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Microfungal spores (Ustilago maydis and U. digitariae) immobilised chitosan microcapsules for heavy metal removal

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ABSTRACT

Designing effective chitosan-based biosorbents from unexploited biomass for heavy metal removal has received much attention over the past decade. *Ustilago*, loose smut, is a ubiquitous fungal plant pathogen infecting over 4000 species including maize and weed. This study aimed to establish whether the spores of the phytopathogenic microfungi *Ustilago* spores can be immobilised in cross-linked chitosan matrix, and it reports findings on heavy metal sorption performance of chitosan/*Ustilago* composite microcapsules. Immobilisation of *Ustilago maydis* and *U. digitariae* spores (from maize and weed) in chitosan microcapsules was achieved via glutaraldehyde cross-linking. The cross-linked microcapsules were characterised using scanning electron microscopy, FT-IR spectroscopy and thermogravimetric analysis. Sorption capacities of chitosan-*U. maydis* and chitosan-*U. digitariae* microcapsules were investigated and compared to cross-linked chitosan beads: Cu(II): 66.72, 69.26, 42.57; Cd(II): 49.46, 53.96, 7.87; Cr(III): 35.88, 49.40, 43.68; Ni(II): 41.67, 33.46, 16.43 and Zn(II): 30.73, 60.81, 15.04 mg/g, respectively. Sorption experiments were conducted as a function of initial metal ion concentration (2–10 mg/L), contact time (60–480 min), temperature (25, 35 and 45 °C), amount of the sorbent (0.05–0.25 g) and pH of the metal solution. The microcapsules with spores exhibited better performance over the plain chitosan beads, demonstrating their potential use in water treatment.

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1. Introduction

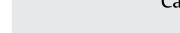
Heavy metal contamination of water bodies is a critical issue. Untreated effluents of the plating, mining and textile manufacturing industries have introduced significant amount of heavy metal ions into the environment (Bilal et al., 2013). Many heavy metal ions have been reported to have detrimental impacts on living organisms (Abdolali et al., 2014; Abou El-Reash, Otto, Kenawy, & Ouf, 2011; Ghasemi et al., 2014). These ions have a recalcitrant nature; that is, they are non-biodegradable and are capable of accumulating in the food chain. Unfortunately, it requires much effort to remove them once they have been introduced into the environment. On the other hand, metal ions also have a tendency to interact with the surfaces providing coordination or chelating sites to bind; thus, making it possible to use various materials with functionalised surfaces in the removal of heavy metal contaminants (Yavuz, Altunkaynak, & Guzel, 2003). In this sense, adsorption is considered

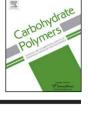
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http://dx.doi.org/10.1016/j.carbpol.2015.11.065 0144-8617/© 2015 Elsevier Ltd. All rights reserved. a simple and versatile tool (Ali & Gupta, 2007), but its effectiveness is largely determined by the selection of the adsorbent (Fomina & Gadd, 2014).

Adsorbents with biological origins have advantages over those of chemical origins; they are nontoxic, biodegradable and abundant in the biosphere (Wang & Chen, 2009). However; biosorbents are not always available in desired form, requiring much chemical modification for fictionalisation or physical treatment to ensure appropriate size and monodispersity (Ngah, Teong, & Hanafiah, 2011). In recent years, due to the functional moieties on their cell walls and their uniformity of size, many bacteria, fungi and algae species, living and dead, have been exploited in studies aimed at developing biosorbents for heavy metal removal (Cataldo, Gianguzza, Pettignano, & Villaescusa, 2013; Rouhollahi, Zamani, Karimi, & Etesami, 2014; Won, Kotte, Wei, Lim, & Yun, 2014).

Fungi are ubiquitous and abundant in the biosphere. Many species have been widely used in heavy metal uptake due to their affinity and selectivity for a wide range of metal ions. However, in literature no attention has been paid to the use of smut fungi genus *Ustilago* in biosorption studies (Wang & Chen, 2009). These organisms are fungal plant pathogens distributed worldwide. They







cause substantial losses in crop yield and biomass (Gallart, Mas, & Verdu, 2009) by infecting over 4000 species (Ruiz-Herrera, Ortiz-Castellanos, Martínez, León-Ramírez, & Sentandreu, 2008). Ustilago maydis and Ustilago digitariae are two common Ustilago species. These biotrophic fungal pathogens cause smut disease in maize (Mueller et al., 2008) and weed, Digitaria (Gallart et al., 2009).

Chitosan is a cationic biopolymer produced by alkali-catalysed deacetylation of chitin, and there has been extensive research regarding its metal binding nature (An, Jung, Zhao, Lee, & Choi, 2014; Lang et al., 2013; Muzzarelli, 2011; Shukla, Mishra, Arotiba, & Mamba, 2013). In designing composite biosorbents, chitosan carriers have been preferred for the immobilisation of fine particles due to the ease of cross-linking with them (Abdel-Mohsen, Aly, Hrdina, Montaser, & Hebeish, 2012). Cross-linked chitosan composites have received much attention in recent years due to their efficiency in heavy metal removal (Kadouche et al., 2012; Karthik & Meenakshi, 2014; Ngah et al., 2011; Zhang, Xia, Liu, & Zhang, 2015). So far, various materials such as algal biomass (Liu et al., 2011), bentonite (Huang, Liu, Zhang, & Yang, 2015), graphene oxide (Ge & Ma, 2015) and lignin (Nair, Panigrahy, & Vinu, 2014) have been incorporated into cross-linked chitosan matrix to enhance the affinity of chitosan for contaminants. However, there are no reports on the preparation of chitosan composite microcapsules with microfungus spores for heavy metal removal.

Designing biosorbent with microfungal spores and chitosan can be beneficial in some ways: (1) These fungal pathogens are abundant and widely distributed in many areas; (2) collection of these smut spores, particularly swollen host tissue of smut on the ears of maize, can help to reduce the area of the infected fields, preventing the spread of the disease and thereby lowering the use of chemical fungicides (Gallart et al., 2009; Kassa, Menzies, & McCartney, 2015); (3) size (10 μ m) (Hu, Linning, & Bakkeren, 2003) and (4) surface characteristics of the spores (Won et al., 2014) facilitates preparation of chitosan microcapsules without need of any pretreatments; and (5) the cell walls of these spores have functional groups which are capable of interacting with metal cations (Won et al., 2014).

The present study aimed to provide insights into the production of smut spores immobilised cross-linked chitosan microcapsules for heavy metal sorption. The spores of *U. maydis* and *U. digitariae* were easily fixed in chitosan matrix via cross-linking of chitosan polymeric chains with glutaraldehyde. Characterisation studies were carried out by Fourier Transform Infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA) and scanning electron microscope (SEM). Cu(II), Cd(II), Cr(III), Ni(II) and Zn(II) sorption performance of the microcapsules were evaluated and compared to that of the cross-linked chitosan beads without smut spores.

2. Materials and methods

2.1. Materials

Chitosan powder (medium molecular weight), NaOH, nitrate salt of cadmium ethanol and ethylenediaminetetraacetic acid disodium salt (EDTA-Na₂) were obtained from Sigma–Aldrich. The nitrate salts of the metals (Cr, Cu, Ni and Zn), acetic acid and glutaraldehyde solution (25% in water, v:v) were purchased from Merck. Methanol was from Analar Normapur. In the experiments double distilled water was used.

2.2. Smut spore collection

The plants (*Digitaria*) infected by loose smut (*U. digitariae* (*Kunze*) *Rabenh*) (May 2013; Aksaray, Turkey) and the smutted

(*U. maydis*) maize ears (September 2013; Kayseri, Turkey) were collected. The smutted panicles of the weed and ears of the maize were removed and allowed to air-dry. In isolation of spores the method reported in an earlier work was followed (Bhuiyan, Croft, James, & Cox, 2012). Briefly, the dried samples were crushed and sieved through a metal mesh (1 mm \times 1 mm) to remove any plant debris.

It has already been reported that non-covalently-bound proteins or proteins bound through alkali-sensitive linkages on the cell of Ustilago spores can be released by mild alkali treatment (Ruiz-Herrera et al., 2008). Also, a recent study demonstrated that alkali solution treatment of Ustilago spores could effectively remove the melanin pigment from the spores (Chen, Wang, Shu, Zhu, & Zhou, 2015). Therefore, following the light microscope examination, the isolated spores were rinsed with water and then treated with 0.5 M NaOH solution for 12 h to remove any organic or inorganic residues in the hyphae and mycelial components of the spores. Subsequently, treated spores were rinsed with distilled water to neutrality and were allowed to air-dry. On the other hand, when preparing microcapsules with untreated spores, chitosan solution lost its viscosity and got thinner; this made the formation of spherical microcapsules in coagulation solution (mixture of water, methanol and NaOH) (infra vide) impossible. Additionally, untreated spores in coagulation solution gave decomposition products by giving the solution dark brown colour. To prevent the chitosan solution from getting thinner and the leakage of decomposition products in the coagulation solution, spores were first subject to the alkaline treatment in NaOH solution and then they were used.

2.3. Preparation of the sorbents

Chitosan solution of 2% (w:v) was prepared by dissolving 3.00 g of chitosan in acetic acid solution (150 mL, 2% v:v). The mixture was stirred with a magnetic stirrer for 24h to assure the complete dissolution of chitosan. Then, 1.50g of microfungi spores (U. maydis or U. digitariae) was added into the chitosan solution and agitated for 4h. Formation of the U. maydis or U. digitariaechitosan microcapsules was achieved by dropping the mixture of microfungi spores-chitosan into a gelation solution containing NaOH, water and methanol (60 g:200 mL:300 mL) (Pal, Pan, & Saha, 2013). The resulting microcapsules were kept in the gelation media overnight. Then, they were separated by filtration and were washed with distilled water until neutrality. Then, the cross-linking of the microcapsules was carried out by refluxing wet microcapsules in a solution of methanol and glutaraldehyde (methanol: 90 mL and glutaraldehyde solution: 0.9 mL) at 70 °C for 6 h with a gentle stirring. The cross-linked microcapsules were recovered with a sieve, washed first with ethanol and then with distilled water. The wet microcapsules were air-dried at room temperature. The same preparation and characterisation method was observed for preparation of the plain chitosan microbeads without microfungal spores.

2.4. Characterisation of Ustilago spores immobilised chitosan microcapsules

Scanning electron microscopy (Scanning Electron Microscope EVO LS 10 ZEISS) was employed to examine the surface morphology of the smut spores immobilised chitosan microcapsules and the plain chitosan microbeads. FT-IR spectra of the microcapsules and the plain chitosan microbeads were recorded with a Fourier Transform Infrared Spectrophotometer (Perkin Elmer 100 FT-IR). Thermal degradation of the microcapsules was performed with an EXSTAR S11 7300 under nitrogen atmosphere (heating rate: 10 °C/min).

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