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Preparation and characterisation of biodegradable pollen–chitosan microcapsules and its application in heavy metal removal

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HIGHLIGHTS

- Preparation of biodegradable, biocompatible and nontoxic pollen–chitosan microcapsule.
- Characterisation of pollen–chitosan microcapsules by SEM, FTIR, TGA and EA.
- Application in heavy metal removal: Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II).
- The novel pollen–chitosan biosorbents showed higher performance in Cd(II) removal.
- *C. sempervirens* pollen–chitosan microcapsules showed the highest removal performance.

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ABSTRACT

Biosorbents have been widely used in heavy metal removal. New resources should be exploited to develop more efficient biosorbents. This study reports the preparation of three novel chitosan microcapsules from pollens of three common, wind-pollinated plants (*Acer negundo*, *Cupressus sempervirens* and *Populus nigra*). The microcapsules were characterized (Fourier transform infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy and elemental analysis) and used in removal of heavy metal ions: Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II). Their sorption capacities were compared to those of cross-linked chitosan beads without pollen grains. *C. sempervirens*-chitosan microcapsules exhibited better performance (Cd(II): 65.98; Cu(II): 67.10 and Zn(II): 49.55 mg g^{-1}) than the other microcapsules and the cross-linked beads. *A. negundo*-chitosan microcapsules were more efficient in Cr(III) (70.40 mg g^{-1}) removal. *P. nigra*-chitosan microcapsules were found to be less efficient. Chitosan–pollen microcapsules (except *P. nigra*-chitosan microcapsules) can be used in heavy metal removal.

1. Introduction

Heavy metal ions are discharged into water bodies via industrial operations such as mining, metal finishing, plating, tannery and fertilizer production. Water bodies that have been contaminated with heavy metal ions are posing risks to the environment (Bilal et al., 2013). Certain heavy metal ions, even in small amounts, are capable of bio-accumulating in the tissues of living organisms and are responsible from developing various diseases and disorders (Abou El-Reash et al., 2011). Many attempts employing various techniques (e.g. co-precipitation, solid phase extraction, ion-exchange separation and adsorption) have been made to remove or recover heavy metal ions from waste waters. However, amongst the techniques mentioned, adsorption manifests itself as an effective and simple method (Sarkar and Majumdar, 2011). Many studies have shown biosorbents are excellent adsorbents (Wan Ngah et al., 2011).

Researches on developing biodegradable and eco-friendly biosorbents demanding less chemical treatment during production are on the rise in the last decades. Various sorbents with biological origin, like fungi (Damodaran et al., 2014), algae (He and Chen, 2014), bacteria (Kieu et al., 2011) and yeasts cells (Machado et al., 2010) have been developed for removal and recovery of metal ions from aqueous solutions. Biosorbents have been proved to be effective and, in some cases, superior to the chemical resins

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in some ways: they are effective, low cost, available in large quantities and more importantly have already carry functional groups including amino, carboxyl, hydroxyl and carbonyl (Wang and Chen, 2009).

Chitosan is a naturally occurring carbohydrate polymer which can meet the above mentioned traits: it is biocompatible, biodegradable and nontoxic to human and environment and shows antimicrobial and antioxidant activities (Muzzarelli, 2011). These excellent physicochemical features have put chitosan in a unique position amongst the biopolymers: it has found broader applications in a number of fields including pharmaceutics and medicine (Ong et al., 2008), food industry (Aider, 2010), textile (Alonso et al., 2009) and water treatment (Hu et al., 2013).

Chitosan also has high affinity towards metal ions due to metal ion binding groups (e.g. $-NH_2$ and –OH) on its polymeric chains (Wu et al., 2010). Chitosan, in raw (Paulino et al., 2007) or functionalized (Wang et al., 2013) form, is one of the widely utilized biosorbents in removal or recovery of heavy metal ions. Among the chitosan-based sorbents, chitosan composites have gained attention and have been considered as an alternative to the conventional biosorbents in recent years. Various chitosan composites with biological materials (e.g. cellulose, cotton, oil palm ash, silk and alginate) have been prepared and used in heavy metal removal (Wan Ngah et al., 2011; Wang and Chen, 2014). However, chitosan composites adsorbents with pollen grains have not been reported in the literature.

This is the first study to report the preparation and use of pollen–chitosan composite microcapsules in heavy metal removal. Pollen grains were preferred: (1) since pollens are biomaterial, (2) they are already fine powder and therefore can be easily covered with chitosan and (3) they can be harvested in large quantities when needed. Modification of chitosan composites is easily achieved via crosslinking in glutaraldehyde solution by forming Schiff base. On the other hand, azomethine formation from free amino groups on chitosan polymer reduces metal sorption capacity of the polymer by eliminating coordination sites for metal ions. This study aimed to find out whether pollen grains entrapped in chitosan matrice are capable of counterbalancing this loss and enhancing metal binding capacity of cross-linked chitosan by increasing metal sorption sites, surface area and the porosity of the microcapsules. Chitosan composite microcapsules with pollen grains from three common plant species were prepared: *Acer negundo*, *Cupressus sempervirens* and *Populus nigra*. Pollen grains from these plants can be harvested easily because these anemophilous plants are wind-pollinated and therefore produce large quantities of pollen grains (Çeter et al., 2011). The present work deals with (1) preparation of three different chitosan–pollen microcapsules, (2) characterisation of the microcapsules employing Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and elemental analysis (EA) and (3) assessment of the heavy metal (Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II)) sorption capacities of the three biosorbents and glutaraldehyde cross-linked chitosan beads without pollen grains.

2. Experimental

2.1. Pollen samples collection and identification

The male cones from *P. nigra*, *C. sempervirens* and *A. negundo* were collected in Kastamonu, Turkey and were identified with reference to the guide book by Coode and Cullen (1965). The cones were kept in an oven at 25 °C for 1–2 days to release the pollen grains. The pollen grains were sieved to remove any other material and 95% of pollen purity was ensured. Then, the pollen grains were kept at −20 °C.

The plant samples are kept at the palynology laboratory at Vocational College, Kastamonu University. *P. nigra* L. (08.04.2013, Voucher: Ceter 56) and *A. negundo* L. (30.03.2013, Voucher: Ceter 49) cones were collected from the garden of Kastamonu University Vocational College and *C. sempervirens* L. (30.03.2013, Voucher: Ceter 50) cones were from the garden of Kastamonu İlbank.

2.2. Materials

Chitosan powder (medium molecular weight), $Cd(NO_3)_2{\cdot}4H_2O$ and NaOH were obtained from Sigma–Aldrich. Glutaraldehyde solution (GA) (25% in water, v:v), the metal salts ($Ni(NO_3)_2{\cdot}6H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, $Zn(NO_3)_2{\cdot}4H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$), acetic acid and HCl were purchased from Merck. Methanol was obtained from AnalaR Normapur.

2.3. Preparation of chitosan–pollen microcapsules and cross-linked chitosan beads

Chitosan (1.000 g) was dissolved and stirred in 50 ml of 2% acetic acid solution. 0.500 g of pollen grains was added to the chitosan solution. To ensure homogeneity, the mixture was stirred for 2 h. Then, the mixture was transferred into a burette. The mixture was dropped into a coagulation solution (100 ml of water, 150 ml of methanol and 30.0 g NaOH) (Pal et al., 2013). The microcapsules were kept in the coagulation solution overnight. Then, they were removed from the solution by filtration. The microcapsules were rinsed with plenty of distilled water to neutrality. Then, the microcapsules in water were recovered by a sieve and transferred into cross-linking reaction solution (mixture of 30 ml of methanol and 0.3 ml of GA) and stirred gently under reflux at 70 °C for 6 h. Finally, to remove any unreacted GA molecules, cross-linked microcapsules were rinsed with ethanol and water and finally dried at room temperature. Cross-linked chitosan beads without pollen grains were also prepared following the same method.

2.4. Characterisation of the pollen–chitosan microcapsules

2.4.1. FT-IR spectroscopy

The IR spectra of pollen–chitosan microcapsules were recorded with a Perkin Elmer FT-IR Spectrometer over the frequency range of 4000–625 cm^{-1}.

2.4.2. Elemental analysis

Elemental analysis of the pollen–chitosan microcapsules was performed using Thermo Flash 2000.

2.4.3. SEM analysis

The pollen–chitosan microcapsules were coated with gold for SEM analysis by Sputter Coater (Cressingto Auto 108). The surface characteristics of the samples were examined by a QUANTA FEG 250 scanning electron microscope.

2.4.4. TGA analysis

Thermogravimetric analysis of the microcapsules were conducted using EXSTAR S11 7300 at a heating rate of 10 °C min^{-1}. The samples were heated up to 650 °C.

2.5. Heavy metal sorption experiments

The pollen–chitosan microcapsules or cross-linked chitosan beads (0.1000 g) were added to metal solution (25 mL of 10 mg L^{-1} at metal solution pH; Cd(II): 5.35, Cr(III): 4.63, Cu(II): 5.18, Ni(II): 5.34, Zn(II): 5.34) and agitated on a shaker (Heidolph Promax 2020) at 200 rpm for 4 h. Then, the sorbent was removed from the solution with a filter paper. The metal ion concentration in