}$ : 0.24 mmol/g,  $\text{Pb}^{2+}$ : 0.19 mmol/g)<sup>[27]</sup> Nordmann fir leaves ( $\text{Cd}^{2+}$ : 0.07 mmol/g,  $\text{Pb}^{2+}$ : 0.10 mmol/g)<sup>[14]</sup> lichen (*Cladonia furcata*) ( $\text{Pb}^{2+}$ : 0.06 mmol/g)<sup>[18]</sup> lichen (*Parmelina tiliaceae*) ( $\text{Pb}^{2+}$ : 0.37 mmol/g)<sup>[19]</sup> or red algae ( $\text{Cd}^{2+}$ : 0.48 mmol/g,  $\text{Pb}^{2+}$ : 0.51 mmol/g)<sup>[17]</sup> The higher sorption capacities were determined in the case of some microorganism biosorbents: *Staphylococcus xylosus* ( $\text{Cd}^{2+}$ :

2.22 mmol/g), *Pseudomonas sp.* ( $\text{Cd}^{2+}$ : 2.47 mmol/g)<sup>[26]</sup> or pecan nutshell ( $\text{Pb}^{2+}$ : 1.02 mmol/g)<sup>[8]</sup> This shows that our pectin-based biosorbents are interesting choices for heavy metal removal.

## Conclusions

In our studies hybrid pectin-based biosorbents with polysaccharide additives (gellan, xanthan and carob gum) were obtained. The ratio of pectin to additive was 1:1; only in the case of xanthan gum the ratio was 1:3. The presence of secondary additives in pectin-based beads was confirmed by Raman spectra of raw and obtained materials. The SEM micrographs show the influence of composition and preparation temperature on the structure of examined materials. Generally, all materials prepared at 70°C are more homogenous and, in the case of gellan and xanthan gum, more porous, than those prepared at 22°C. At higher temperature there are also greater differences between the structures of beads with various additives. These differences are not strongly reflected in sorption capacities of the studied biosorbents. Generally the sorption capacities of sorbents with various additives as well as without them are rather the same, only in the case of sorbent with carob gum the  $q$  decreases by about 10–20%. The maximum sorption capacity was determined in pH 4–6 and equals 0.85 and 0.70 mmol/g for lead and cadmium, respectively. This shows that our biosorbents are good alternatives to others reported in literature.

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