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Letter to the Editor

Modification of chitosan with carbamoyl benzoic acids for testing its coagulant-flocculant and binding capacities in removal of metallic ions typically contained in plating wastewater

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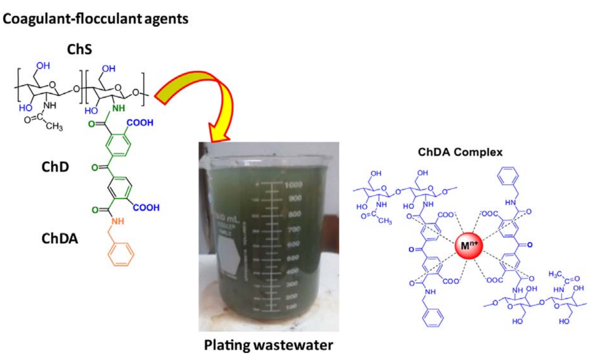
GRAPHICAL ABSTRACT



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ABSTRACT

This paper proposes the use chitosan modified with carbamoyl benzoic acids as new coagulant-flocculant agents for metals removal from aqueous solutions. The grafted chitosan species as chitosan dianhydride (ChD) and chitosan dianhydride-amine (ChDA) improved the removal of Cu^{2+}, Pb^{2+}, Ca^{2+}, Cr^{3+}, Zn^{2+} and Ni^{2+}, compared with chitosan alone. Zeta potential measurements predict doses and allowed to calculate binding constants between the new coagulant-flocculant agents and metallic cations (from 10^4 to 10^5 M^{-1}). After the coagulation-flocculation, solids were analyzed by SEM and EDS. SEM images show the texture of solids depending on the functional group grafted on chitosan. EDS study of solids containing chitosan dianhydride-metals (average of all scanner areas) revealed the wt% of metals: Cr (10.45%), Cu (5.95%), Ni (5.22%), Zn (4.36%), Pb (1.37%), Cd (0.31%) and Ca (0.10%) For recovered solids containing chitosan dianhydride-amine-metals, the observed wt% appeared in the same order: Cr (12.44%), Cu (6.75%), Ni (5.75%), Zn (5.12%), Pb (1.82%), Cd (0.59%) and Ca (0.12%).

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1. Introduction

Recently, wastewater treatment has been carried out using diverse types of natural polymers such as chitosan to innovate the coagulation-flocculation processes [1]. However, due to the presence of various pollutants in industrial wastewater, the effectiveness of the treatment depends on the quantity and type of polyelectolyte. For this reason, the combination of natural and synthetic materials to improve their performance represents a new challenge for material science and environmental engineering. In the case of coagulant-flocculant agents, the scope is to combine a biopolymer with a synthetic polymer to obtain better metal binding agents as well as biodegradable and eco-friendly chemicals, recommended for primary wastewater treatments. Among the biopolymers, chitosan has been described as a non-toxic cationic linear molecule with high molecular weight and biodegradable [2,3]. Some authors have also shown that chitosan works well for heavy metals removal [4,5]. However, its use is limited because of its low solubility in water [6]. Due to chitosan usefulness, it has been reported that a modification of a chitosan matrix improved its environmental applications [7–9], antimicrobial ability [10] and pharmacological uses [11]. However, there are almost no reports about the combination of chitosan and inexpensive synthetic compounds as carbamoyl benzoic acids that could have advantages over synthetic polymers in wastewater treatment. In this work, it is expected that the modification of chitosan with carbamoyl benzoic acids increase the polymer solubility and binding properties to remove metals typically contained in plating wastewater. From the environmental point of view, the chemical modification of chitosan (aldehydes, acids) [4] represent an attractive alternative to conventional treatments. In particular, the new compounds are expected to present a synergistic effect combining chitosan eco-friendly characteristics [12] and the binding power if carbamoyl benzoic acids with heavy metals.

Concerning the quality of wastewater, turbidity and color are caused by very small particles identified as colloids [13,14]. In the case of metallic ions, they remain suspended in water for long time and can pass through very fine filters. To remove these metallic ions coagulation-flocculation processes are usually performed [15]. Coagulation aims to destabilize suspended particles facilitating agglomeration [16]. In general, these particles coalesce to form a floc that can be readily removed by decantation procedures and filtration. It is important that coagulation-flocculation processes are properly used [17], to prevent the production of small or very light solids and provides insufficient decantation; while the water reaching the filters contain a large amount of floc particles which quickly dirty filters and require frequent washings. On the other hand, when the flocs are fragile, it breaks into small particles that can pass through the filter and alter water quality.

Trying to find the correct combination of a natural polymer as chitosan and a synthetic metal binder we found a study of a supramolecular compound cross-linked with metallic ions, as well as a chemical modification of chitosan with diverse groups to improve the separation of metallic ions used in biomedical field [18]. To our knowledge there are no reports on the anchorage of carbamoyl benzoic acids in chitosan. In a previous work, carbamoyl benzoic acids were tested as separation agents of Pb^{+2} by combining chelating and coagulation-flocculation process [5]. It is also important to mention that carbamoyl benzoic acids did not work to separate other metals, for this reason this paper propose to modify chitosan molecule with carbamoyl benzoic acid to test its capacity to remove metallic cations including Pb, Cu, Cd, Zn Ni, Cr, and Ca that are typical in industrial waste water.

2. Materials and methods

2.1. Materials and reagents

Deionized water (resistivity: 18.2 MΩ, MilliQ. Advantage A10) was used for sample preparation in all experiments. 3,3′,4,4′-benzophenonetetracarboxylic dianhydride, benzyl methyl amine and low molecular weight chitosan (**ChS**) were purchased from Sigma-Aldrich in highest available purity (> 99%). All solvents were of spectroscopic or HPLC grade. Zeta potential data was recorded on a Stabino Particle Charge Mapping. The measurements were done at room temperature in porcelain cuvettes. Sample solutions used to study the pH dependence of the potential zeta were prepared adjusting to the desired pH, with 0.1 M NaOH and 0.1 M HCl. The effect of metal cations upon the zeta potential was examined by adding a few microliters of stock solution (0.1% w/w) of the study metal cations to a known volume of the solution (10 mL). The addition was limited to 0.3 mL, so that dilution remained insignificant [19]. ^{1}H NMR spectra were obtained in a Bruker 400 MHz NMR Spectrometer at a probe temperature of 25 °C with TMS as the internal standard. The FT-IR spectra were recorded on an FT-IR ATR Spectrum Two Perkin Elmer. Metal ion concentrations were determined using Agilent Technologies 4200 MP-AES. Various formulations of the derivatives were placed in cylindrical glass cells and submitted to separation kinetics in a Turbiscan Lab®. For metal estimation in solid phase formed from coagulation-flocculation tests. The solid samples were examined in a SEM ZEISS EVO-MA15, equipped with a EDS (energy dispersive spectroscopy) BRUKER detector.

2.2. Preparation of chitosan derivatives

To prepare chitosan dianhydride, **ChD**, the procedure was as follows: **ChS** (1 g) was gradually added, under constant mechanical stirring, into 100 mL aqueous acetic acid 0.7% (v/v). After complete dissolution, 6 mL of 3,3′, 4,4′-benzophenonetetracarboxylic dianhydride (0.67 g) in ethanol were added dropwise. To prepare Chitosan dianhydride-amine, **ChDA**, the above mentioned mixture was combined with benzylamine (0.4 mL added dropwise). Each derivative ethanol solution was stirred in a water bath at 50 °C for 5 h. After preparation both derivatives were precipitated by adding an adequate amount of acetone. A final purification step was done for 24 h. M.p. > 400 °C.

2.3. Zeta potential vs. pH plots for the *ChD* and *ChDA* derivatives

The zeta potential plots of ***ChD*** and ***ChDA*** derivatives were performed to evaluate the pH influence over the surface charge, in particular to determine the amine protonation capacity. The measurements were done at room temperature in porcelain cuvettes. The experiments were done for ***ChD*** and ***ChDA*** (0.1%) derivatives within a pH range of 2–11 using 0.1 M NaOH and 0.1 M HCl to adjust the desired value.

2.4. Affinity study *ChD* and *ChDA* derivatives with different metal cations

The binding properties of ChD and ChDA with different metal cations (Cu^{2+}, Pb^{2+}, Ca^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Cr^{3+}) were studied in aqueous solutions to establish their application as new coagulation-flocculation agents for environmentally important metal cations. The chitosan derivatives were titrated by successive increment of equivalent number of cations followed by zeta potential measurements.

2.5. Turbiscan lab® Expert stability analysis

After obtaining zeta potential plots, the proper dose of each chitosan derivative were chosen and added to a synthetic wastewater (**SWW**). Stability tests were carried out, performing a transmittance scan every 25 s for 4 h. The measurement principle for this technique is based on detecting the changes in transmission and backscattering, as a function of particle movements.