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SHORT COMMUNICATION

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New chitosan–calcium pectinate pellets and their adsorption capacity

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Abstract A new simple procedure to prepare chitosan–calcium pectinate pellets from a chitosan solution in acetic acid was developed. Porous beads were prepared by mixing a chitosan solution in acetic acid and a pectinate solution in water. The obtained suspension was dropped into a $CaCl_2$ solution. These pellets were studied as adsorbents for Pb(II) and Cd(II) in acidic aqueous solutions because chitosan is a biopolymer with the capacity of adsorbing heavy and transition metal ions. Kinetics data were reported for conditions under which these contaminants were adsorbed in low concentrations.

Keywords Chitosan–pectinate pellets · Biopolymer · Lead · Cadmium · Adsorption

Introduction

Chitin, poly-β(1→4)-*N*-acetyl-D-glucosamine, is one of the most abundant natural polysaccharides and is largely available in the exoskeletons of shellfish and insects. The deacetylation of chitin yields chitosan (poly-β(1→4)-D-glucosamine). A wide variety of applications of chitin, chitosan, and their derivatives as functional materials has been reported [1].

Pectin is an anionic polysaccharide present in the primary cell walls and intercellular regions of higher plants. It is a linear chain of α-(1→4)-linked D-galacturonic acid units with varying amounts of methoxyl esters. Its methoxyl content, which is expressed as the degree of methylation (DM), implies specific industrial applications. The galacturonosyl backbone is interrupted by the insertion of (1→2)-linked α-L-rhamnose units (typical amounts of 1–4%).

Recent studies in environmental quality standards demonstrate the need for improved wastewater treatment of dilute metal-containing effluents. Biosorption, or sorption to material of biological origin, is recognized as an emerging technique for the depollution of heavy-metal-polluted streams. Several sorbents can be used: bacterial, algal, or fungal biomass, as well as biopolymers [2, 3]. Among the biopolymers, chitin and the deacetylated form chitosan exhibit high sorbent capacities for heavy metals [2, 3]. Chitosan is a well-known biopolymer whose high nitrogen content confers a remarkable ability for the sorption of metal ions from dilute effluents. However, its sorption performance in both equilibrium and kinetic terms is controlled by diffusion processes [3].

Previously, we have proposed a method of preparing beads using chitosan for the remotion of heavy and transition metal ions [4]. Also, in previously published papers [5–7], we presented theoretical and experimental studies of Hg^{+2} and Pb^{+2} adsorption using chitosan powder, pectin powder, and chitosan–pectin pellets. We showed the results for Hg^{2+} and Pb^{2+} adsorption and we proposed an intra- and intermolecular chelation for models for pectin and chitosan using the extended Huckel method, PM3 and MM2. We could conclude that pellets of chitosan–pectin, using chitosan in powder, were better than either chitosan or pectin alone. The adsorption of heavy metals reached 100% when pellets were used, and the kinetics data of Hg^{+2} and Pb^{+2} adsorption onto pellets

were clearly different from those obtained with chitosan or pectin alone. In another paper, the results for Cd^{+2} adsorption were presented and they were compared with those obtained for Hg^{+2} and Pb^{+2} [8].

The goals of this work are to propose a new and simple procedure for preparing chitosan–calcium pectinate pellets using a chitosan solution in acetic acid and to apply them in Pb(II) and Cd(II) adsorption from an aqueous system.

Experimental

Materials

Two different kinds of chitosan were used in this work, and they were obtained in our laboratory (Laboratorio de Investigaciones Básicas y Aplicadas en Quitina) from crustacean exoskeletons applying different operational conditions. Their characteristics are presented in Table 1. The pectin used was obtained from citrus fruits (Sigma), partially methoxylated with degrees of methoxylation of 8, 31, and 72%, with an anhydro galacturonic acid content of 79%.

Preparation of sodium pectinate solution

We prepared a solution containing 1.0 g pectin in 90.0 mL distilled water (pH 4.0). The pH of the solution was monitored during dissolution and adjusted to a final pH of 11.0 using sodium hydroxide 2 M. The final volume was adjusted to 100.0 mL.

Preparation of chitosan solution

A solution of chitosan (1% w/v) in aqueous acetic acid (1% v/v) was prepared. The final pH was 4.1.

Preparation of pellets

The chitosan (soluble)/pectin system (pellets from dissolved chitosan) was prepared by mixing sodium pectinate and chitosan solutions in different ratios (2.0/1.0, 3.0/1.0, 4.0/1.0, 5.0/1.0, 7.0/1.0, and 10.0/1.0) [4–7]. The obtained suspensions were homogenized with a magnetic stirrer, and then they were immobilized by dropping them into a solution of $CaCl_2$ (4% w/v). The resulting beads were kept in this solution for 12–24 h at ambient temperature to harden them. The pellets were washed with distilled water and kept under refrigeration at between 4 and 7 °C until they were used.

To prepare the chitosan (flakes)/pectin system (pellets from undissolved chitosan), we mixed the chitosan flakes with a suspension of sodium pectinate. The suspension (pH 10.0–11.0) was inmobilized by dropwise addition into a $CaCl_2$ solution [4, 5].

Table 1 Chitosan characteristics

Deacetylation (%)	Viscosity (spindle 21 and rpm 50)	Water content (%)	Ash content (%)
86	6.9 cP	3.51	1.18
81	31 cP	2.79	1.16

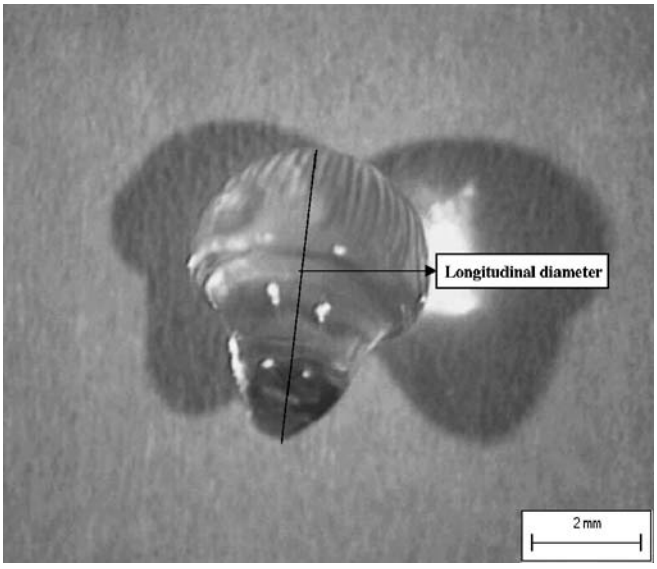

Fig. 1 Microphotograph of a wet pellet

Adsorption study

The kinetics of adsorption for Pb(II) and Cd(II) by pellets were measured in a batch mode at different times. The heavy metal salts used were $Pb(NO_3)_2$ and $Cd(NO_3)_2$, and

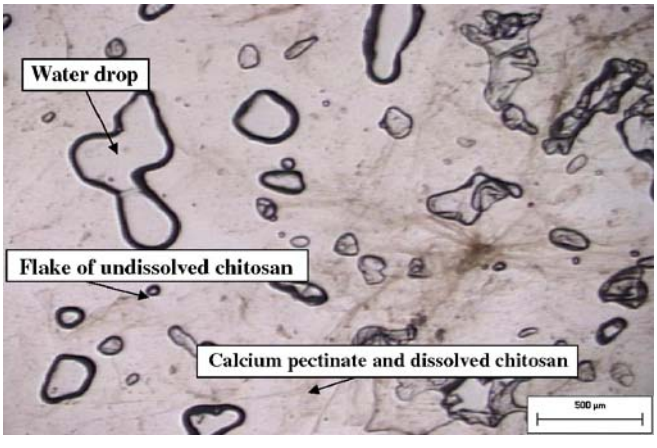

Fig. 2 Microphotograph of a pellet cross section showing a matrix of calcium pectinate and dissolved chitosan

Table 2 Size and weight of pellets

Characteristic	Value
Longitudinal diameter	3.32 mm±0.04
Wet weight	31.6 mg±1.6

the initial concentrations were 6.50 and 0.79 ppm for Pb(II) and Cd(II), respectively, in 15.0 mL of 0.01 M $NaClO_4$ solution at pH 5.0. Both solutions were freshly prepared. The mass of adsorbent used in each case was 1.00 g.

The solutions were contacted with sorbent and stirred using a magnetic horizontal stirrer at 20±1 °C. Then, the solutions were filtered using a glass sheet. The Pb(II) and Cd(II) initial and final concentrations were determined by a Hitachi, Z-61000 model, atomic absorption spectrophotometer with lamps cathode hue. The determinations were done in duplicate.

Measurement of pH variations

The solution pH, before and after the adsorption procedure, was measured using a Metrohm Herisau pH meter. The pH of the interior of the pellets was determined by an Orion electrode centered in a sharo knife-shaped blade.

Optical microscopic studies

Microscopic observations were made in an Olympus BH-2-UMA optical microscope equipped with a Sony CCD IRIS/RGH photographic camera.

X-ray fluorescence spectrometry study

The data were obtained with a Philips PW 1400 spectrophotometer with an RH anode, working at 60 kW and 40 mA with a LiF200 vacuum atmosphere.

Results and discussion

Pellet obtainment

The pellets obtained as described in the experimental section showed different behaviors. The pellets formed with pectin of lower DM and chitosan of higher degree of deacetylation (DD) have shown better behavior, in accordance with those obtained using chitosan in powder. It was not possible to obtain pellets using 72% DM pectin. The ratio of 5.0/1.0 of pectin (8% DM) and chitosan (86% DD) was chosen because the pellets were uniform, consistent, and reproducible. The percentage of water in the gel material was 96%. Once the pellets were obtained, the next step was to characterize them.

Physical appearance (optical microscopic studies)

To evaluate the physical appearance of the pellets, an optical microscopic study was done. Figure 1 shows the microphotograph of a wet pellet. A gelatinous and opalescent appearance, with uniform and transparent edges, is observed. The shape of the pellets was not spherical, but mushroom-like. The cross section is shown in Fig. 2. A homogeneous phase of dissolved calcium pectinate and chitosan, with very few flakes of undissolved chitosan and some water drops, can be seen.

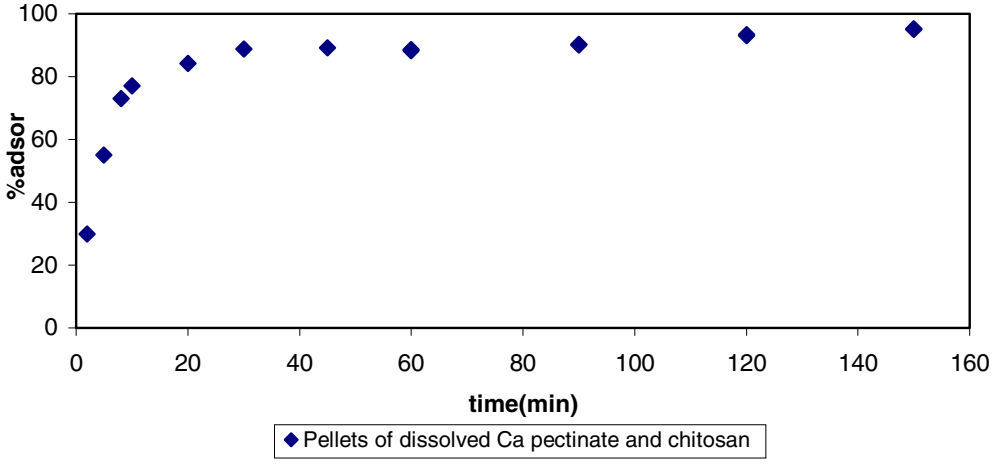

Fig. 3 Adsorption kinetics of cadmium (II) on new pellets (initial and final pH values were 6.0 and 6.8, respectively)

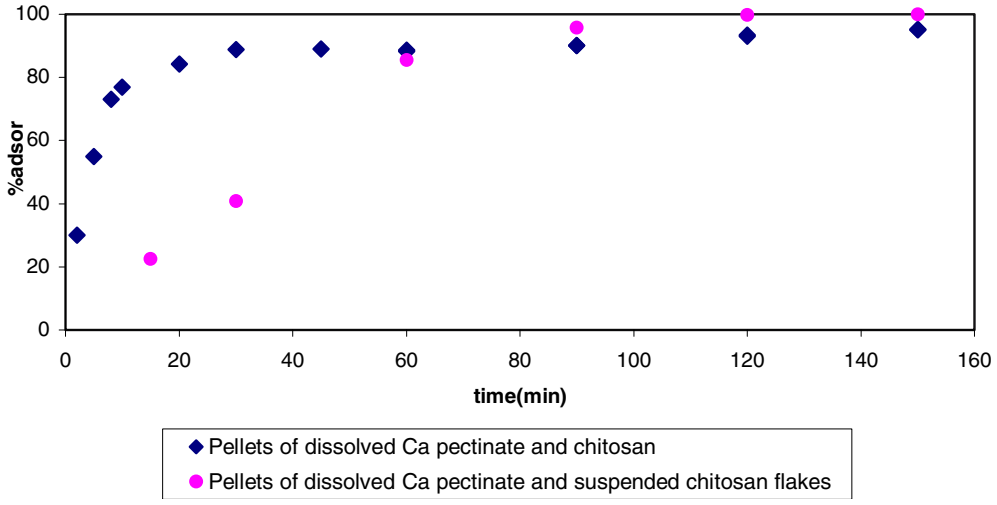

Fig. 4 Adsorption kinetics of cadmium (II) on both kinds of pellet

Size and weight

To determine the size and weight of the pellets, 20 of them were evaluated and a statistical study was performed. The obtained data and their confidence limits at 99% are shown in Table 2.

Cd and Pb adsorption in biopolymers

In Fig. 3, the adsorption kinetic behavior for cadmium can be observed. A removal of 87% was obtained in 20 min. After this time, the adsorption kinetic behavior continued in a stable way and achieved 95% removal after 150 min. The pH values of the solution before and after the adsorption process were 6.0 and 6.8, respectively. The predominant species at pH values lower than 7.5 was Cd^{2+}. Taking into account the pH values, the amine group of chitosan is the most important active site in the coordination of cadmium ions [8, 9].

In Fig. 4, a comparison of the kinetic adsorption process between the obtained pellets from both dissolved calcium pectinate and chitosan and those obtained from dissolved calcium pectinate and undissolved flakes of chitosan is shown. Significant differences at a confidence level of 1% exist between both behaviors for periods of time shorter than 50 min. In this case, the cadmium adsorption kinetics are better for the dissolved chitosan–calcium pectinate pellets than for the other pellets. This could be due to a better arrangement of the exposed groups of both polymers in the pellet. For periods of time longer than 50 min, 100% removal is obtained for both pellets. In Fig. 5, the kinetic behavior of lead is very similar to that of cadmium. The adsorption maximum (88% removal) is achieved at 120 min.

The pH values of the solution before and after the adsorption process are 6.1 and 6.5, respectively. Taking

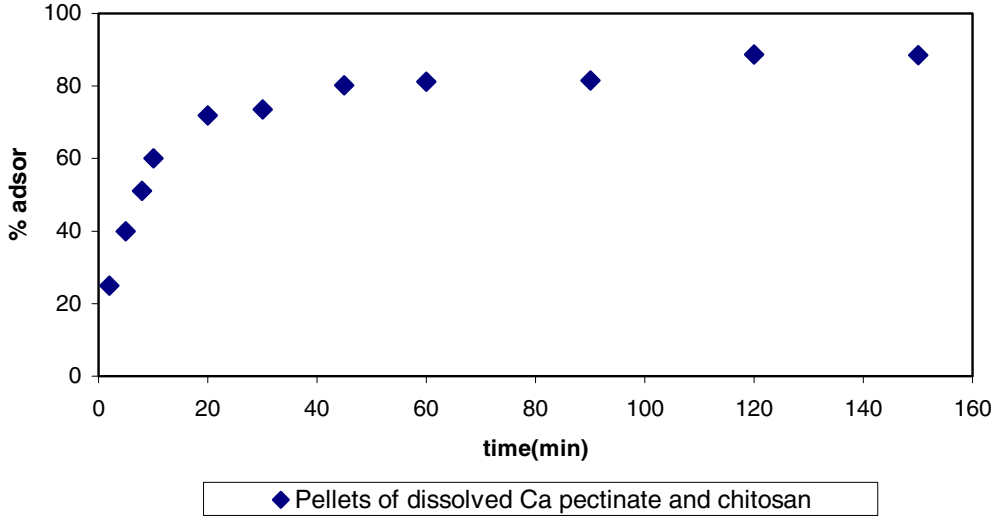

Fig. 5 Adsorption kinetics of lead (II) on new pellets (initial and final pH values were 6.1 and 6.5, respectively)

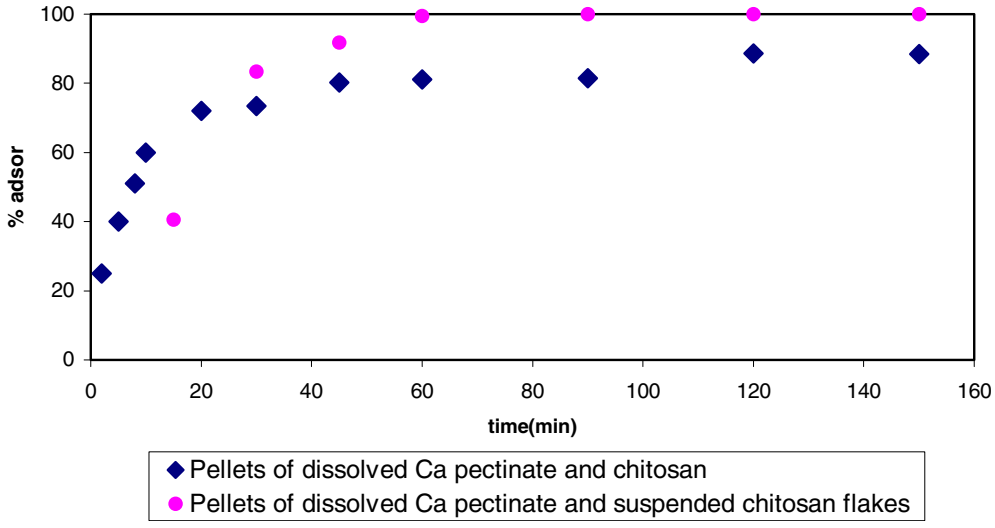

Fig. 6 Adsorption kinetics of lead (II) on both kinds of pellet

into account the predominant equilibrium at these pH values, the predominant species is Pb^{2+}. In Fig. 6, a comparison of the kinetic adsorption process of lead using both kinds of pellets is shown. Significant differences exist between both pellets at periods of time shorter than 40 min, and the adsorption capacity is higher with the pellets with both dissolved polymers. For periods of time longer than 40 min, differences exist between both pellets, and the lead adsorption kinetics are better for the pellets obtained from undissolved chitosan.

X-ray fluorescence spectrometry study

To complete the study of the adsorption process, an X-ray fluorescence spectrometry was performed. The goal of this analysis was the detection of cadmium and lead in the whole pellet and in pellets whose external surfaces were eliminated. The thickness of the eliminated external surface could not be determined. In each case, the samples were compared with pellets that were not exposed to contaminants (unused blank pellets).

Examples of the obtained spectra for whole pellets and for the interiors of the carved pellets are shown in Figs. 7 and 8, respectively. Lead was detected in whole pellets and in carved pellets, though in a much lower concentration. The same results were obtained for Cd. These results suggest that the adsorption on the surface happens at the beginning, and then a diffusion through the pellet pores takes place, as in the pellets obtained from chitosan flakes. In this work the maximum capacity of pellet adsorption was not determined.

Conclusions

An obtainment procedure of a new bioadsorbent is described. It has a very good adsorption capacity for lead and cadmium, solving in this way a very serious problem originated by cadmium and lead contamination, and it is also very efficient when traces of these ions are found in large volumes of residual liquids.

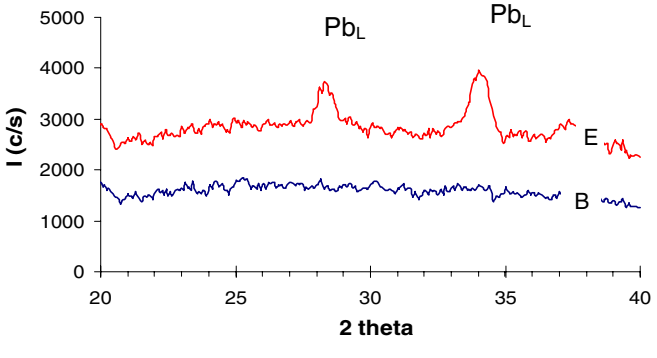

Fig. 7 X-ray fluorescence spectrometry of lead-contaminated whole pellets (*E* entire, *B* blank)

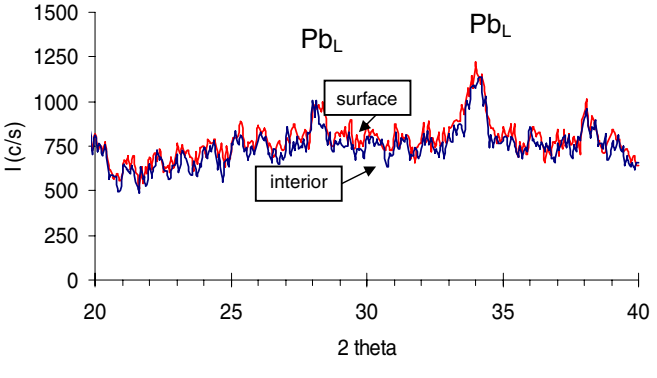

Fig. 8 X-ray fluorescence spectrometry of lead-contaminated pellets (entire and interior)

The comparative kinetic studies made between pellets of chitosan–calcium pectinate obtained from chitosan flakes and these new pellets obtained from dissolved chitosan demonstrated that adsorption is faster for the latter pellets, increasing the adsorption percentage for shorter periods of time, always with under pH control.

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