

Adsorption of Pb (II) from Aqueous Solutions by Pectic Acid Microspheres

Fen Li¹, Jianjun Li^{1,3}, Xiaoyan Wen², Xiaoyong Li¹, Yanhong Bai¹, Yun Yang¹ and Zhao Xu^{1*}

¹Department of Chemistry, Xi'an Jiaotong University, Xi'an 710061, China

²Xi'an Modern Chemistry Research Institute, Xi'an 710065, China

³Key Laboratory of Resource Biology and Biotechnology in Western China (Northwest University), Ministry of Education, School of Life Science, Northwest University, Xi'an 710069, China

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Abstract: Pectin or modified pectin is used to remove the heavy metal ions in aqueous solution. The adsorption ability of pectin microspheres (PMs) and pectic acid microspheres (PAMs) for Pb (II) in aqueous solution were characterized by the parameters such as pH, initial concentration, and contact time for Pb (II) removal in this work. The results showed that adsorption for 150 min at pH 5 was the optimal condition. The maximum adsorption capacity of PMs and PAMs for Pb (II) was 127 mg·g⁻¹ and 325 mg·g⁻¹, respectively. Five-cycle reusability tests demonstrated microspheres could be repeatedly used. All the results confirmed that PAMs which presented outstanding adsorption capability and reusability could be a good candidate for wastewater purification.

1 INTRODUCTION

Heavy metal pollution has drawn much attention because of its high toxicity and nonbiodegradability (Jorgetto et al., 2015). The heavy metal accumulated in water would affect people's health through various ways to a certain extent. Researches showed that excessive heavy metal ions which could damage the human brain and nervous system are intangible risk for human beings (Chojnacka, 2010). For these reasons, it has always been an urgent task for researchers engaged on environmental security to seek more reasonable ways of treating water pollution.

The mainly methods of removing heavy metals are chemical precipitation (España et al., 2006), adsorption (Shariful et al., 2017), membrane filtration (Mortaheb et al., 2010), ion-exchange (Fonseca et al., 2005), electrodialysis (Mohammadi et al., 2005), and so on. Compared with conventional methods, bioadsorption (Chen et al., 2017) is recently considered as the most advisable method for heavy metal removal due to its efficiency, reproducibility, and environmental friendliness. According to reports (Celus et al., 2017), pectin is regarded as a suitable candidate among the available bioadsorbents. In this study, pectin and modified pectin were used to

remove the heavy metal in an aqueous solution.

Pectin substances belonging to the group of natural biopolymers are the ionic plant polysaccharides (Liu et al., 2003). Their capacity in aqueous solutions was proved in numerous studies mainly due to their unique properties such as hydrophilicity, biodegradability, nontoxicity (Serguschenko et al., 2007). But pectin had a low adsorption capacity when directly used to remove heavy metal ions because esterified residues were not active. Thus, in our work pectin was modified to improve the adsorption ability.

In this study, the work aims at investigating the different adsorption ability of pectin, and pectic acid (PA) which was prepared from pectin by pH-modification. Batches of experiments were performed to evaluate its adsorption capacities for Pb (II) in either single or binary metal ion solutions at various pH values, contact time, and initial concentrations. The results showed that the adsorption ability of PAMs is higher than that of PMs and their high adsorption performance would provide great potential for water treatment. The highlight of this research is that PAMs was efficient in removing Pb (II) with 325 mg·g⁻¹ from aqueous solutions at pH 5; PAMs that have absorbed Pb (II) are readily removed from aqueous solutions and can be reused;

high selective for Pb (II) of PAMs was showed in mixed aqueous solutions of Cd (II) and Pb (II).

2 METHODS AND MATERIALS

2.1 Materials

Citrus pectin (CAS: 9000-69-5) was purchased from Sigma Biotechnology Co. (America). $\text{Pb}(\text{NO}_3)_2$, CaCl_2 and $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ were got from Xi'an Chemical Reagent Factory. All other reagents were of analytical grade. The water used to prepare the solutions was deionized water.

2.2 Preparation of PA and PAMs

2.2.1 Preparation of PA

The PA was prepared by method as described (Ilse et al., 2009). Briefly, 10g citrus pectin powder was dissolved in 500 ml $1.0 \text{ mol} \cdot \text{L}^{-1}$ NaOH ethanol solution on a magnetic stirrer for 5 h at 4°C . Placed overnight, the solution was filtered and the residue was dissolved into 50% ethanol (v/v) adding $3 \text{ mol} \cdot \text{L}^{-1}$ HCl until the $\text{pH}=1.5$. After 1.5 h, the solution was filtered and the residue was dissolved in 250 ml 50% ethanol (v/v) containing 1% HCl stirring at 25°C for 0.5 h. The mixture was filtered and the resultant composites were washed with 50% ethanol (v/v) with three times. After freeze-dried, the PA was obtained. The esterification degree of pectin and PA were determined using titrimetric method (Afanas'Ev et al., 1984) and the results were 47.90% and 0.90%, respectively.

2.2.2 Preparation of PAMs and PMs

The PA solution was prepared by dissolving 0.3 g of PA powder in 10 mL of deionized water (3%, w/v). Using syringe (1 mL, 0.45 #) added the pectin solution to the calcium chloride solution (5%, w/v) dropwise, the needle was about 5 cm from the liquid level. After 20 min, PAMs were collected through a membrane filter separation, and then washed thoroughly by deionized water. PMs were prepared using the same procedure as PAMs, excepting the concentration of calcium chloride solution was used as 10%.

2.3 Characterization of PA and PAMs

FTIR (Fourier Transform infrared) spectra of PA, pectin and microspheres were obtained by an FTIR

spectrometer (Nicolet AVATAR 360, Thermo Instrument Company, Madison, USA) at the wave number range of $400\text{-}4000 \text{ cm}^{-1}$. SEM (TM-1000 SEM, Hitachi, Japan) was used to observe the surface microstructure and morphology of PAMs and PMs.

2.4 Adsorption Experiments of Pb (II)

2.4.1 Adsorption Experiments

The experiments were performed at pH (1, 2, 3, 4, 5, 6), contact time (10, 20, 30, 60, 90, 120, 150, 180, 210, and 240 min) and initial concentration of Pb (II) ($50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 600, 700 \text{ mg} \cdot \text{L}^{-1}$). To test the selective adsorption, a total of 50 mg of microspheres was added into 100 mL mixed solution which contains Cd (II) and Pb (II) with the initial concentration of $250 \text{ mg} \cdot \text{L}^{-1}$ at initial pH 5.0. The reusability of microspheres was evaluated via sequential cycles of adsorption-desorption in a binary ion mixture system of Cd (II) and Pb (II). After adsorption for Cd (II) and Pb (II), the microspheres were collected, washed with deionized water and constantly stirred for 1 h in 0.002M Na_2EDTA solution for desorption. Then, the microspheres were filtered and washed thoroughly until Cd (II) and Pb (II) concentration in the filtrate was almost equal to zero. The collected microspheres were further used in the next adsorption cycle. The regeneration tests were conducted for five times under the same conditions to evaluate the reusability of microspheres.

2.4.2 Calculation of Adsorption Capacity

The concentration of metal ions was measured by a flame atomic absorption spectrophotometer (AA1700, FULI Instrument, China). The adsorption capacity (q_e) was calculated by the equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where q_e ($\text{mg} \cdot \text{g}^{-1}$) is the adsorption capacity, C_0 ($\text{mg} \cdot \text{L}^{-1}$) and C_e ($\text{mg} \cdot \text{L}^{-1}$) are respectively initial and final concentrations of metal ions, respectively. V (L) is the volume of the metal ion solution, and m (g) is the mass of the dried adsorbent.

3 RESULTS AND DISCUSSION

3.1 Characterization of PA and PAMs

3.1.1 FTIR Analysis

To investigate the chemical structure of PA and PMs, the results of FTIR are shown in Figure 1. The main characteristic absorption bands of pectin were summarized as follows: 3346 cm^{-1} (-OH group), 1731 cm^{-1} (-C=O in free carboxylic acid groups), 1607 cm^{-1} (-C=O in non-free carboxyl group) (Martinez et al., 2012). The peak at 1607 cm^{-1} of PA disappeared demonstrating that the non-free carbonyl group in PA decreased, and the peak of 1730 cm^{-1} increased, indicating that the free carboxyl group increased. For PMs, the intensity at 1730 cm^{-1} and 3327 cm^{-1} became weaker, compared with pectin spectrum. For PAMs spectrum, new bands at 1416 cm^{-1} appeared and 3229 cm^{-1} dropped off compared with PA spectrum, indicating that pectin and PA had a cross-linking reaction successfully with Ca (II).

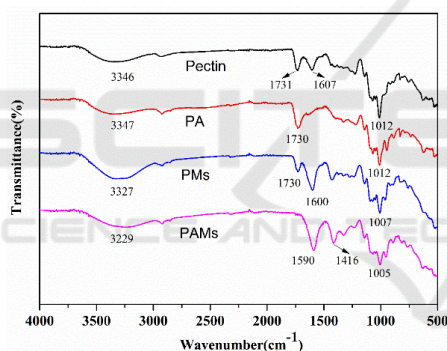


Figure 1: FTIR spectra of pectin, PA, PMs, and PAMs.

3.1.2 SEM Observation

The images of PMs and PAMs at different magnification were recorded via SEM in Figure 2, by which the surface morphology and texture of each sample was mapped out. The surface of PMs with fewer folds exhibits some small cracks and there are more uniform folds on the PAMs surface. The mean diameters of two microspheres all were 2 mm and had an integral surface, which could facilitate the separation and recycling of samples.

3.2 Effect of pH on Adsorption

The initial pH of aqueous solutions is an important parameter that greatly influences the adsorption property of an adsorbent. The experiments on effect

of pH were performed at initial pH 1.0-6.0 in which Pb (II) solution with initial concentration of 130 $\text{mg}\cdot\text{L}^{-1}$ and adsorption time lasted 240 min. The results are displayed in Figure 3. At pH 1.0, both of PMs and PAMs have the lower adsorption rate; when the pH increased from 2.0 to 6.0, the adsorption rate of PMs increased while that of PAMs tends to a plateau. At pH 6.0, the adsorption rate of PMs and PAMs for Pb (II) respectively reached maximum values, about 69% and 95%, respectively. That may be because -COO groups on microspheres donated their electron pairs to Pb (II) to form complex, when the pH was low, the carboxyl group in pectin was protonated and the complexation of Pb (II) with the active group was reduced. The degree of protonation decreased with the pH rising, and the number of active group participating in the complexation increased. There are more carboxyl groups binding site with Pb (II) in PA compared with pectin, so the adsorption capacity of PAMs is higher than PMs's. When the value of pH in the solution reached to 6.0, Pb (II) have tended to precipitate. There would be less amount of Pb (II) remained consequently showing a high adsorption rate in the result. The initial pH of the Pb (II) solution was close to pH 5.0, while the adsorption rate of the microspheres at pH 4 was almost equal to that of them at pH 5, so the optimization of pH in equilibrium adsorption is 5.0.

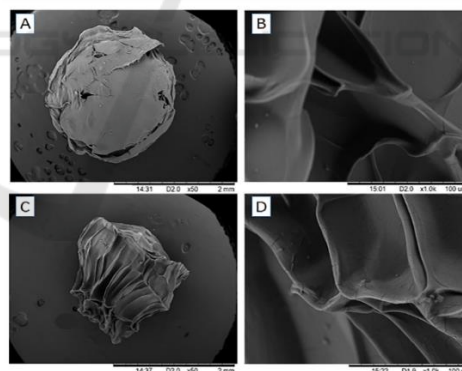


Figure 2: SEM images of PMs (A×50 and B×1000) and PAMs (C×50 and D×1000).

3.3 Effect of Contact Time on Adsorption

The experiments on influence of contact time were conducted with initial Pb (II) concentration of 130 $\text{mg}\cdot\text{L}^{-1}$ at pH 5.0. Figure 4 shows the effect of contact time on Pb (II) adsorption of two kinds of microspheres. After 90 min, the amount of adsorption of PMs and PAMs on Pb (II) were 74% and 96%,

respectively. Then, the adsorption capacities increased slowly with the increase of contact time until reaching adsorption equilibrium at 150 min. It was a slow process in which the metal ion diffusion into pores and the adsorption by interior surface while almost all facial adsorption sites of microspheres have been occupied. The maximum adsorption capacity of PMs and PAMs was $95.74 \text{ mg}\cdot\text{g}^{-1}$ and $123.84 \text{ mg}\cdot\text{g}^{-1}$ at pH 5.0.

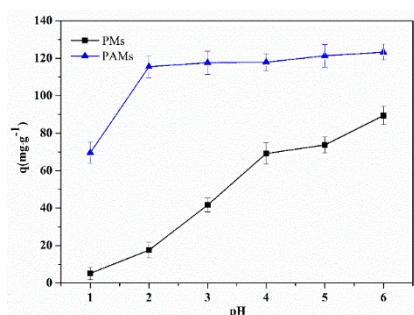


Figure 3. Effects of pH on adsorption.

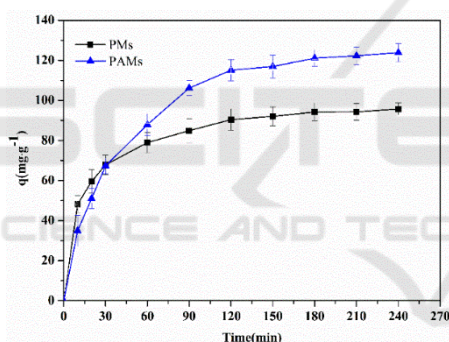


Figure 4: Effects of contact time on adsorption.

3.4 Effect of Initial Concentration on Adsorption

The experiments on impact of initial Pb (II) concentration were carried out at pH 5.0 for 150 min. The effects of the initial Pb (II) concentration on the adsorption of the microspheres are shown in Figure 5. For PAMs, the amount of the adsorbed ions increased slowly until approached the plateau at $C_0 = 600 \text{ mg}\cdot\text{L}^{-1}$. The maximum adsorption capacity of PAMs were $325 \text{ mg}\cdot\text{g}^{-1}$. Obviously, it was about 2.5 times as much as that of PMs ($127 \text{ mg}\cdot\text{g}^{-1}$), which indicated the ability of chelating with metal ions of PAMs was significantly improved by modified within the experimental.

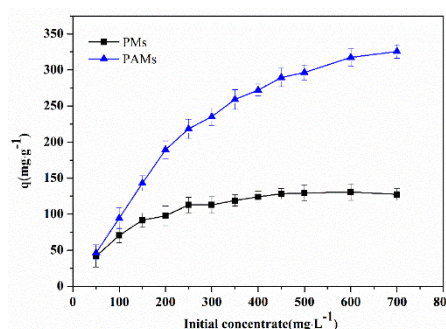


Figure 5: Effects of initial Pb (II) concentration on adsorption.

3.5 Selective Adsorption

The tests of selective adsorption were carried out in a binary ion mixture system of Cd (II) and Pb (II) at pH 5.0 and with different contact time. The results of the selective adsorption of PMs and PAMs for Cd (II) and Pb (II) are shown in Figure 6. The results indicated that the adsorption capacity of PAMs for Pb (II) was higher than that of Cd (II) in the binary metal ion solution. Moreover, the selectivity of PAMs for Pb (II) is superior to PMs.

3.6 Desorption and Regeneration

The adsorption-desorption tests were repeated five times in a binary ion mixture system. The results are shown in Figure 7. After the 5th cycle, the adsorption capacity of the PMs and PAMs for Pb (II) dropped to 15.66% and 9.64%, respectively, and remained constant almost after the second cycle. However, the adsorption capacities of PAMs for Pb (II) were even $143.47 \text{ mg}\cdot\text{g}^{-1}$ with the existence of Cd (II). PAMs's adsorption capacities was about 2.2 times that of PMs's at the 5th recycle. These results indicated that PAMs were of desirable reusability and stable chemical property.

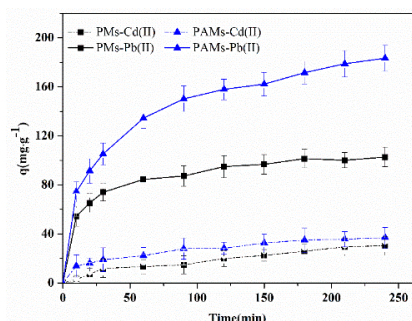


Figure 6: Effects of contact time on adsorption for Cd (II) and Pb (II).

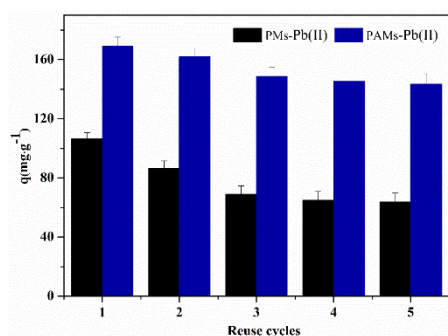


Figure 7: Results of five consecutive adsorption-desorption for the reuse of microspheres for Pb (II) adsorption.

4 CONCLUSION

In this work, PMs and PAMs were successfully fabricated through crosslinking with calcium ions. The maximum adsorption capacity for Pb (II) of PAMs was about 2.6 times of PMs which implied that the adsorption ability of PAMs greatly increased. And the selective adsorption capacity for Pb (II) of PAMs was better than that of PMs. Moreover, the result of regeneration experiments showed that the removal efficiency for Pb (II) of PAMs was more than 54% after five adsorption-desorption cycles in a binary ion mixture system. All the results above implied that the newly-prepared PAMs might be the promising adsorbent for Pb (II) in aqueous solutions.

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