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Comparison of Cd(II) preconcentrations by using magnetized *Pleurotus erygnii* and *Coprinus micaceus* and its determination in real samples

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ABSTRACT

The utilization of the magnetized *Pleurotus erygnii* and *Coprinus micaceus* with γ-Fe_2O_3 nanoparticles as biosorbents for magnetic solid phase extraction (MSPE) of Cd(II) were investigated in details. The surface structures of magnetized *P. erygnii* and *C. micaceus* were investigated by the Fourier transform infrared (FT-IR) spectroscopy, scanning electron microscope (SEM) and energy dispersive X-ray (EDX). The best process conditions were tested and determined as pH 5, 3 mL min^{-1} flow rate, 100 mg of *P. erygnii* and *C. micaceus* on 75 mg of γ-Fe_2O_3 nanoparticles, 5 mL of 1 mol L^{-1} HCl as eluent, and 400 mL of sample volume for both biosorbents. The limit of detections (LOD) were achieved as 0.054 ng mL^{-1} and 0.040 ng mL^{-1} for magnetized *P. erygnii* and *C. micaceus*, respectively. Preconcentration factors were determined as 80 for both magnetized biosorbents. The recommended methods were validated using certificated reference materials. Cd(II) in different real samples were determined by ICP-OES (inductively coupled plasma optical emission spectrometry) after preconcentration with developed methods.

1. Introduction

The management of toxic metal ions in soil, water and food samples has been a major public concern. Especially, water bodies near the industrial zone polluted with toxic metals such as cadmium (Cd), lead (Pb) and copper (Cu) put the lives of living organisms in danger and contaminate the ecosystem of the world. According to international agencies, Cd has been regarded as a latent metabolic toxicant because of being detrimental to all living organisms. [1]. Cd cannot be biodegraded in the environment and accumulates in living organisms, causing serious diseases such as heart and blood vessels, erythrocyte destruction, renal degradation, skeletal deformities, chronic pulmonary and nervous system problems [2,3]. Besides, it is known as a carcinogen [4]. Cd has many uses, including batteries, pigments, metal plating, metallurgical and alloy industries and plastics [5,6]. According to the World Health Organization (WHO), the allowable value of Cd for portable public water supplies is fixed by below 3 ng mL^{-1}. In respect to the low amount of Cd in natural samples such as water, soil and food, sensitive methods are required for accurate and precise determinations of Cd in these samples.

Different spectroscopic techniques have been used to detect Cd in food samples but preconcentration and/or separation stages are continuously necessary to repeat in order to obtain sufficient sensitivity [7,8]. For this aim, several extraction techniques, including liquid-liquid microextraction (LLME) [9], dispersive liquid-liquid microextraction (DLLME) [10,11] and solid phase extraction (SPE) [12–14] can be applied before instrumental measurement. In terms of simplicity, efficiency and economically, among them SPE, has proven to be the best application for this goal [15,16]. For the SPE process, various organic and inorganic adsorbents, including polymeric resins, magnetic nanoparticles, activated carbons, bentonites and sepiolites etc. are used. In order to improve the properties of the surface structure of the adsorbent and increase its selectivity, microorganisms such as fungus, algae, and bacteria could be used as biosorbents in SPE process [8].

There have been many biosorption investigations with fungi. In most of these investigations free cells were used. There have not been enough studies with magnetized *Pleurotus erygnii* and *Coprinus micaceus* in literature for the preconcentration and determination of toxic metals in real samples. In addition to these, there are no investigations related to the comparison of different magnetized fungal biosorbents for preconcentration processes. This reason makes this investigation interesting. The aim of the present work was to perform a comparative study

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of the analytical characteristics of MSPE using the *Pleurotus erygnii* and *Coprinus micaceus* immobilized with γ-Fe_2O_3 nanoparticles for preconcentration of Cd(II) in real samples and quantification by ICP-OES.

2. Materials and methods

2.1. Biological materials

P. erygnii and *C. micaceus* as biomass were collected in Sülün, Afyonkarahisar, Turkey.

2.2. Preparation of P. erygnii and C. micaceus for immobilization and synthesis of γ-Fe_2O_3 magnetic nanoparticles

Once the biological materials have been gathered, they were cleaned with pure water to remove contaminants. After then, they were dried at room temperature for one week. Dried *P. erygnii* and *C. micaceus* were ground in a porcelain bowl to make a fine powder. In order to kill all cells, they were kept in an oven for one day at 80 °C. Finally, *P. erygnii* and *C. micaceus* were inoculated with malt agar at room temperature for one day. The absence of micelles of *P. erygnii* and *C. micaceus* demonstrated a positive result, meaning that *P. erygnii* and *C. micaceus* had completely died. γ-Fe_2O_3 nanoparticles were prepared by procedure indicated in literature [17].

2.3. Immobilization of P. erygnii and C. micaceus with γ-Fe_2O_3 magnetic nanoparticles

100 mg of the dried *P. erygnii* and *C. micaceus* were separately added to the aqueous suspension containing γ-Fe_2O_3 nanoparticles and then refluxed for 1 h at 65 °C. Quantitative adsorption of dried biomass was achieved after the filtration and then checked gravimetrically. In addition, unbounded particles were removed by washing with distilled water. It was then dried for 24 h at 90 °C.

2.4. Preparation of column for magnetic solid phase extraction

The magnetized *P. eryngii* and *C. micaceus* with Fe_2O_3 nanoparticle (100 mg) were separately weighed. It was added to 5 mL purified water and mixed until being homogeneous in the magnetic stirrer for 2 h. Polyethylene columns, 1 cm × 10 cm, were cleaned with 1 M HCl and purified water, respectively before usage. The mixture was then slowly added to the polyethylene column. Procedures for column preparation were detailed in our recent study [18].

2.5. General sorption studies

The model solution of 30 mL of Cd(II) at 50 ng mL^{-1} was applied to MSPE process. pH of the solution was adjusted to 6 by considering our previous experiences. The metal solution was passed through the packed MSPE column at flow rate of 1 mL min^{-1}. The concentration of Cd(II) was measured in elution solution (5 mL of 1 mol L^{-1} HCl) by ICP-OES.

2.6. Biosorption capacities and MSPE column reusability

To determine the biosorption capacities of magnetically charged *P. erygnii* and *C. micaceus*, 100 mL of 1 mg L^{-1} Cd(II) solution at optimum pH values were mixed with 50 mg *P. erygnii* and *C. micaceus* was loaded with magnetic iron oxide nanoparticles at 120 rpm for 120 min at 25 °C, using a shaker. Before the determination of residual amounts of Cd(II) by ICP-OES, magnetized *P. erygnii* and *C. micaceus* were separated from the solution using a magnet. The concentrations of the Cd(II) in upper solution and pellet (after acid digestion with concentrated HNO_3 acids) were measured by ICP-OES.

The biosorption capacity of a biosorbent, which is obtained from the mass balance on the sorbate in a system with solution volume V, is often used to acquire the experimental adsorption isotherms. Under optimum conditions, the biosorption capacities (q_{eq}) of both biosorbents for each concentration of studied metal ions at equilibrium were calculated by the following equation:

$$q_{eq} = \frac{(c_o - c_{eq})V}{X}$$

where c_o is the initial concentration of solution, c_{eq}, the concentration of solution at equilibrium, V the volume of solution and X the mass of biosorbent.

Reusability of the column was tested by using the same column repeatedly for the preconcentrations of Cd(II). When the recovery of Cd (II) was under 95%, the number of use was accepted as the maximum cycle number.

2.7. Sample preparation

The proposed process was validated by performance according to certified reference materials: NWTM-15 (Fortified water-trace elements), EU-L-2 (SCP SCIENCE EnviroMAT Wastewater) and NCS DC 73351 (Tea) which were present in the laboratory. The tap water was sampled in Diyarbakır, Turkey. Milk, mineral water, rice, honey, carrot, tomato, pepper and black tea samples were bought in local markets. Liquid samples were directly applied to SPE procedure after pH adjustment. 10.0 mL of concentrated HNO_3:HCl (1:1) was added to the sample for pre-digestion. They were heated until dryness. The samples were added to a 5.0 mL mixture of HNO_3:HCl:H_2O_2 (1:1:0.2) and then transferred to a temperature and pressure controlled microwave oven (Speedwave MWS3, Berghof-Germany) to complete the digestion. It was diluted to the required volume before SPE procedure.

3. Results and discussion

3.1. Surface studies

Fig. 1a and b show the FT-IR spectra of magnetized *P. erygnii* with γ-Fe_2O_3 with and without Cd(II), respectively. The peak at 578 cm^{-1} was assigned to the stretching vibration of Fe—O bond. The broad band at approximately 3270 cm^{-1} attributed to the presence of surface hydroxyls of γ-Fe_2O_3. The peaks at 1029, 1149 and 1699 cm^{-1} could attribute to the C—N stretching of amine and C═O stretching of carboxyl functionalities of fungal surface, respectively. In Fig. 1a and b, there was no significant difference after loading Cd(II). However, double and sharp peaks at about 2900 and 3676 cm^{-1}, were attributed to complexation of Cd(II) with surface functionalities of *C. micaceus* (Fig. 2b). By considering SEM images, it can be concluded that prepared sorbents had homogenous structures (Figs. 1c, d and 2c, d). EDX images confirmed that Cd(II) bound on magnetized *P. erygnii* and *C. micaceus* (Figs. 1e and 2e).

Hard and soft acids and bases theory should be considered also to understand the interactions of Cd(II) with fungal surface. Cd(II), as a soft acid, has affinity to functional groups such as CN^-, CO, SCN^-, R_3P, R_2S, RSH, RS^- as soft bases. As a conclusion, the above-mentioned functionalities could be possible on fungal surface even if not detected. The concentrations of these can be low as that they may not be measured by FT-IR due to low sensitivity.

3.2. Effect of solution pH

The pH of a solution is the critical step of metal adsorption process. It is the key parameter that governs the adsorption of a metal ion on an adsorbent [1,19]. In addition, pH greatly affects the biosorption capacity of a metal owing to differences in the biomass cell wall compositions [20]. In order to detect the best pH for the quantitative recovery of Cd(II), pH of the initial solution were tested in the pH range of 2–9. The