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Chitosan/mangiferin particles for Cr(VI) reduction and removal

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ABSTRACT

In this work, chitosan/mangiferin particles (CMP) were prepared by spray-drying technique and characterized by SEM, DLS, FTIR, HPLC–UV and adsorption studies to investigate a possible application as a preventive material in cases of human and animal contamination with Cr(VI). CMP presented sizes ranging from nano to micrometers. Chitosan and mangiferin (MA) presence in the powder was confirmed by FTIR and MA quantification (136 μg/mg) was performed using a calibration curve prepared by HPLC–UV. Adsorption capacity of Cr(VI) onto CMP was compared with chitosan and investigated in a batch system by considering the effects of various parameters like contact time, initial concentration of adsorbent and pH. Cr(VI) removal is pH dependent and it was found to be maximum at pH 5.0. The results showed that CMP has a potential application as a preventive material in cases of human or animal contamination with Cr(VI).

1. Introduction

Contamination with Cr(VI) has been reported to be a health problem regarding the toxicity of Cr(VI) species to human beings and other living organisms. Respiratory exposure to Cr(VI) has been a problem between welders and workers in industries. Carcinogenicity, genomic dysregulation, stomach and skin tumors, lung cancer, effects on osteoclasts and osteoblasts functions are some of the observed damages [1–7].

Chitosan is a natural copolymer of β-(1 → 4)-D-glucosamine and β-(1 → 4)-N-acetyl-D-glucosamine obtained from the easily available chitin [8,9]. Chitosan polymer and derivatives have been investigated in its ability to adsorb Cr(VI) ions[9–12]. Mangiferin (MA) is a natural xanthone compound found in many parts of *Mangifera indica* L. besides other trees. MA has been reported to show many biological activities such as antioxidant, analgesic, immunomodulatory, anti-HIV, antitumor and others [13–15]. Phenolic compounds have been reported to be involved in Cr(VI) reduction and removal [16].

Many authors have reported the use of different materials to remove Cr(VI) from industrial wastewaters [17–21] but not much have been investigated about the preparation of materials for Cr(VI) removal from living organisms.

In this work, chitosan/mangiferin particles (CMP) were prepared encapsulating MA for Cr(VI) removal. It was observed that MA improved the adsorption ability of chitosan. Chitosan/MA capsules may be used as a poison preventive material in cases of human contamination with Cr(VI) ions.

2. Experimental

2.1. Materials

Chitosan with molar mass of 7.82×10^4 g/mol and degree of deacetylation of 89% was obtained from Primex ehf, Iceland. MA was isolated from the bark of *M. indica* L. Tween 80, a non-ionic surfactant, was purchased from Synth Chemicals. All other chemicals used were of analytical grade.

2.2. Production and characterization of CMP

2.2.1. Spray-drying encapsulation of MA

The preparation of CMP was performed in a spray-dryer equipment büchi, Switzerland, model B-290. The inlet and outlet air

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temperatures were maintained at 160 °C and 60 °C, respectively, pump feed of 60% and aspirator volume flow of 100%. The spray-drying formulations were performed using a commercial chitosan. For that, a mass of polysaccharide (0.5 g) was dissolved in 100 mL of 1% acetic acid and gently stirred overnight at room temperature. Afterwards, 50 mg of MA was added to the solution which was stirred for 2 h. Surfactant Tween 80 was used as emulsifier at a concentration of 0.1% per bioactive immediately before the addition of MA to the solution. During spray-drying procedure, the dispersion was continuously homogenized using a magnetic stirrer.

2.2.2. Scanning electron microscopy (SEM)

The surface of the polymer encapsulated formulation was observed using a FEI Inspect S50 Scanning Electron Microscope (at low energy of 10 kV). The samples were deposited on carbon tapes and coated with gold, using vapor deposition techniques. The surface was scanned using a magnification between 10,000 and 40,000×.

2.2.3. DLS measurements

DLS experiments were performed in triplicate using an instrument Zetasizer Nano ZS (Malvern, UK) for particle size determination. CMP sample was dissolved in acetic acid 1%, diluted and dispersed with ultrasound before measurements.

2.2.4. Infrared spectroscopy

Fourier transform IR spectrum (FT-IR) was recorded with a Shimadzu IR spectrophotometer (model 8300) in the range of 400 and 4000 cm^{-1} as KBr pellets.

2.2.5. Analytical HPLC

High performance chromatography analyses were conducted on a liquid chromatograph (Agilent Technologies 1260 Infinity) using a reverse-phase C18 ODS column 250 mm × 4 mm, 5 μm (Latek, Eppelheim, Germany). The mobile phase consisted of 2% acetic acid in water (solvent A) and methanol (solvent B) with the following gradient profile: 95% A for 3 min; reduced to 75% A over 12 min; to 60% A over 24 min; to 50% A over 30 min; to 0% A over 35 min; continuing at 0% A until completion of the run. The flow rate of the mobile phase was 1.0 mL/min. Phenolic compounds in the eluant were detected at 257, 278, and 340 nm with a diode-array UV detector.

CMP was suspended in methanol at a concentration of 1.3 mg mL^{-1} for MA extraction, vortexed for 1 min (Votex Kasvi K40-1020) placed in an ultrasound bath (Quimis Q335D) for 5 min and then shaken in an Eppendorf mixer (Thermomixer C) at 25 °C, 600 rpm for 2 h. Following that, the sample was centrifuged (Eppendorf centrifuge 5415R) for 5 min at 14,000 rpm and supernatants (20 μL) samples were then analyzed by HPLC–UV.

2.3. Batch equilibrium experiments

2.3.1. Preparation of stock solution

The stock solutions of Cr(VI) were prepared by dissolving 2.82 g L^{-1} $K_2Cr_2O_7$ in ultrapure water resulting in approximately (approx.) 1000 mg $L^{-1}$of Cr(VI) solution. Different concentrations ranging from 10 mg L^{-1} to 100 mg L^{-1}were prepared. Solution pH was changed using hydrochloric acid or sodium hydroxide.

2.3.2. Adsorption experimental analysis

Adsorption experiments were carried out in batch mode at room temperature (25 ± 2 °C). A shaker was used at a fixed agitation speed of 110 rpm for all batch experiments. In order to investigate the interaction between Cr(VI) and CMP, the effect of pH on percentage removal was carried out, followed by further observation of the time contact (kinetic reaction) and adsorption dosage on adsorption capacity at an optimized pH value. Only one parameter was changed at a time while others were maintained constant during the experiments. In the first set of experiment, percentage adsorption was studied at various pH values (1, 4, 5, 6 and 7) for chitosan and CMP (0.6 g L^{-1}), initial Cr(VI) concentration of 50 mg L^{-1} and the predetermined time of 60 min in a rotary shaker at a speed of 110 rpm using a 100 mL Erlenmeyer. In the second set of experiments with CMP, the contact time ranged between 0 and 24 h at pH 5 and at an initial [Cr(VI)] = 50 mg L^{-1}. For the third set of experiment, CMP doses changed (0.2–2.0 g L^{-1}) while other parameters such as initial Cr(VI) concentration (50 mg L^{-1}), optimum time and optimum solution pH was kept constant. All experiments for CMP were performed in comparison to chitosan.

2.3.3. Chromium quantification

Total chromium concentration (Cr_{TOTAL}), after the adsorption test, was determined by atomic absorption spectrometry (Varian AA240FS). The concentration of Cr(VI) ions in solution was determined using a colorimetric method with 1,5-diphenylcarbazide using a UV–Vis spectrophotometer (Thermo Scientific Evolution 100) at 540 nm as described in the standard methods [22]. Each trial was performed in duplicate. The reduced Cr(III) was calculated by the difference between the Cr_{TOTAL} and Cr(VI) in the solution.

Controls were conducted using adsorbent in ultrapure water blank and adsorbent-free Cr(VI) solutions. The percentage removal of Cr(VI) was calculated by using following equation:

$$R\ (\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (1)$$

where C_0 (mg L^{-1}) is the initial concentration and C_e (mg L^{-1}) is the equilibrium metal concentration. The adsorption capacity, q (mg g^{-1}), is defined as the mass of substrate bound/gram of adsorbent. Eq. (2) shows the mathematical equation for the calculation of the adsorption capacity:

$$q\ \left(\frac{mg}{g}\right) = \frac{(C_0 - C_e)xV}{m} \quad (2)$$

in which C_0 and C_e are those described in Eq. (1), V (L) is the volume of the sample solution and W (g) is the mass of the adsorbent. For each sample, two replicates were performed and the average was taken for calculation.

2.4. Diagrams of chromium ion speciation

A diagram of chromium species distribution as a function of pH for Cr(VI) ions was constructed with HYDRA (hydrochemical equilibrium-constant database) software [23]. These diagrams were built for a defined Cr(VI) concentration using potassium dichromate (50 mg L^{-1}) as reference.

3. Results and discussion

3.1. Production and characterization of CMP

3.1.1. Scanning electron microscopy (SEM)

The morphology obtained for CMP was observed by SEM as shown in Fig. 1. The particles presented heterogeneous sizes between micron and nanometers. Some agglomerates or bigger particles could also be observed as well as broken particles due to the high temperature used for spray drying. The average measured size for the micro and nanoparticles were 2.64 μm and 460.54 nm, respectively. Most particles presented app. spherical shape and a rough surface characteristic of chitosan particles [8].

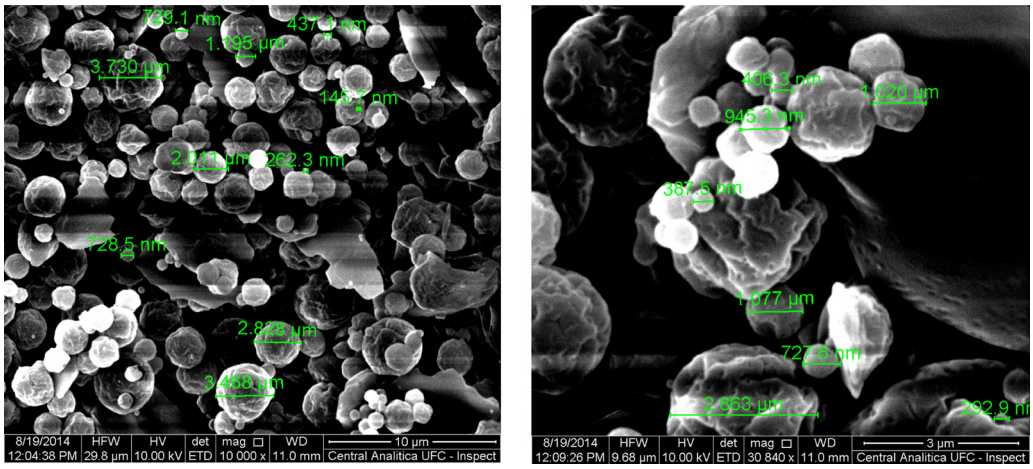

Fig. 1. SEM micrographies for chitosan/mangiferin particles.

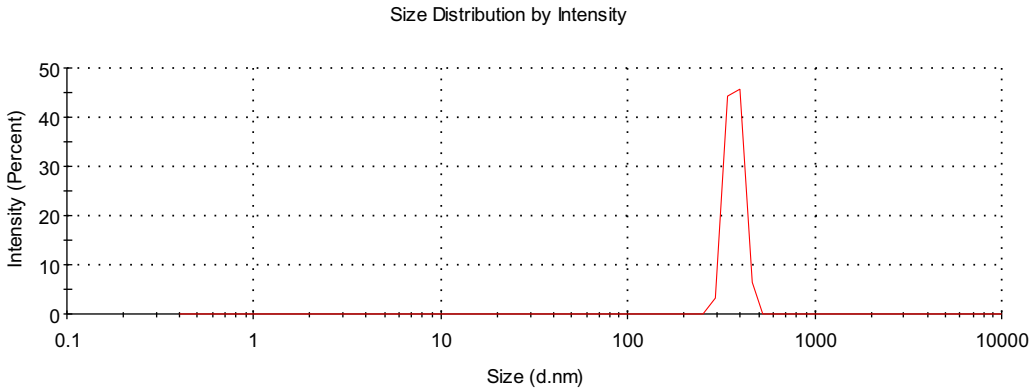

Fig. 2. DLS particles size distribution graph.

3.1.2. *Dynamic light scattering (DLS) measurements*

DLS measurements were performed to determine the particle size for CMP in solution. Fig. 2 shows the particle size distribution graph. Three measurements were performed and a mean hydrodynamic diameter value of 467.7 nm was determined. It is possible to observe that the mean particles size observed by DLS was smaller when compared to SEM particle sizes which were in micro-nanometer range. For DLS experiments, CMP sample was dissolved in 1% acetic acid promoting chitosan dissolution and possibly forming self-assembly nanoparticles. That is probably the reason why no microparticles were observed in solution. Heidari et al. [24] prepared nanoparticles of chitosan and polymethacrylic acid for metal adsorption and observed particles in aqueous solution ranging from 41 to 560 nm. They observed that a higher content of chitosans in the nanoparticles caused an increase in the particles sizes.

3.1.3. *Infrared spectroscopy (IR) of the encapsulated materials*

The main assignments and the "fingerprint" region from the IR spectra (Fig. 3) for CMP are shown in Table 1 [25–27]. The assignments for chitosan in CMP are characterized by the appearance of a band at 1560 cm^{-1} attributed to NH_2 and NH functional groups, also noted in the spectrum of chitosan itself as shown in a previous publication [25]. The weak absorptions in the range of 1510–1530 cm^{-1} and near 1630 cm^{-1} indicate the presence of a protonated amine group from chitosan [26]. The band at 1735 cm^{-1} may be due to the effect of the surfactant Tween 80 addition to the formulation promoting intermolecular interactions.

The presence of MA in the encapsulated samples was confirmed by the appearance of a high intensity peak at around 1494 cm^{-1} in the samples (Fig. 3), which is likely a shifted absorption band of MA at 1520 cm^{-1}. This band is not present in the chitosan spectra

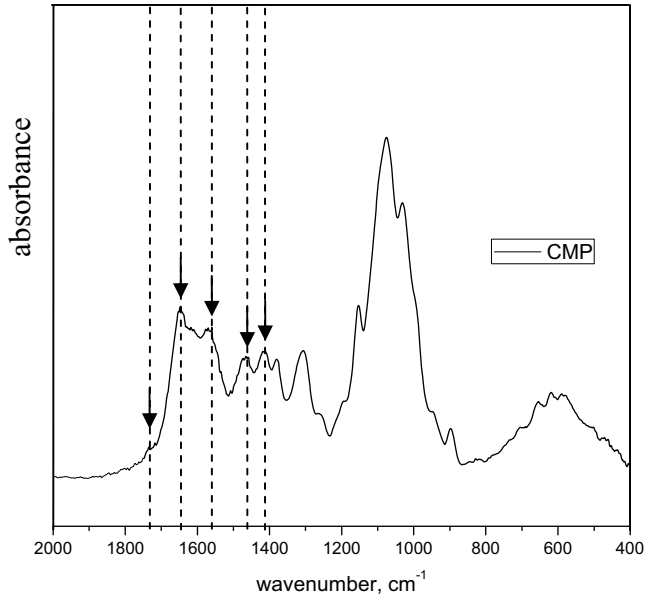

Fig. 3. FTIR spectrum for chitosan/mangiferin particles.

Table 1
Assignment of FTIR bands for chitosan/mangiferin particles [25–27].

Chitosan	Mangiferin	CMP	Assignment (cm^{-1})
1652		1649	νC=O (amide I) of chitosan and OH from trace or bound water
1560		1564	δNH_2 from amine and δNH (amide II) of chitosan
1520		1521	$\delta_s NH_3^+$ of chitosan
	1520	1494	νC=C aromatic ring of mangiferin
1425		1405	$\delta_s CH_2$ of chitosan
1380		1375	$\delta_s CH_3$ of chitosan
1155		1151	νC—O—C of chitosan
	1094	1100	—OH aromatic of mangiferin
1077		1103	νC—O—C of chitosan
1033		1021	Skeletal vibration involving νC—O of chitosan
920–580		920–580	Pulsation and some types of pyranose ring deformation

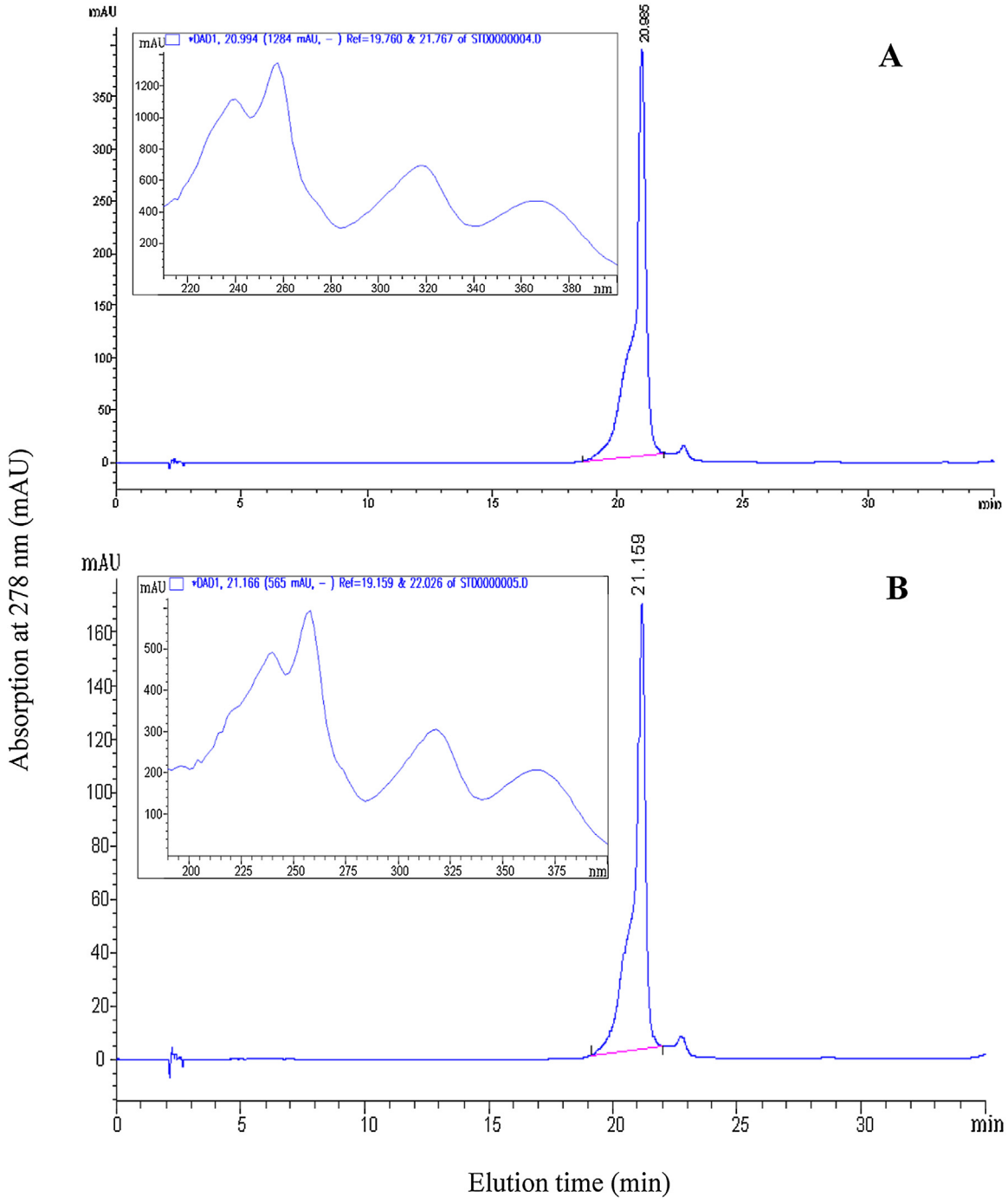

Fig. 4. HPLC chromatograms coupled with UV spectra for mang (A) and CMP (B).

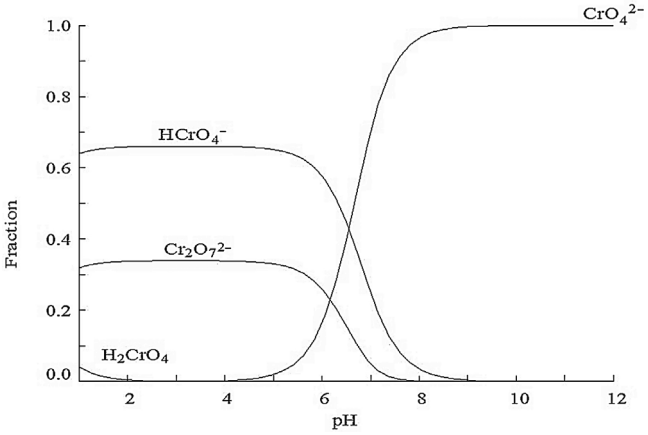

Fig. 5. Chromium speciation as a function of pH (Cr(VI) = 50 mg L^{-1}).

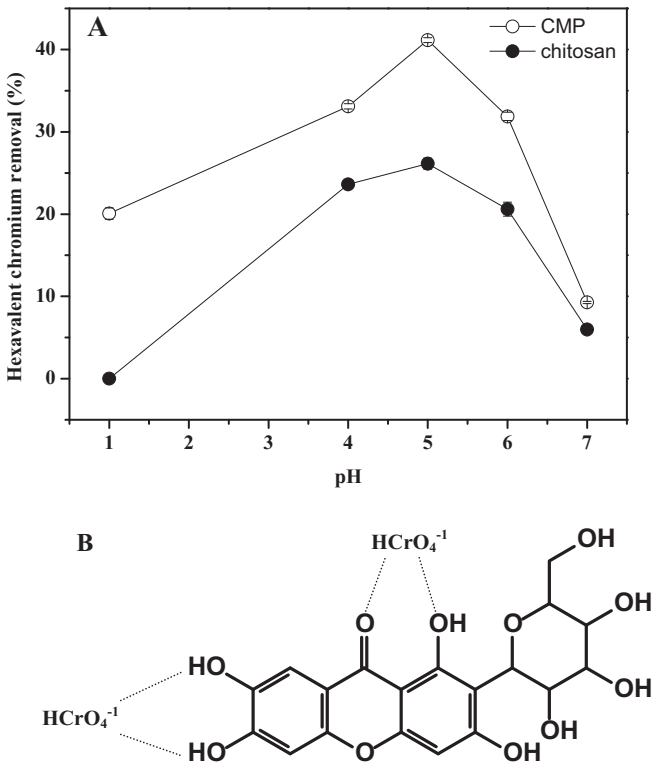

Fig. 6. Effect of pH of the solution to study the removal of chromium(VI) obtained by chitosan (●) and CMP (○) materials (A) and proposed interactions between MA and chromium(VI) species (B).

alone [25] and it was suggested in the previous work that it may be assigned to another conformation of MA molecule [8]. It is also possible to observe an intensification of the band at approx. 1100 cm^{-1} in the sample spectra compared to that of chitosan itself which may be due to the high absorption band at 1094 cm^{-1} for MA.

3.1.4. Analysis and quantification of MA in CMP by HPLC–UV

MA was detected and quantified in CMP by HPLC–UV. In the chromatograms of purified MA, an intense peak with a retention time (t_r) of approx. 21 min was observed (Fig. 4A). The HPLC–UV spectra of MA displayed the characteristic wavelengths at 240, 258, 274, 318 and 366 nm, in agreement with that published by Schieber et al. [28]. In the chromatogram of CMP, a low intensity MA peak at t_r = 21 min was detected (Fig. 4B). Standard curve was prepared in MeOH (optical absorbance at 278 nm *vs.* concentration, 50–1000 μM) for MA quantification. The equation was calculated by linear fit (Abs = 22.58 + 5.33 [MA], R = 0.9983). After extraction in MeOH and injection in the HPLC–UV, the integration value was obtained and the amount of MA in the encapsulated sample was then quantified using the standard curve equation. The MA concentration value in CMP was 136 μg/mg. That concentration was much higher than that observed in a previous work [8] and one of the reasons for that may be the stirring procedure during the spray-drying procedure resulting in a more homogeneous material. Even though the polymer chains may enhance the solubility of MA in aqueous medium, it was possible to observe that dispersion was formed and the stirring during spray-drying procedure ensured that a more homogenized material was obtained after drying.

3.2. Cr(VI) adsorption studies

3.2.1. Diagrams of chromium ion speciation

Fig. 5 shows the distribution of chromium species as a function of pH for Cr(VI) at a concentration of 50 mg L^{-1} (simulated using HYDRA software). The concentration of 50 mg L^{-1} corresponds to the initial concentration of chromium in the solution for chromium adsorption experiments. $HCrO_4^-$ and $Cr_2O_7^{2-}$ are the predominant species at the experimental concentration (Fig. 5) and these are the dominant components in a pH lower than 6.8. When the pH is above 6.8, CrO_4^{2-} is the dominant component of hexavalent chromium so initial solution pH is an important parameter for metal ions adsorption [23,29–32].

3.2.2. Effect of initial solution pH

The effect of solution pH on Cr(VI) removal by CMP is shown in Fig. 6A. Chitosan and CMP showed 26.14% and 41.13% removal of Cr(VI) at pH 5, respectively. That means a significative Cr(VI) adsorption improvement of 57.34% by CMP. At pH 5, values of Cr_{TOTAL} and Cr(VI) in both solutions were compared but no differences were found, indicating that only adsorption process of metal was involved. Vieira et al. [23] prepared a crosslinked chitosan for chromium reduction and removal. Anyway, the reduction process was most promoted by the crosslinker glutaraldehyde. In this study, it was observed that chitosan promoted only adsorption and that it may also occur by the hydroxyl and carbonyl groups of the natural compound MA at pH 5 (Fig. 6B) which explains the adsorption improvement of CMP shown in Fig. 6A.

After subtracting the Cr_{TOTAL} and Cr(VI) concentration values in the solutions, it was possible to determine the percentage of chromium reduction in aqueous solution, indicating the redox process. At pH 1, chromium adsorption by chitosan was not observed, however, CMP reduced 20.06% of Cr(VI) to Cr(III). That may be an important result as pH 1 represents the gastric environment pH, showing that CMP may reduced Cr(VI) already in the upper gastrointestinal tract. CMP showed improved Cr(VI) removal capacity in all pH range studied (1–7) showing that the material may be also used to remove Cr(VI) species in other environments of the gastrointestinal tract. At low pH values, it was observed the solubilization of chitosan due to the quaternization of the amine groups releasing MA to the medium and promoting the redox process [33,34].

MA (0.6 g L^{-1} and at pH 1) was placed in contact with hexavalent chromium and it was verified the ability of chromium reduction. It was found that 49.98% of Cr(VI) was removed *via* the reduction process. After analysis, the solution was evaluated by HPLC–UV (Fig. 7) and two peaks were observed: a first one with a retention time at approx. 23.6 min which presented the same MA UV spectrum (Fig. 7A) and a second with a retention time at approx. 24.2 min showing a different UV spectrum (Fig. 7B), probably due to a change in MA structure. That may be an indicative of the MA ability to

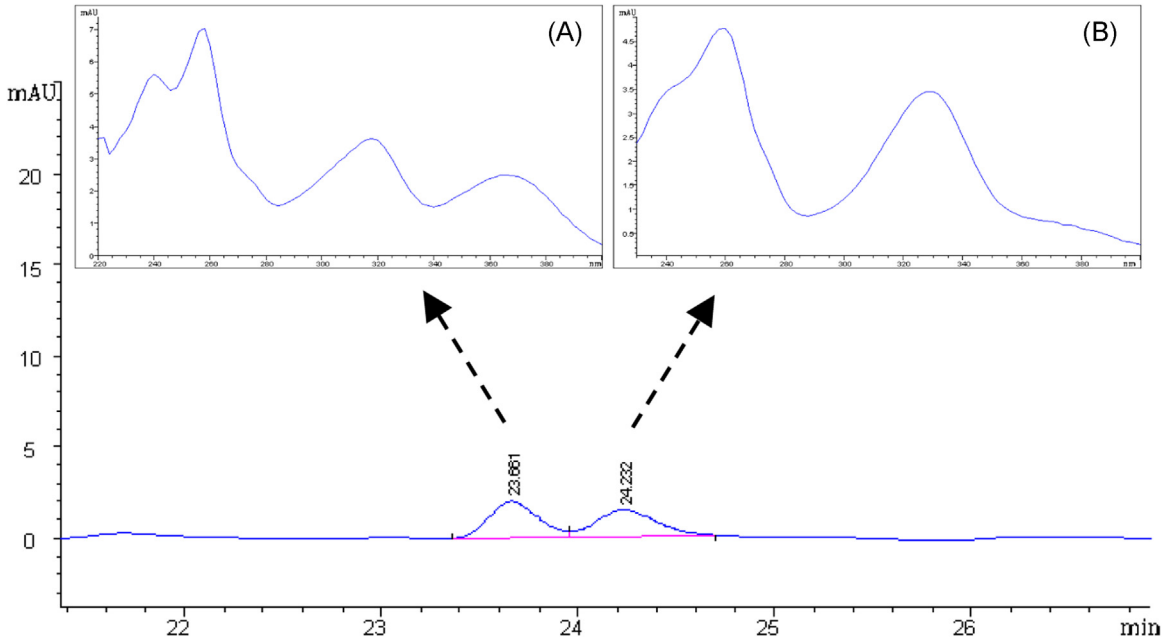

Fig. 7. HPLC chromatogram of the solution CMP + chromium after 1 h contact time. UV spectrum of mang (23.6 min) (A) was compared to the signal generated from the compound (24.2 min) (B).

reduce Cr(VI) to Cr(III) species. The shift on MA peak retention time when compared to Fig. 4 (t_r = 21 min) may be related to possible reactions between MA molecules and Cr(VI) species.

Agarwala et al. [35] demonstrated that MA has the potential to modulate cytotoxicity caused by mercury and may be attributed to quenching of radical oxidative species (ROS) generated in the cells due to oxidative stress induced by metal. Another advantage for MA is its nontoxicity at lower concentrations what makes it a safe compound to be used for chromium removal.

The pH_{PZC} of chitosan is 9.4 and the —NH and —OH present on the surface of this polymer are protonated in acid medium [36] promoting the electrostatic interaction between the adsorbent–sorbate systems. It was then decided to maintain the pH 5 for further experiments as it showed the best results.

3.2.3. *Effect of contact time and adsorbent dosage*

The influence of contact time on the adsorption capacity of chitosan and CMP (dose of 0.6 g L^{-1} at pH 5), at initial Cr(VI) concentration of 50 mg L^{-1} and at room temperature was determined (Fig. 8A). The removal of Cr(VI) increased with contact time. It was observed that the removal efficiency increased rapidly within the first 15 min and then continued to increase slowly until equilibrium at approx. 120 min. The rapid uptake among the first 15 min illustrated a high affinity between Cr(VI) and the adsorbent [32]. In 60 min it was observed the initial level and the time of experiment was defined. Both materials show similar behavior, differing only in the adsorption capacity (q).

Adsorbent dosage in solution is an important parameter. It determines the capacity of each adsorbent to remove a fixed initial concentration of Cr(VI). The adsorption capacities, qt, for 0.2 g L^{-1}, 0.4 g L^{-1}, 0.6 g L^{-1}, 1.2 g L^{-1} and 2 g L^{-1} were evaluated to be 60.56 mg g^{-1}, 54.92 mg g^{-1}, 45.41 mg g^{-1}, 29.94 mg g^{-1} and 21.09 mg g^{-1} respectively (Fig. 8B). Nair et al. [37] used chitosan–lignin composites for Cr(VI) removal using the material at a concentration of 4 g L^{-1} and it was observed a adsorption capacity value of 24.5 mg g^{-1}, showing not much difference for those obtained in this work.

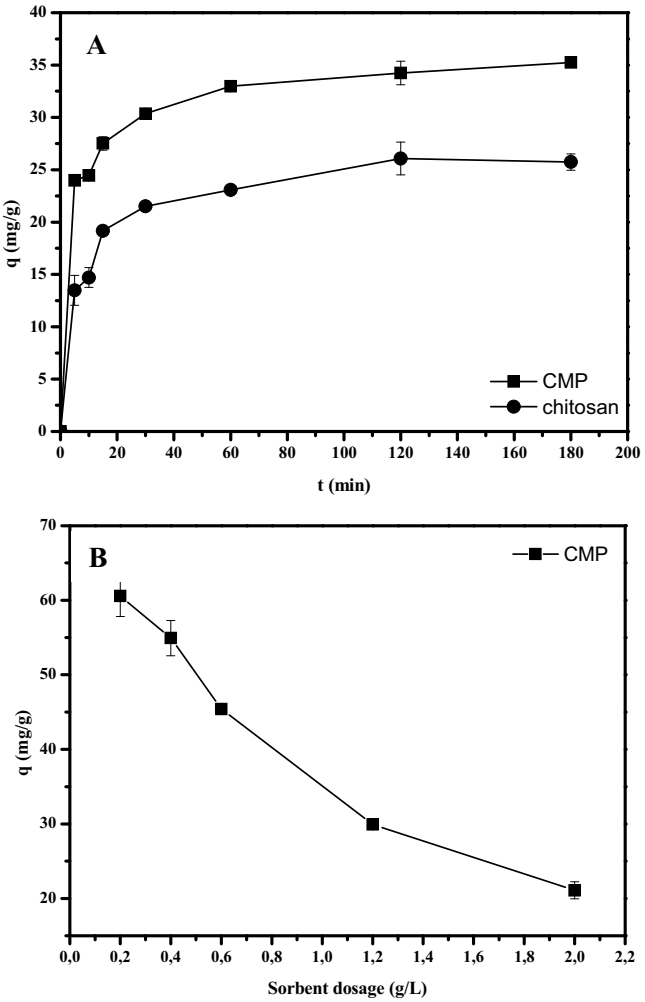

Fig. 8. Effect of contact time of the solution to study the removal of chromium(VI) obtained by chitosan (●) and CMP (■) material (A); effect of CMP dosage to study Cr(VI) removal (B).

4. Conclusions

Chitosan/mangiferin particles (CMP) were prepared by spray-drying technique and characterized by SEM, DLS, FTIR, HPLC–UV and adsorption studies for possible applications as a preventive material in human and animal contaminations with Cr(VI) species. SEM micrographies showed that CMP presented sizes ranging from nano to micrometers. DLS analyses for CMP dissolved samples presented hydrodynamic diameter around 468 nm. Chitosan and MA presence in the powder was confirmed by FTIR and MA was quantified as 136 μg/mg of chitosan particles. Adsorption experiments for chromium(VI) removal were performed and compared with chitosan. CMP showed improved adsorption when compared to chitosan itself. Chromium(VI) adsorption by chitosan and CMP showed to be pH dependent showing Cr(VI) reduction at pH 1 (gastric environment pH) and adsorption being most efficient at pH 5 when CMP improved Cr(V) removal in 57.34% compared to chitosan. It was also observed that besides adsorption, MA is also possibly removing chromium(VI) by redox process. Cr(VI) removal by CMP showed to be time and concentration dependent showing its maximum removal at approx. 120 min and also did show fast action in removing and reducing chromium(VI) in the first 30 min, what is an important parameter for a possible application as a poisoning prevention material in humans and animals. Further investigations should focus on the preventive evaluation of CMP in cells and living organisms.

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