Research Article

Pectin-based Hydrogels Produced from Banana and Mango Peels as a Potential Approach to Removing Heavy Metal Ions from Contaminated Water

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Abstract
The release of harmful compounds from manufacturing processes into the environment causes a variety of environmental problems. In the low concentration range, conventional removal methods are frequently either too costly or insufficiently successful. On the other hand, hydrogel-based biosorption demonstrated to be economical and effective. Biohydrogels suitable to adsorb heavy metal contaminants from water were prepared using pectin obtained from a mixture of banana and mango peels and combined with carboxymethyl cellulose using calcium chloride as a crosslinker. The hydrogel's internal structure and surface morphology as well as their swelling behavior, swelling-shrinking cycles, and water adsorption capacity under different external pressures were evaluated. The adsorption capacity and the influence of pH and temperature were assessed using Pb(II), Cu(II), Cd(II), and Ni(II). The reusability was investigated by adsorption-desorption cycles. The findings demonstrated a porous structure, more than 80% swelling at pH higher than 5 and within 30 min in contact with the medium, and the capacity to retain water at pressures of up to 400 kPa. With a reusability of five adsorption-desorption cycles, and the ability to adsorb more than 70 mg of each heavy metal ion per gram of dried hydrogel in the resulting order; Cu(II)>Pb(II)>Cd(II)>Ni(II).

Keywords: Carboxymethyl cellulose, Heavy metal ions, Hydrogels, Pectin extraction, Water treatment

1 Introduction

The availability of clean water is one of the biggest ecological issues brought on by fast industrialization and growing urbanization. This is mainly due to the release of harmful organic and inorganic contaminants into the environment, including Cu, Pb, Ni, Cd, Zn, Hg, As, Ag, and Cr, which are extremely dangerous and carcinogenic even at low concentrations [1], [2]. There are several methods available for removing these contaminants, including chemical precipitation, evaporation, ion exchange, distillation, electrodialysis, and membrane separation [3]–[5]. The use of inexpensive adsorbents in adsorption processes is receiving growing attention since it is straightforward, efficient, and economical, all aspects that make them an appropriate option for removing heavy metal ions from contaminated wastewater [6]–[9]. Hydrogels are among various highly adsorbent materials that have drawn much interest because of their exceptional qualities, high porosity, and swelling behavior. Hydrogel-based adsorbents have been used for many years in several industries, but only in the past ten years have they been employed for eliminating pollutants from wastewater [10]. Hydrogels thanks to their cross-linked network, and the existence of chemical groups, such as carboxyl, amino, and hydroxyl, can absorb and hold large volumes of water [11], [12]. Most of the hydrogels available on the market are made of synthetic polymers, such as polyacrylates; however, in the last decade, interest in utilizing natural polymers has increased because of their environmental friendliness. Using and valuing biomass, such as food or agricultural waste, to produce biopolymers is of interest in addition to the biological nature of the polymers. Hydrogels based on polysaccharides and polysaccharide derivatives offer particular application potential due to their particular features, which include biodegradability, easy availability, and widely distributed sources [13]. Hydrogels having interesting features have been made from polysaccharides and or a combination of polysaccharides such as cellulose, pectin, chitosan, alginate, and starch [14]–[16]. Therefore, many researchers have looked into the effective remoting of heavy metals using polysaccharides-based hydrogels.

Pectin is an anionic polysaccharide that is present in numerous plants, particularly fruit peels. Its structure is based on residues of polygalacturonic acid joined by one to four glycoside linkages. With a pK_a of 3.5, the carboxylic groups are in ionic form at pH values greater than 3.5 with a tendency to interact with cations, especially divalent cations like Ca^{+2}, to form crosslinking point with a structure known as an "egg-box" [17]–[19]. This structure enables the retention of various compounds within the gel matrix. Furthermore, pectin's negative charge allows it to interact with positively charged species, such as heavy metal ions, as has been widely shown [20]–[24]. Generally, to enhance the mechanical properties, pectin is mixed with other natural or synthetic polymers or undergoes chemical modification [25]. Herein, we combined pectin obtained from mango and banana peels, following the protocol reported in our previous work [26], with commercial carboxymethyl cellulose (CMC).

CMC is an anionic chemical derivative of cellulose that finds extensive use in different industrial spheres, including biomedical, healthcare, and the environment [27]. Its features, such as pH sensitivity, low toxicity, hydrophilic nature, low cost, and gelation properties, make it a suitable material for hydrogel preparation [28]. The hydroxyl and carboxylic groups displaced along the chain groups make the hydrogels highly swollen with CMC.

In the present work, pectin was obtained by extraction in acidic media from two sources; mango (Kesar) and banana (Cavendish) peels. The reason for the choice is that in tropical and subtropical areas of the world, bananas are a significant fruit crop. The peels of bananas make up 40% of the fresh fruit's weight, and bananas are generally discharged as solid waste at a high expense.

A significant amount of banana peel is lost or used as inexpensive animal feed due to the expansion of the banana-processing industry and the rise in the manufacturing of fruit goods. However, it is not environmentally friendly or economically viable. As a result, the banana processing sector has been looking for ways to use banana peels as a pectin supply [29], [30]. Mangoes, like bananas, are one of the most significant tropical fruits. They are utilized extensively as dried fruits, fruit bars, flakes, concentrates, jams, concentrates, juice, and nectar. [31]. Byproducts from the mango industry can account for as much as 60% of the fruit weight, which poses a significant disposal issue [32]. A large amount of research that has been published in the literature claims that the pectin content in mango peels can reach 23%, making mango peels excellent sources of fruit [33]. Like bananas, the type, geographic origin,

harvesting method and extraction technique of bananas can affect their content.

In accordance with our previous work [26], pectin was extracted from the selected biomass via a 5 L batch reactor equipped with an ultrasound horn. The adoption of ultrasound assisted extraction permits to perform the extraction at 50 °C, which is lower compared to the traditional extraction temperature, (which can reach 80 °C). Also, it reduces the extraction time. The molecular weight and the methoxy content of the extracted pectin have been measured. To produce the hydrogels, pectin has been mixed with carboxy methyl cellulose at a weight ratio of 3:1 in favor of pectin and using calcium chloride as a crosslinking agent. The prepared hydrogels were characterized in terms of swelling and swelling–shrinking cycles, the effect of pressure on water uptake, surface morphology, and inner structure. To study the ability of the hydrogel to remove heavy metal ions from contaminated waters, Pb(II), Cu(II), Cd(II), and Ni(II) ions were considered. A set of experiments was carried out to evaluate the influence of pH, ion concentration, contact time and temperature on the hydrogel adsorption performance. Moreover, the possibility of reusing the hydrogels was evaluated by adsorption/desorption cycles using Na_2EDTA to desorb the heavy metal ions. The results indicate pH-dependent swelling of the hydrogels, with equilibrium reached within 20 min. In addition, the swelling properties of the hydrogels tended to be preserved for up to 5 swelling–shrinking cycles. Adsorption studies indicate an increase in adsorption with the increase in the ions concentration and contact time. The maximum adsorption was reached mostly within the first hour of contact. The highest adsorption was at pH values 4.0–7.0. The presence of interfering ions, Na^+, K^+, Mg^{+2}, and SO_4^{-2} slightly decreases the adsorption capacity due to a possible competitive effect. The present study and the preliminary results, show the possibility of valorizing mango and banana peels by extracting pectin and using it for developing innovative adsorbent materials with potential for application in water purification. Compared to other related work, pectin has not been chemically modified and no post extraction or additional treatments were performed to enhance the adsorption properties.

2 Materials and Methods

2.1 *Materials*

Pectin was obtained from mango (Kesar) and banana (Cavendish) peels. Calcium chloride, sodium hydroxide, sodium carboxymethyl cellulose (average Mw 250.000, substitution degree 0.9), Na_2EDTA, lead chloride, copper chloride, cadmium chloride, and nickel chloride were purchased from Merck. All chemicals were reagent grade and used as received.

2.2 *Methods*

2.2.1 Pectin extraction

Pectin was extracted from a mixture of banana and mango peels following a procedure reported in our previous work with minor changes [26]. A total of 0.5 kg of banana peels and 0.5 kg of mango peels were collected from house waste, separated from other residues, washed with hot tap water, cut into 3x3 cm thick slices, and then dried at 50 °C for 48 h. The pectin was extracted via a 5 L batch reactor equipped with an ultrasonic horn. 250 g of dried biomass, 125 g of banana, and 125 g of mango peels were loaded in the reactor, and then 2 L of HCl 0.1 M aqueous solution was added and mechanically stirred for 1 h at 50 °C. Compared with other reported extraction methods [33]–[35], a lower temperature has been adopted because of the use of ultrasonication, which enhances the extraction, allowing a reduction in the temperature [36]. Ultrasounds in pulse mode were applied 2 min ON/1 min OFF at 20 kHz. The resulting slurry was filtered to separate the two fractions. The liquid fraction was centrifuged for 10 minutes at 8000 rpm, and the supernatant was poured into a 5 L glass beaker, followed by the addition of methanol until precipitation occurred [36]. Following five minutes of centrifugation at 8000 rpm, the precipitate was recovered, rinsed with methanol, and dried in an oven at 50 °C until a stable weight was achieved. The pectin yield was determined as follows in Equation (1):

$$Yield(\%) = \frac{M_{PEC}}{M} x100 \quad (1)$$

where M_{PEC} is the mass (g) of pectin and M is the mass (g) of dried banana and mango peels.

2.2.2 Pectin characterization

The equivalent weight (W_{eq}), the -OCH_3 content and the chemical structure of the extracted pectin were investigated. To calculate the W_{eq}, 0.5 g of pectin powder was soaked in 5 mL of ethanol and 100 mL of distilled water. Afterward, 0.3 mL of phenol red indicator and 1 g of NaCl were added, and the mixture was left under stirring until complete dissolution of pectin. A 0.1 N NaOH solution was slowly added until the solution turned rose color (pH 7.5). The equation determines the W_{eq} (Equation (2)):

$$W_{eq} = \frac{W_S}{V_{NaOH} \times N_{NaOH}} \times 1000 \quad (2)$$

where W_{eq} (g/mol) is the equivalent weight, W_s (g) is the weight of the sample, and V_{NaOH} and N_{NaOH} are the volume (mL) and normality (N) of the alkali, respectively.

To determine the methoxyl (-OCH_3) content, the neutralized solution obtained in the previous step, was mixed with 25 mL of 0.25 N NaOH, stirred for 30 min and then titrated to the same endpoint by adding 25 mL of 0.25 N HCl solution [37]. The -OCH_3 content was calculated as follows in Equation (3):

$$Methoxyl(\%) = \frac{V_{NaOH} x N_{NaOH} x 31}{W_S x 1000} x100 \quad (3)$$

where 31 represents the molar mass of the -OCH_3.

The chemical structure of the pectin and the presence of the main chemical groups were studied by attenuated total reflectance- Fourier transform infrared spectroscopy (FTIR–ATR, Thermo Fisher Scientific). The spectra were recorded at 200 scans with a resolution of 4 cm^{-1} in the range 4000–400 cm^{-1}.

2.2.3 Pectin-CMC hydrogel preparation

CMC and pectin were combined to produce the hydrogels. In short, pectin and CMC were dissolved in a 3:1 weight ratio in 0.1 M NaOH water solution at 50 °C while being stirred. Following the formation of a homogenous mixture, 10% w/v $CaCl_2$ solution was added, and the mixture was left for 24 h at room temperature to let the hydrogel to form. Afterward, the hydrogels were rinsed with distilled water and dried at 50 °C until they reached a stable weight.

2.2.4 Swelling and swelling/shrinking cycle measurements

The swelling represents an important parameter, which directly influences the adsorption capacity of the hydrogels. Herein the influence of the pH and temperature on the swelling was studied as follows; 1 g of dried hydrogel in cylindrical shape and dimension 7 cm × 2 cm was soaked in 100 mL of media (pH 2, 5, 7, and 8) at room temperature (25–28 °C) or in cooled environment (4 °C). At defined time intervals, the sample was removed, wiped with filter paper, and the weight measured. The swelling was calculated via the following Equation (4):

$$S(\%) = \frac{W_s - W_0}{W_0} x100 \quad (4)$$

where W_S and W_0 represent the hydrated and dried weight (g).

Swelling-shrinking cycles were carried out to investigate the possibility of reusing the hydrogels. One gram of dried hydrogel was soaked in the media to fully hydrate. Afterward, the hydrogels were withdrawn, wiped with a filter paper, the weight recorded and then dried at 60 °C. The swelling was calculated in each cycle via equation (4), and a total of 5 cycles were performed.

2.2.5 Hydrogel's surface morphology and inner structure

Using a scanning electron microscope (Nova NanoSEM 450 (FEI)), the dried hydrogels' internal structure and surface morphology were studied.

2.2.6 Effect of pressure on hydrogel water uptake

The assessment of hydrogel water intake under varying pressures offers important insights into the ability of hydrogels to hold fluid in a setting where pressure variations influence water transport. [38]. A cylindrical shape hydrogel (size 4 × 2 cm) sample (was placed within a vessel with a membrane wall, and pressures up to 400 kP_a were applied to accomplish the measurements. The amount of distilled water that diffused out of the vessel through the membrane due to the increase in pressure was recorded and used to calculate the water retention by the hydrogel as a function of pressure [38].

2.2.7 Heavy metal adsorption evaluation

The heavy metals adsorption was investigated under different pH, time, concentration, and the presence of interfering ions (Table 1) as reported in sections 2.3.1 and 2.3.2. For the desorption and regeneration studies, the wet hydrogels were first incubated with 2 mol/L Na_2EDTA for two hours and then cleaned with distilled water to remove any remaining unabsorbed ions [39].

The procedure was repeated thrice. The adsorption–desorption cycles were conducted five times using the regenerated hydrogels for the next adsorption measurement. The cycles were run using 250 mg of dry hydrogels in an aqueous solution at pH 5 containing 50 mg/L of heavy metal ions.

Table 1: Operative parameters to evaluate the adsorption of different heavy metal ions by pectin/CMC hydrogels. In bold are reported the intervals of the parameter tested (variables), while in italics are the other operational conditions (constant).

Metal	pH ion	Time (min)	Concentration (mg/L)
Pb(II)	**1–7** Time:60 min Mass Hydrogel: 250 mg Conc: 50 mg/L	**10–600** pH 5.0 Mass Hydrogel: 250 mg Conc: 50 mg/L	**5–150** pH 5.0 Mass Hydrogel: 250 mg Time: 60 min
Cu(II)	**1–7** Time:60 min Mass Hydrogel: 250 mg Conc: 50 mg/L	**10–600** pH 5.0 Mass Hydrogel: 250 mg Conc: 50 mg/L	**5–150** pH 5.0 Mass Hydrogel: 250 mg Time: 60 min
Cd(II)	**1–7** Time:60 min Mass Hydrogel: 250 mg Conc: 50 mg/L	**10–600** pH 5.0 Mass Hydrogel: 250 mg Conc: 50 mg/L	**5–150** pH 5.0 Mass Hydrogel: 250 mg Time: 60 min
Ni(II)	**1–7** Time: 60 min Mass Hydrogel: 250 mg Conc: 50 mg/L	**10–600** pH 5.0 Mass Hydrogel: 250 mg Conc: 50 mg/L	**5–150** pH 5.0 Mass Hydrogel: 250 mg Time: 60 min

2.2.8 Effects of pH, time, and concentration

The influence of pH on metal ion absorption was evaluated in the pH range of 1.0–7.0. 100 mg of dried hydrogels of cylindrical shape (4 cm × 2 cm, cylindrical shape) were poured into 20 mL of a 50 mg/L solution of the heavy metal ions (separately). The mixture was left under mild stirring, then the hydrogels were taken out and the ion concentration in the solutions was obtained by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700x, Agilent Technologies, USA). The following equations were used to determine and evaluate the extraction (E%), which indicates the suitability of the hydrogel in removing heavy metal contaminants (Equation (5)).

$$(\%) = \frac{C_I - C_F}{C_F} \times 100 \quad (5)$$

where C_I is the initial concentration of the ions (mg/L), and C_F represents the concentration after adsorption (mg/L).

The effects of time (10–600 min) and ion concentration (5–150 mg/L) on adsorption were evaluated following the same procedure described above.

2.2.9 Interfering species Effects of pH, time, and concentration

Different ions can hamper the adsorption of metal ions [40], [41]. Here, the influence of magnesium sulfate, sodium, and potassium chloride was evaluated. A solution containing heavy metals (50 mg/L), separately, and 100 mg of hydrogel (4 cm × 2 cm, cylindrical shape) was supplemented with 5 mg of each interfering species. The mixture was left for 60 minutes under stirring in a media (pH 5) at room temperature. Equation (4) was used to determine the amount of ions that were removed.

3 Result and Discussions

3.1 *Pectin extraction yield and characterization*

The most commonly used approach for extracting pectin is acidified hot water (pH 1.5–3.0 at 60–100 °C) [42], [43]. However, alternative approaches, such as enzyme-assisted extraction [44], [45], ultrahigh-pressure extraction [46], microwave-assisted extraction [47], subcritical fluid extraction [48], moderate electric field extraction [49], ultrasound pulses [50], ultrasonication [26], [51] or a combination of these techniques, such as ultrasound-microwaves [52], have been reported to maximize the extraction yield. The molecular weight and degree of methylation vary by the kind and provenance of the biomass and according to the pH, temperature and time of extraction [53].

In the present case, as a source of pectin, peels from mango fruit and unripe banana, purchased from a local supermarket, were used. As reported in previous studies, the content of pectin in such biomasses is expected to reach 20% in mango, depending on the type and maturation state, and up to 21% in unripe banana peels [54], [55]. The pectin yield obtained comprises 13–17% of the initial biomass. Herein, the final yield of pectin refers to the mixture of mango and banana peels, and the contribution of a single biomass was not calculated. The extraction yield is comparable to the average values reported in previous work using similar biomasses separately or in a mixture [56]–[58]. However, as mentioned above, the geographical area, harvesting period, and extraction conditions play important roles in the final yield of pectin. The obtained pectin resulted in a molecular equivalent weight of 356.45 ± 5.52 g/mol and a methoxyl (MeO) content of 11.41 ± 0.35. When divalent cations occur, typically calcium, gelation is made possible due to the low MeO concentration [59]. In the gelation process, the creation of intermolecular conjunction zones between smooth sections of different chains takes place with the creation of the so-called "egg box" structure. The ability to create gels rises as the degree of methylation decreases. Conversely, in the high-MeO pectin, the acetyl groups prevent gel formation with calcium ions while giving pectin emulsions exceptional stabilizing properties [60]. As the methoxy concentration and equivalent weight of pectin from various sources differ, the results are related to the pectin in the mixture. At this stage of the study, it was not essential to define the amount of pectin coming from each biomass separately.

In the Figure 1, the FTIR-ATR spectra of the extracted lignin are reported. As can be seen, the typical peaks related to pectin are observable. The O-H stretching is observable at 3300 cm^{-1} while the peak around 2900 cm^{-1} refers to the C-H stretch. The peak in the range between 1600–1800 cm^{-1} is ascribed to the C=O stretching. The large band in the range 1100–1300 cm^{-1} is characteristic of polysaccharides and the C-O stretch of ester and carboxylic groups [41].

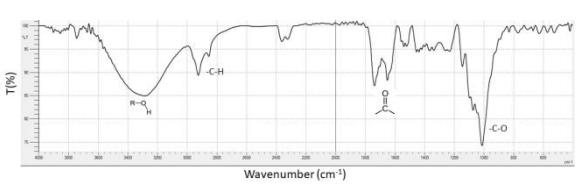


Figure 1: FTIR-ATR spectra of the extracted pectin.

3.2 *Swelling and water retention evaluation*

The swelling is an increase in the weight of a hydrogel caused by water absorption and is fundamental in the metal ions adsorption process [61]. The trend in Figure 2(A) shows that the maximum swelling occurred within 30 min at room temperature, with the rate affected by the pH of the solution. At pH 5.0 and higher at room temperature, all of the carboxylic groups that are displaced along the pectin structure (pK_a 3.5) are deprotonated, which results in repulsion and, ultimately, the expansion of the polymer chains. This causes the greatest degree of swelling [62]. It is known that the temperature can affect the swelling behavior. For such reason, the swelling behavior was studied also in cooled conditions (4 °C). The trend in Figure 2(B) shows how the swelling is reduced, from 10% to 40%, when the temperature dropped from 25–28 °C to 4 °C, with particularly emphasis on pH < 5. This is mostly due to the reduction in the chain's movement, which reduces the uptake and displacement of the water molecules within the hydrogel matrix [63], [64]. As the swelling directly affects the adsorption capacity, it is expected that by decreasing the temperature, also the heavy metals adsorption would be reduced.

To determine the durability and reusability of the hydrogels, swelling–shrinking cycles were also carried out at different pH values. According to the graph in Figure 2(B), there were no noticeable variations in swelling during the first two cycles, but from the third cycle to the fifth cycle, there was a decrease, particularly at pH 8.0. With the reduction in swelling, the performance of the hydrogels decreases, which affects their capacity to absorb heavy metals as well as their reusability.

It has been demonstrated that external pressure influences swelling, especially in some applications where hydrogels are buried in soil [65]. Here, swelling was tested at pressures of up to 400 kP_a to assess the swelling under different pressure conditions [38]. A water retention curve, with the water retention (kg/kg) expressed as a function of the external pressure, is shown in Figure 2(C). The pattern demonstrates the hydrogels' ability to retain water at pressures up to 400 kP_a. This pattern is similar to that observed in an earlier investigation that examined pectin-sodium acrylate hydrogels [39]. These outcomes validate the potential to assess the application of the prepared pectin-based hydrogels for soil conditioning in addition to the adsorption of contaminants from wastewater and other polluted waters.

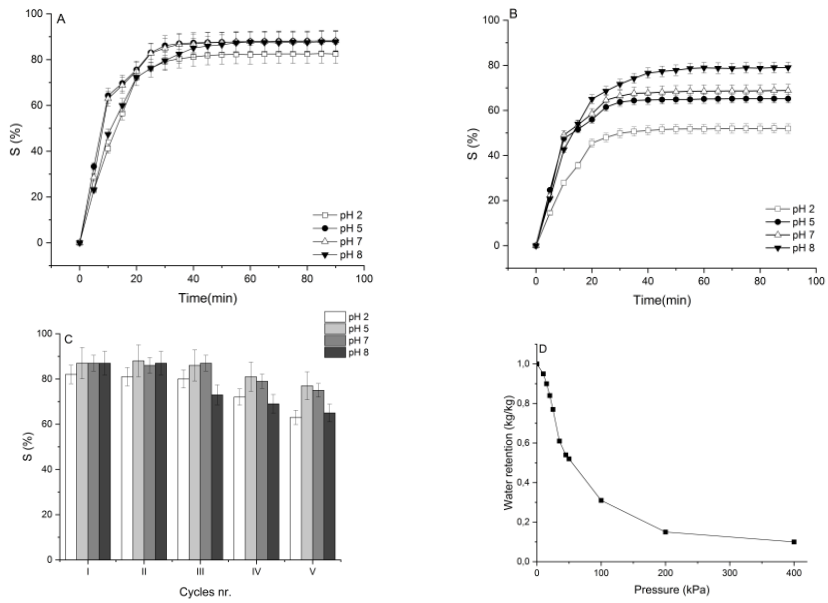


Figure 2: Influence of pH on hydrogel swelling at room temperature (A) and at 4 °C. (B) The number of swelling–shrinking cycles at room temperature. (C) Water retention versus external pressure. The experiments were repeated thrice (n=3).

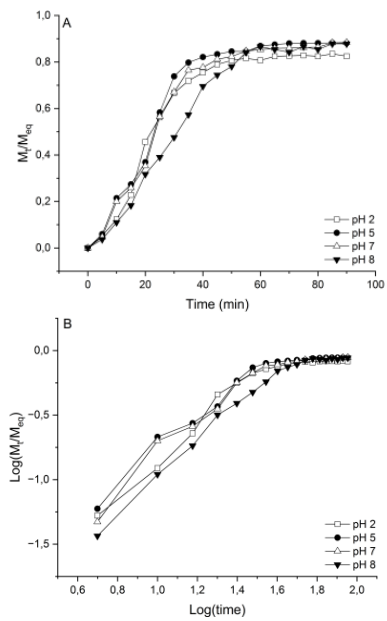


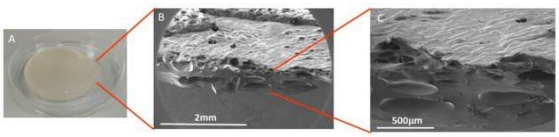
Figure 3: **(**A) Diffusion water rates at different pH values and (B) logarithmic curves.

By plotting Mt/Meq and its logarithm (logMt/Meq) against time (t) and the logarithm of time (log(t)), respectively, the hydrogel swelling profile was studied (Figure 3(A) and (B). A cylinder-shaped hydrogel (4 cm × 2 cm dried) was chosen to assess the possible water transport mechanism since the hydrogel geometry affects water diffusion into the matrix. According to Ganji *et al*., [66], the water diffusion process is Fickian or Case I for *n* values equal to 0.45, and anomalous transport, which results from Fickian diffusion and controlled relaxation, for values between 0.45 and 0.89. For *n* equal or higher than 0.89 a zero-order or Case II model, in which the diffusion is controlled by the relaxation of the polymer chains, and a super Case I model, in which the water diffusion process is achieved by the macromolecular relaxation of the polymer chains represent the driving force. Because of the hydrogel's cylindrical shape, the n values in this instance ranged from 0.5 to 0.9 subject to pH, suggesting non-Fickian diffusion with a propensity for macromolecular relaxation. Ionized COO-groups, whose content rises with pH, may be linked to these results [67], [68]. Electrostatic repulsion among the polymer chains was the cause of the hydrogel network's expansion. It pertains only to pH values that are more than or equal to 5.0.

3.3 *Morphological investigation via SEM*

The SEM micrographs in Figures 4(B) and (C), show a non-uniform porous structure with different-sized pores. Upon immersion, water molecules diffuse and displace within the inner structure, hydrating the hydrophilic groups—also known as, the primary

bound water. When the hydrophobic groups interact with water molecules to form hydrophobically bound water molecules, a secondary bond is formed. In this case, some of the key factors are the crosslinker type and concentration as well as the porosity. Based on numerous studies, a porous structure is essential for promoting the absorption of water into the hydrogel structure and thus improving swelling [69]–[71]. Figure 4(B) shows that a small surface of the hydrogels with a few randomly displaced pores probably caused by the drying process in the oven.



(A) (B) (C)

Figure 4: **(**A) Photo of hydrated hydrogel (7 cm × 3 cm) and (B), (C) the corresponding scanning electron micrographs. (B) magnification 120x, 5.00Kv, scale bar 2 mm and (C) magnification 150x, 5.00Kv, scale bar 500 µm.

3.4 *Influence of pH, time, concentration and temperature on the adsorption capacity*

One of the most serious environmental issues is the removal of heavy metal ions from wastewater or contaminated natural waters. The effectiveness of removing a contaminant depends on the kind of water or wastewater, the contaminants, and the method of removal. Adsorption is one of the most effective techniques because of its high efficacy, affordability, and minimal impact on the environment. Three primary steps constitute the pollutant sorption process: first, pollutants migrate from the bulk solution to the surface of the adsorbent material, in this case, the hydrogel, and then they are adsorbed. The contaminants are displaced within the adsorbent structure during the last stage. pH, temperature, contact time, and the concentrations of the pollutants and sorbent may influence the outcome, as has been demonstrated [72], [73].

The characteristics of the heavy metal ions, in particular their ionic radius, atomic weight, coordination geometry, and electronegativity, have a major impact on the interaction with the adsorbent material. It has been reported that ions with smaller atomic weights and radii are better adsorbed, especially in multiple adsorption settings [74]. For each heavy metal contaminant, the influence of pH, contact time, and ion concentration on the adsorption capacity were assessed separately. Figure 5(A)–(C) show the extraction percentages.

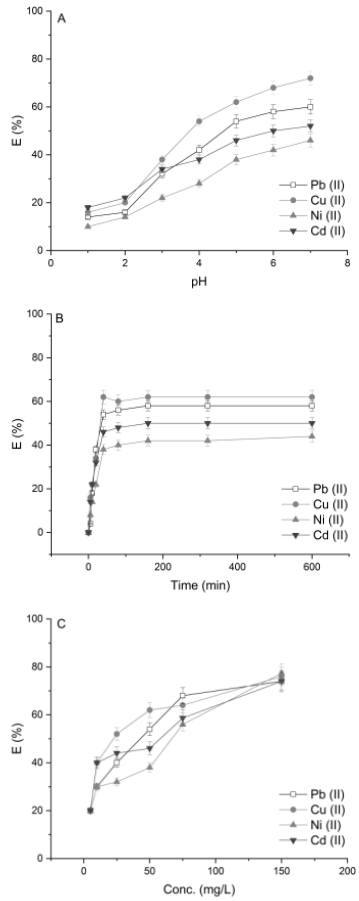


Figure 5: Effects of (A) pH, (B) time and (C) initial ion concentration on ion removal by the hydrogels. The experiments were carried out at room temperature three times (n=3).

As has been extensively documented and explained, the environmental pH significantly affects the absorption process as it influences the surface chemistry of the adsorbent material and its interaction with the metal ions [75]–[79]. The maximum adsorption occurs at a specific pH for each metal ion. The ideal pH range for cationic metals is the acidic region, whereas the ideal pH range for anionic metals is the basic zone. The patterns in Figure 4(A) indicate how increasing the pH improves ion extraction, with Cu(II) exhibiting the most effective results. The protonated form of the functional groups (-COOH) is responsible for the reduced extraction of the pectin

carboxylic groups when the pH < pK_a (pK_a 3.5); in this instance, the metal ions remain restricted inside the hydrogel's three-dimensional structure. Conversely, by increasing the pH, the carboxylic groups are deprotonated, and more adsorption sites are available with a subsequent increase in the adsorption efficiency E (%) [75]. Among the considered heavy metal ions, in the individual adsorption, Cu(II) showed the highest affinity while Ni(II) was the lowest, regardless of the pH of the solution.

Figure 5(B), which shows the contribution of the contact time to E (%), shows a similar pattern. The time of contact, also adsorption efficiency as widely described [76]. To evaluate it 50 mg/L heavy metal ions and 100 mg dry hydrogel were used, and the experiments were carried out at pH 5, at which the best adsorption was observed. As expected, an increase in E (%) was observed for longer contact time, even if the majority of the adsorption occurred in the first 60 min when equilibrium was achieved by the saturation of all the adsorption sites. This trend is in agreement with other reported studies, in which fruit peels were used to prepare adsorbent materials, and reported how in the first 30 min had rapid adsorption after which the process slowed down significantly [77].

The results of the individual adsorption revealed the sequence Cu(II)>Pb(II)>Cd(II)>Ni(II), regardless of pH and contact time (Figure 6(A) and (B). Another factor that directly affects absorption is the initial ion concentration. Indeed, as shown [78], [79], a rise in extraction is observed at a rate that differs on the basis of the type of metal ions when the concentration of heavy metal ions is increased without changing the concentration of the adsorbent. When 100 mg of hydrogel was used, the extraction in this case (Figure 4(C)) did not increase linearly with the concentration of ions; rather, it tended to achieve its maximum value at the ion concentration of 150 mg/L. The extraction percentage is comparable in all of the metal ions assessed at the biggest concentration, in contrast to the previous case in which pH and contact time had an impact.

In Figure 7(A)–(C) the amount of metal ions adsorbed, expressed in mg, under different pH, contact time and concentration are displayed. However, this can be enhanced by adjusting the crosslinking agent or the pectin-to-CMC ratio. The ability to recover and reuse hydrogels is one of their primary benefits over other adsorbent materials. In general, chelating agents, acid or alkaline treatment can be used to desorb the metal ions [74]. In this case, the hydrogels were regenerated using a solution of 2 mol/L Na_2EDTA The efficiency of metal ion desorption for each cycle is resumed in Figure 6(C). The results illustrate how at the end of each cycle more than 90% of the ions were desorbed making the adsorption sites free. With the best results for Cu(II) and Pb(II), the regenerated hydrogels are capable of removing metal ions for up to five cycles, according to the data provided in Figure 7(A). After the third cycle, a slight decline in performance was observed under the following conditions: 50 mg/L concentration, pH 5.0, 60 min of contact, and 100 mg of dried hydrogel. This is most likely because the material structure is deteriorating.

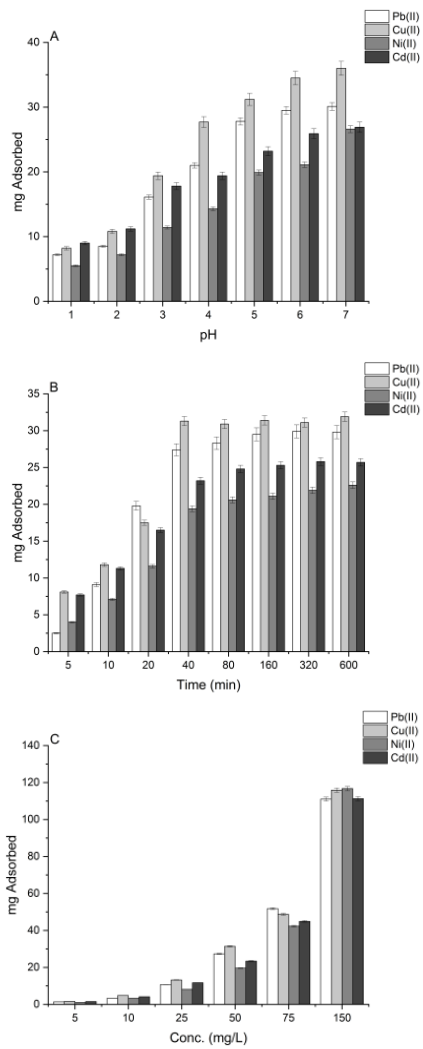


Figure 6: Amount of metal ions adsorbed, expressed in mg, under different (A) pH, (B) contact time, and (C) concentrations are displayed. Experiments were repeated thrice (n=3).

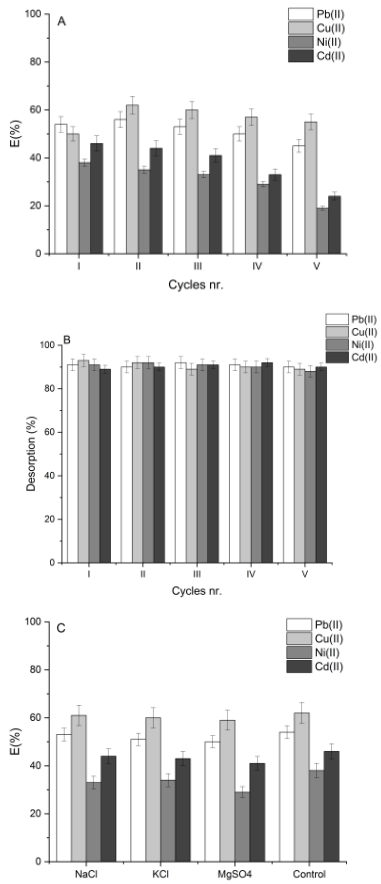


Figure 7: (A) Reusability of the pectin-based hydrogels. (B) Desorption of heavy metal ions by the hydrogels for each cycle. (C) Effects of interfering ions (5 mg/L) on heavy metal removal. The experimental conditions were as follows: heavy metal ion concentration, 50 mg/L; pH, 5.0; 60 min; and 100 mg of dried hydrogel. The control represents the solution containing the heavy metal ions in the absence of the interfering ions. The experiments were performed thrice (n=3).

The possibility to use the hydrogels for up to 5 adsorption-desorption cycles, indicates good regeneration property, which may render the very potential for the practical application. Moreover, compared to other reported studies either regarding biopolymer or synthetic polymer based hydrogels in which the reusability is limited up to three cycles [80], [81]. Cu(II)>Pb(II)>Cd(II)>Ni(II) is the ion affinity preserved in all cycles except the first. The reusability of the hydrogels is favorable, according to these values and those reported in Figure 7(A) (swelling cycles).

3.5 *Effects of Interfering Species and adsorption-desorption cycles*

Due to competitive phenomena, the presence of additional ions may have a detrimental effect on the hydrogel's adsorption ability [82], [83]. The effects of 5 mg/L KCl, $MgSO_4$, or NaCl on the pectin-CMC adsorption ability were evaluated. The results resumed in Figure 6C illustrate how the presence of interfering species results in a minor decrease in the extraction percentage for all ions. Among the evaluated interfering species, the presence of SO_4^- had the greatest effect on the extraction percentage. Ni (II) seems to be the metal ion most impacted by the presence of other ions that undergo major reduction. Cu(II) appears to be less impacted. This was expected, as Cu(II) seems to have the highest affinity.

4 Conclusions

Pectin from a mixture of banana and mango peels was mixed with CMC at a weight ratio of 3:1 to produce hydrogels that can potentially be used in the future as a material to remove heavy metal ions from contaminated water. The hydrogels reach the equilibrium within 60 minutes from the contact and exhibit pH-dependent swelling behavior. Apart from their high degree of swelling, the produced hydrogels can hold water when subjected to up to 400 kP_a external pressure and preserve the performances for up to five swelling-shrinking cycles. The findings demonstrate that the swelling mechanism is driven by non-Fickian diffusion when taking into account the cylindrical structure. A smooth surface and a non-homogeneous porous structure emerged via SEM investigation. The results from adsorption tests showed that heavy metal ions might be removed from contaminated water: Pb(II) > Cd(II) > Ni(II) > Cu(II). The adsorption capacity is directly affected by concentration, pH, and time. The data showed that the hydrogels were able to remove over 70% of each heavy metal ion in the polluted water under the best circumstances, which included a pH of 5.0 or higher, a contact time of max 60 min, and an ion concentration of up to 150 mg/L. Such achievement is comparable with hydrogels based on polysaccharides and for some ions slightly lower than hydrogels based on synthetic polymers. However, the advantages are given by the higher number of adsorption-desorption cycles, which the presented hydrogels can stand and the low environmental impact of the process.

The current study is in line with the nowadays interest in finding and developing innovative bioadsorbent materials as an alternative to synthetic ones. The proposed strategy aims to valorize banana and mango waste but also has the objective of reducing the possible cost of the material by using mild extraction conditions supported by ultrasound and minimizing post extraction treatments and/or modification of the obtained pectin. Moreover, the study demonstrates the possibility of using a mixture of pectin, coming from different sources, to produce hydrogels. Despite, additional characterization and studies are required, in particular, in simultaneous adsorption of the heavy metal ions, but also other types of pollutants, like organics, the outcomes demonstrate not only the adsorption ability but also how the hydrogels can be easily recovered and reused, which could make them preferable to the common adsorbent like activated carbon.

The main limitation related to the study is that the adsorptions were evaluated for each metal ion individually, which is not fully representative of the real condition in which multiple ions are present, in various concentrations and phenomena like competition for the adsorption sites or interactions between the ions can occur and affect the adsorption.

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Author Contributions

A.D.M. and A.D.: conceptualization; A.D.M. and K.O.: methodology; A.D.M., W.F., and A.S.: validation; A.D.M., M.I.B., A.R.P.A., Y.W., A.S.: investigation; A.D.M. and K.O.: data curation; A.D.M. and W.F.: writing—original draft preparation; A.D.M. and W.F.: writing—review and editing; supervision Antonio Di Martino. All the authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflicts of interest.

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