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Removal of Cu (II), Co (II) and Ni (II) Ions from Aqueous Solutions Using Modified Sporopollenin

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Abstract
In this study, (E)-2-((2-hydroxynaphthalen-1-yl)methyleneamino)pyridin-3-ol(HNMAP) compound was immobilized on sporopollenin of Lycopodium clavatum spores. The obtained structure was characterized by infrared spectroscopy (IR) and scanning electron microscopy (SEM). This newly synthesized compound has been used as an adsorbent in the separation of heavy metals. Batch method was used to separate Cu (II), Co (II) and Ni (II) ions from waste waters. In addition, different experimental parameters such as pH, concentration and duration of interaction were selected to effectively separate heavy metals from aqueous solution and wastewater. The experimental results were applied to Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm equations. Thermodynamic parameters such as free energy (ΔG^0), entropy (ΔS^0) and enthalpy (ΔH^0) were calculated from the experimental results to explain the mechanism of the sorption. As a result, this adsorbent has been successfully used to separate Cu (II), Co (II) and Ni (II) from aqueous solutions and waste water.

Keyword: *Immobilization, Wastewater, Heavy metals, Sporopollenin*

INTRODUCTION

Heavy metal levels are increasing day by day in drinking and irrigation waters. This increase leads to a serious threat to human health and ecological systems [1]. Many heavy metals such as Pb, Cd, Co, Ni, Cr and Hg have toxic effects on living organisms.

These metals can harm flora, fauna and other living things even in very small quantities. Their accumulation in humans causes kidney failure, nervous system damage and bone softening, as well as other serious illnesses [2].

Many methods such as precipitation, adsorption, ion exchange, photocatalyst and membrane are used to separate heavy metal ions. Adorption method is widely used for elimination of the heavy metal ions. For this method, adsorbent materials such as resins, clays, silica gel, activated carbon and biological materials [1] are used. For this purpose, one of the most widely used materials in recent times is the sporopollen [3].

Sporopollenin of Lycopodium clavatum spores has a stable aromatic structure and contains carbon, hydrogen, and oxygen. Sporopollenin is produced by monomer structures of the macromolecular sporopollenin. It has a stable, cross-linked structure and an aromatic character that contains carbon, hydrogen, and oxygen with a stoichiometry of $C_{90}H_{144}O_{27}$. The modification of sporopollenin was achieved via chemical immobilization of the appropriate organic groups onto sporopollenin surface [4-5].

MATERIALS AND METHODS

Materials

Sporopollenin (Merck Darmstadt Co.) was used as adsorbent in this study. $Cu(NO_3)_2$, $Co(NO_3)_2$ and $Ni(NO_3)_2$, (3-Chloropropyl)trimethoxysilane [CPTS] and (E)-2-((2-hydroxynaphthalen-1-yl)methyleneamino)pyridin-3-ol (HNMAP) were purchased from Merck. All chemicals used in the study were analytical graded. Ultra pure water was used in experimental study.

Instruments

Infrared spectra were measured in the range of 650–4,000 cm^{-1} by a Perkin Elmer 100 FT-IR spectrometer (KBr pellets, 21 ℃ temperature, 39% moisture, 1 atm pressure). The pH values were monitored with pH meter. The thermostatic shaker was used for the sorption experiments. The heavy metal concentrations were determined by UV-Visible Spectroscopy. All aqueous solutions were prepared with ultra pure distilled water obtained from a water purification system (Millipore Milli-Q Plus).

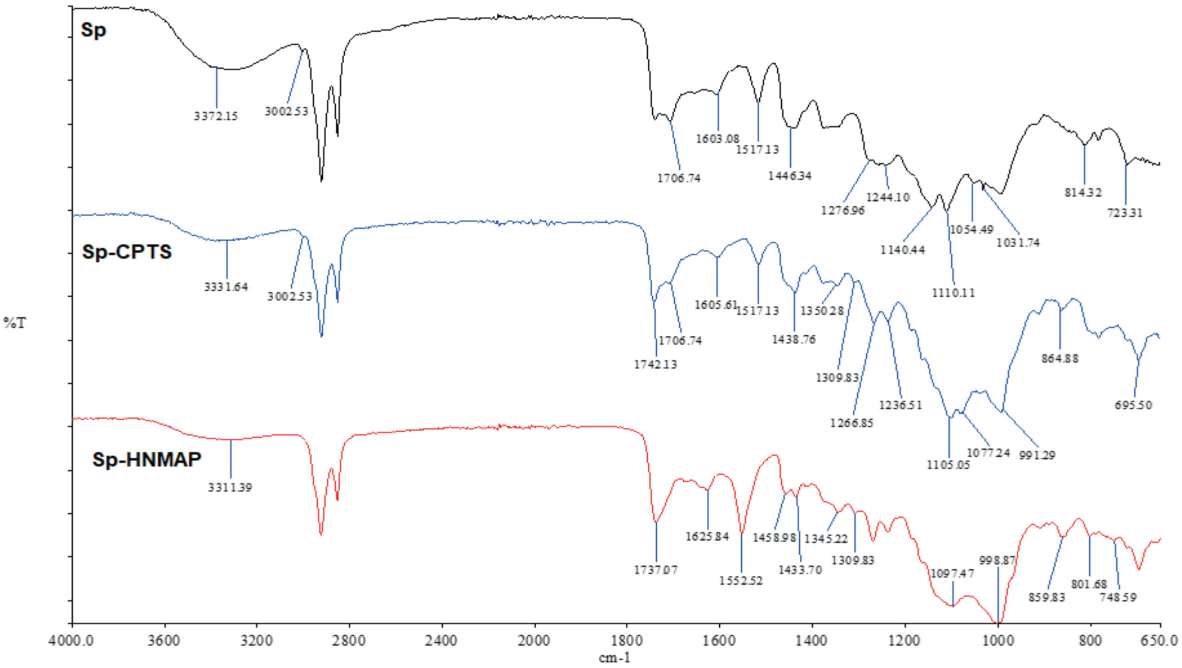
RESULT AND DISCUSSION

Characterization

The immobilized sporopollenin was characterized by FTIR and SEM. The infrared spectra of the prepared surface were shown in Fig.1.

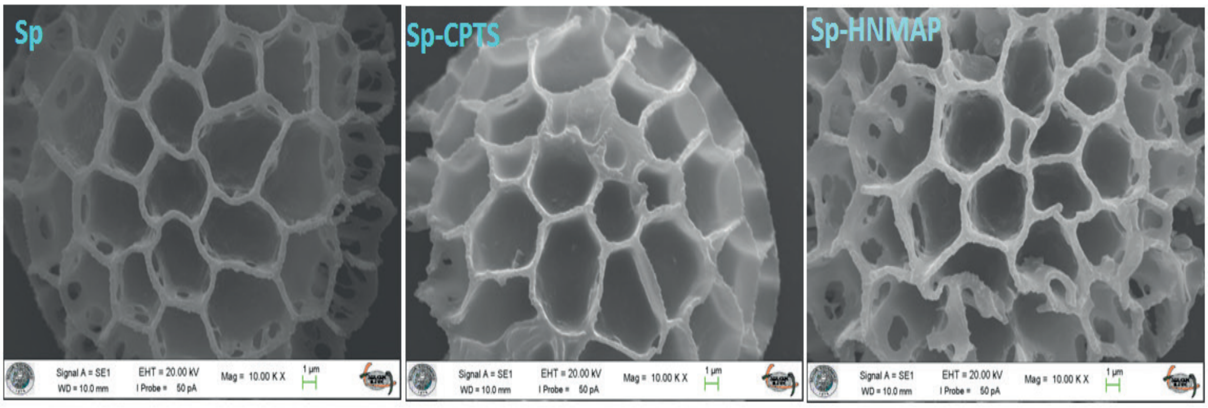
It is observed between 3400 and 3200 cm^{-1} of the purely sporopollenin peak. CH_2 stretching vibration in Sp-CPTS was shifted from 2920 cm^{-1} to 2840 cm^{-1} (Sp). Spectra of Sp-HNMAP have broad –OH peak at 3100 cm^{-1} because of the –OH groups (Fig.1)[6]. Stretching of C=N group observed at 1644 cm^{-1} indicated primer amine group in Sp-CPTS and Sp-HNMAP and organic substances. The peak at 1204 -1150 cm^{-1} was bending of–C-OH. The peaks at 1479-1500 and 2860 cm^{-1} were interpreted as stretching of C=C and C-H in the benzene ring respectively [7].

Figure 1. FTIR spectra of Sp, Sp-CPTS and Sp-HNMAP.



SEM images of pure sporopollenin are shown in Figure 2(a). The structure of the Sp- CPTS compound is shown in Figure 2(b). Figure 2(c) shows NHMAP showing a very smooth morphology after immobilization to the Sp-CPTS surface. The surface of the sporopollenin coated with NHMAP shows an irregular morphology. The presence of NHMAP on the surface of sporopollenin confirms immobilization.

Figure 2. SEM images of Sp (a), Si- CPTS (b) and Sp-HNMAP (c).



CONCLUSION

According to the results obtained from experimental studies, the best chromium removal was carried out at pH = 5.0, with 0.075 g adsorbent, at 323.15 ^{0}C temperature, in concentration of 40 mg/L in 180 min. FT-IR spectroscopy and SEM techniques confirmed the immobilization of SP-HNMAP. Adsorption is mostly found to be pH dependent. Since the results are consistent with the Langmuir isotherm model, adsorption mechanism is explained by this model.

The calculated thermodynamic parameters [8] have shown that the reactions are endothermic and spontaneous. For spontaneous reactions, ΔG^0 values were negative at 25-50 ^{0}C. ΔG^o value decreased with increase in temperature. The adsorption of heavy metal ions on Sp-NHMAP increased at higher temperatures [8]. The Sp-NHMAP has high capacity to adsorb Cu (II), Co(II) and Ni(II) ions in the wastewater.

This work is very important in terms of characterization, calculation of the thermodynamic properties and the synthesis of Sp-NHMAP and its effective use in the removal of heavy metals in wastewater.

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