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Isotherms and thermodynamics for the sorption of heavy metal ions onto functionalized sporopollenin

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ABSTRACT

In this study, sporopollenin of *Lycopodium clavatum* spores was used for the sorption experiment. Glutaraldehyde (GA) immobilized sporopollenin (Sp), is employed as a sorbent in sorption of selected heavy metal ions. The sorbent prepared by sequential treatment of sporopollenin by silanazing compound and glutaraldehyde is suggested for sorption of Cu(II), Zn(II) and Co(II) from aqueous solutions. Experimental conditions for effective sorption of heavy metal ions were optimized with respect to different experimental parameters using batch method in detail. Optimum pH range of Cu(II) has occurred at $\text{pH} \geq 5.5$ and Zn(II), Co(II) at $\text{pH} \geq 5.0$, for the batch method. All of the metal ions can be desorbed with $10\,\text{cm}^3$ of $0.5\,\text{mol}\,\text{dm}^{-3}$ of ethylenediaminetetraacetic acid (EDTA) solution. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm equations were applied to the experimental data. Thermodynamic parameters such as free energy (ΔG^o), entropy (ΔS^o) and enthalpy (ΔH^o) were also calculated from the sorption results used to explain the mechanism of the sorption. The results indicated that this sorbent is successfully employed in the separation of trace Cu(II), Zn(II) and Co(II) from the aqueous solutions.

1. Introduction

The increasing level of heavy metals in water represents a serious risk to human health and ecological systems [1]. Heavy metals, such as lead, cadmium and mercury, are harmful to living organisms. Indeed, even in very small quantities, some of these metal ions, especially mercury ions, may harm flora, fauna and other living beings. Their accumulation in humans causes kidney failure, nervous system damage and bone softening, as well as other serious illnesses [2]. Sorption is widely used for elimination of the heavy metal ions. Metal sorption through precipitation and complexation is a common approach to reduce metal toxicity in the environment.

Several materials such as activated carbon, resins, clays, silica gel, and biological materials [1] have been studied for sorption of heavy metal ions. Support structure plays a dominant role in mechanical, chemical and thermal stability of sorbent materials. One of the materials is sporopollenin which possesses a high content of functional groups available for modification [3].

The outer wall of spores and pollen contains a highly resistant biomacromolecule, sporopollenin, occurs naturally as a component of spore walls *Lycopodium clavatum* has a stable, cross-linked structure and has an aromatic character that contains carbon, hydrogen, and oxygen with a stoichiometry of $C_{90}H_{144}O_{27}$, which can survive in geological strata over millions of years with full retention of morphology. Sporopollenin is produced by oxidative polymerization of carotenoids and carotenoid esters, which leads to proposed monomer structures of the macromolecular sporopollenin. At present, sporopollenin is generally considered to be a biopolymer and the detailed chemical structure of sporopollenin is as yet unknown [4].

Recently, surface modification of sorbents has garnered intense interest in order to be used as solid supports due to its large surface area, fast sorption kinetics and due to specifications of sorbent [5]. Modification of sporopollenin can be achieved via chemisorptions of the active species onto the sporopollenin surface. In this process, organic reagents or synthesized organic molecules containing the desired organic functional group are directly attached to the supports [6].

Sporopollenin with its polymeric structure would be a candidate sorbent for removal of heavy metal ions from aqueous solutions due to its low cost. However, the literature search indicates that the studies which comprehensively intensify the ability of sporopollenin based materials in complexation process are very few. To the best of our knowledge, there exists no report on the use of sporopollenin from *Lycopodium clavatum* as support for immobilization of glutaraldehyde. The objective of this work was to investigate the Cu(II), Zn(II)and Co(II) sorption performance of Sp-APT-GA as a new sorbent. The focus in the present study is on characterizing the sorption properties of this material. Surface structure of the immobilized sporopollenin was examined by Fourier Transformed Infrared Spectroscopy (FTIR), thermal analysis (TGA), and elemental analysis. Several factors, including solution

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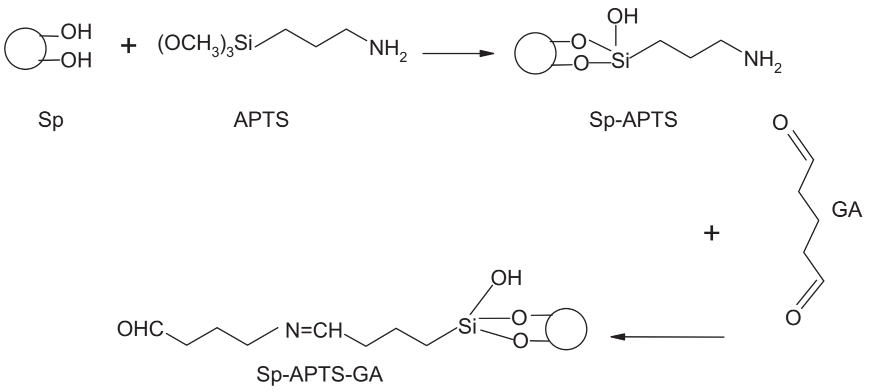

Fig. 1. Possible structure of the sporopollenin bonded glutaraldehyde molecules.

pH, solution concentration, and reaction temperature were studied. Thermodynamics of the sorption process was also studied and thermodynamic parameters such as ΔG^o, ΔS^o and ΔH^o were calculated for the systems.

2. Materials and methods

2.1. Materials

Lycopodium clavatum spores (sporopollenin) with 20 μm particle size obtained from Fluka Chemicals. All the chemicals used were of analytical grade and ultra pure water was used throughout. Toluene (Merck) was distilled and dried. 3-Aminopropyltrimethoxysilane (APTS), glutaraldehyde (25%), EDTA, and Co(II), Cu(II) and Zn(II) nitrates were also obtained from Merck. A series of standard metal solution by appropriate dilution of the stock metal solution were prepared. Solutions of 0.01 M NaOH and HNO_3 were used for pH adjustment.

2.2. Apparatus

An infrared spectrum was obtained in the 400–4000 cm^{-1} range, by Perkin Elmer 100 FTIR spectrometer. Thermogravimetric curves were obtained on a Setaram Termogravimetrik Analyzer/Setsys analyzer at temperature range of 25–800 °C. Elemental analysis was performed with a Leco CHNS 932 microelementel analyzer.

The pH value was monitored with Jenway 3010 model digital pH meter with glass and saturated calomel electrode, calibrated on the operational stage using standard buffer solution at 298 ± 1 K. Selecta-Ivmen 100D thermostatic shaker was used for the sorption experiments. Metal concentration of the supernatant was determined by a flame atomic absorption spectrometer (ContrAA 300, Analytikjena). All aqueous solutions were prepared with ultra pure water obtained from a Millipore Milli-Q Plus water purification system.

2.3. Synthesis of the sorbent

Sporopollenin was selected as a support material for this study and firstly converted into Sp-OH through described elsewhere [7]. Immobilization of the APTS onto sporopollenin was performed as follows: sporopollenin (15.0 g) was suspended in dry toluene (100 cm^3) and 3-aminopropyl trimethoxysilane (APTS) (9 cm^3) was added. The mixture was then refluxed for 72 h and conditioned under vacuum to prevent the reaction between the immobilized amine groups and CO_2 present in the atmosphere [8].

In the next step, approximately 10 g Sp-APTS was treated with 25% of GA solution (33 cm^3) and stirred at 308 ± 2 K for 15 h. After filtration of the suspension, the residue was washed and dried under vacuum at 313 ± 1 K for 72 h to obtain the Sporopollenin-Silanizing compound-Glutaraldehyde (Sp-APTS-GA). Fig. 1 shows a schematic diagram of proposed products of organic compounds anchored on the sporopollenin surface.

2.4. Sorption studies

Sorption studies were carried out by batch process. 20 mg of sorbent with 10 cm^3 of sorbate of various concentration and pH was shaken in a temperature controlled shaker incubator till equilibrium was reached (90 min). The sorption experiment the temperature was controlled at 298 ± 1 K. After extraction, the solid phase was separated by filtered. Residual metal concentration of the supernatant was determined by an AAS. All experiments were performed in triplicate. The amount of cations sorbed by sorbent was calculated as

$$q = \frac{(C_o - C_e)V}{W} \quad (1)$$

where q is the amount of metal ion sorbed onto unit amount of the adsorbent (mmol g^{-1}), C_o and C_e are the initial and equilibrium concentrations of the metal ions in aqueous phase (mmol dm^{-3}), V is the volume of the aqueous phase (dm^3), and W is the dry weight of the adsorbent (g).

2.4.1. Optimum pH studies

The acidity of a solution has two effects on metal sorption. Firstly, protons in acid solution can protonate binding sites of the chelating molecules. Secondly, hydroxide in basic solution may complex and precipitates many metals. Therefore pH of a solution is the first parameter to be optimized [9].

A total of 20 mg of Sp-APTS-GA sorbent was suspended with constant stirring in 10 cm^3 of 10 mmol dm^{-3} of Cu(II), Zn(II) and Co(II) at different pH (2.0, 3.0, 4.0, 5.0, 5.5, 6.0, 6.5, 7.0) values and the mixture was shaked for 90 min at 298 ± 1 K to attain equilibrium. After the equilibrium, the concentrations of the metal ions in solution were directly determined by AAS.

2.4.2. Effect of concentration

The sorption was carried out batch wise in aqueous solution for divalent cobalt, copper and zinc nitrates at 298 ± 1 K. For these sorption measurements, samples of 20 mg of sporopollenin derivatized were suspended in 10 cm^3 of aqueous solution containing variable amounts of each cation, whose concentrations varied over 3.5–25.0 ± 0.01 mmol dm^{-3} range, in a shaker thermostated for 90 min [10]. After equilibrium was established, the suspension was eluted and the amounts of metallic cations remaining in solution were determined by AAS. A scheme given by Fig. 2 shows metal ions sorbed Sp-APTS-GA.