Removal of Pb^{2+} ions from contaminated solutions by microbial composite: Combined action of a soilborne fungus *Mucor plumbeus* and alunite matrix

Tamer Akar [a],*, Sema Celik [b], Asli Gorgulu Ari [c], Sibel Tunali Akar [a]

[a] *Department of Chemistry, Faculty of Arts and Science, Eskişehir Osmangazi University, 26480 Eskişehir, Turkey*
[b] *Department of Chemistry, Graduate School of Natural and Applied Sciences, Eskişehir Osmangazi University, 26480 Eskişehir, Turkey*
[c] *Department of Elementary Education, Faculty of Education, Yildiz Technical University, 34210 İstanbul, Turkey*

HIGHLIGHTS

▶ Fungi–mineral composite was successfully used for the removal of Pb^{2+}.
▶ Composite exhibited high Pb^{2+} sorption capacity in batch and continuous modes.
▶ Results were described by Langmuir isotherm and the pseudo-second-order kinetic model.
▶ Composite sorbent–Pb^{2+} interactions were characterized.

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ABSTRACT

Mucor plumbeus–alunite composite was tested as a new sorbent material for the removal of Pb^{2+} ions from contaminated solutions. Sorption experiments were carried out by varying pH, contact time, sorbent dosage, initial metal ion concentration and flow rate. Zeta potential measurements, FTIR, SEM and EDX analyses were used to characterize the biosorption mechanism. The Pb^{2+} removal capacity of composite sorbent was significantly higher than that of *M. plumbeus*. The experimental results fitted satisfactory to the Langmuir isotherm in comparison to the Freundlich and Dubinin–Radushkevich model. Kinetic studies showed that the process followed the pseudo-second-order mechanism. The intraparticle diffusion played a significant role in first 40 and 50 min for *M. plumbeus* and composite sorbent, respectively. Reusability of composite material and Pb^{2+} recovery were investigated using acidic eluent. The presence of competing metal ions in the sorption medium reduced Pb^{2+} uptake potential of the composite sorbent material but it has still Pb^{2+} binding capacity in real wastewater conditions. Overall the results indicated that the prepared composite sorbent can be used as an effective and economic material for the environmental cleanup.

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1. Introduction

As a result of industrial operations, the toxic pollutants introduced into the aquatic systems are worldwide concern in recent years. Among many organic and inorganic pollutants, heavy metal ions like Pb^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, etc. have a special importance because of their chronic toxicities, accumulation abilities in living tissues and carcinogenic in nature. Hence, it is necessary to eliminate these metals from contaminated effluents before their release into receiving bodies of waters [1–4].

Conventional water treatment processes generally involve some disadvantages such as high operating and maintaining costs, incomplete metal removal, high reagent or energy requirements,

generation of metal bearing sludge or other waste products that require safe disposal [5].

Biosorption is an alternative technology emerged in recent years to threat the metal containing wastewaters with the advantages of low operating cost, minimization of the volume of disposable sludge, high detoxifying efficiency of very dilute effluents [6,7]. Furthermore, this process can be used in situ with proper design, may not need any industrial process operations and can be integrated with many systems in the most eco-friendly manner [5]. Biosorption process is based on the metal sequester ability of biological materials from aqueous systems by either metabolically mediated or non-metabolic mediated pathways uptake [8,9].

In recent years, considerable attention has been devoted to the preparation of new and effective sorbent materials. A number of studies are available in the literature concerning the use of different type of biosorbents for the removal of organic or inorganic

* Corresponding author. Tel.: +90 2222393750/2871; fax: +90 2222393578.
E-mail address: takar@ogu.edu.tr (T. Akar).

pollutants from contaminated media [10–18]. However, only a few referred to the removal of heavy metals by microbial composites [19,20]. In the present study, a new microbial composite material prepared from *Mucor plumbeus* and alunite was assessed for the removal of Pb^{2+} from contaminated solutions. *M. plumbeus* is chosen as a model fungus because of the lack of information in the literature regarding its biosorption potential. On the other hand, there is no report in the literature about the use of alunite as a matrix material in the sorbent system. Furthermore alunite is a natural and abundant mineral. Its use for the preparation of composite sorbent may be an important advantage from the economical point of view. Composite sorbents are considered to be more economic materials when compared with the microbial origin biosorbents.

The goal of this study was to investigate the batch and dynamic flow mode Pb^{2+} removal potential of *M. plumbeus*/alunite composite. Process was evaluated by different kinetic and isotherm models. Zeta potential, FTIR, SEM and EDX analysis were used to characterize the composite sorbent and identify the possible sorption mechanism. Pb^{2+} sorption performance of the suggested material in real wastewater conditions was also tested in addition to its regeneration ability.

2. Materials and methods

2.1. Preparation of the composite sorbent

The fungal strain, *M. plumbeus* ATCC 6795 was obtained from the American Type Culture Collection. It was maintained on potato dextrose agar (PDA) and grown on PDA slants for 7 days at 26 °C. Biomass was produced in the liquid medium with the composition (per liter) of glucose (30 g), KH_2PO_4 (2 g), $MgSO_4$ (2 g), $(NH_4)_2C_4H_4O_6$ (2 g), Yeast extract (1 g), $CaCl_2$ (0.1 g), NaCl (1 g), $(NH_4)_2Fe(SO_4)_2$ (0.1 g) and trace element solution (2 mL). Trace element solution was prepared by mixing $ZnSO_4$ (1 g), $FeSO_4$ (1 g), $(CoNO_3)_2$ (1 g), $(NH_4)_2MoO_4$ (1 g), $CuSO_4$ (0.1 g) and $MnSO_4$ (0.1 g) in distilled water (1 L) [21]. The pH of the liquid growth medium was adjusted to 5.5 before autoclaving at 121 °C for at least 20 min and adding trace element solution. Erlenmayer flasks containing the growth media (100 mL) were innoculated with mycelium suspension (1 mL) obtained shaking sterile water (10 mL) with a mature slope of *M. plumbeus*, under sterile conditions and shaken at 26 °C and 120 rpm for 7 days in a rotary incubator shaker. After this period, fungal biomass was separated by filtration and washed with distilled water. The biomass was dried at 60 °C in an oven and sieved to obtain particle fraction less than 150 μm.

Alunite was provided from Kütahya, Turkey. It was ground, sieved through a 150 μm sieve and calcined at 600 °C for 3 h.

Microbial composite was prepared using a method suggested by Mahan et al. with some minor modifications [22]. Briefly, 5 g of sieved fungal biomass was mixed with 10 g of calcined alunite. The mixture was wetted with deionized water and thoroughly mixed. The paste was heated in an oven at 60 °C to drive off the water. The wetting and drying steps were repeated three times in order to maximize the contact between the fungal biomass and alunite mineral. Composite material was sieved to a particle size of 150 μm for use as a sorbent.

2.2. Preparation of metal solutions and biosorption studies

A stock solution of Pb^{2+} (1000 mg L^{-1}) was prepared by dissolving a weighed quantity of $Pb(NO_3)_2$ (analytical grade, Merck) in deionized water. Other concentrations were prepared by diluting a proper amount of this stock solution. Batch mode biosorption experiments were performed by contacting 0.15 g (except for pH optimization experiments) of both natural and composite sorbents

with 50 mL of metal solutions. The pH values of the test solutions were adjusted to the desired values by adding 0.1 M HNO_3 or 0.1 M NaOH. Biosorption mixture was agitated on a multipoint magnetic stirrer at a constant stirring rate of 200 rpm. After the equilibrium period, sorbent material was separated from the biosorption medium by centrifugation at 4500 rpm for 5 min. The effect of pH on the sorption of Pb^{2+} was investigated by varying the pH values between 1.0 and 6.0. Sorbent dosage was changed from 1.0 to 6.0 g L^{-1} at an initial Pb^{2+} ion concentration of 100 mg L^{-1}. For kinetic evaluation of Pb^{2+} removal process, the contact time was varied from 5 to 90 min. In order to model the equilibrium sorption data Langmuir, Freundlich and Dubinin–Radushkevich isotherm models were tested.

The continuous mode biosorption performance of composite biomaterial was also investigated. Glass columns (internal diameter of 9 mm and height of 10 cm) were used in the continuous mode studies. Composite sorbent was packed between two layers of glass wool into the column. Tygon tubing was used for the connections between solutions and column. Metal solutions were continuously pumped upward through the columns using a peristaltic pump (Ismatec ecoline). The parameters screened are: biosorbent amount (1.0–4.0 g L^{-1}) and flow rate (0.5–7.0 mL min^{-1}). In order to test the reusability feature of the composite material, regeneration studies were conducted by column process under pre-optimized conditions. 0.1 M HNO_3 was used as eluent and efficiency of the regeneration potential of composite material was investigated in four consecutive cycles. The dynamic flow mode biosorption performance of the composite biomaterial was also tested in real waste medium. The wastewater sample was obtained from a local metal processing factory from Eskişehir, Turkey. It was placed in a sterile container, transferred to the laboratory and stored at 4 °C.

The biosorption capacity (q_e) of the sorbent was determined using the following relationship:

$$q_e = \frac{V(C_i - C_e)}{m} \tag{1}$$

where C_i and C_e are the initial and the equilibrium metal ion concentrations (mg L^{-1}), respectively, V is the volume of aqueous solution (L) and m is the weight of the sorbent material (g).

Data presented are the mean values from three independent experiments. The statistical treatment of the results was done using SPSS 15.0 for Windows.

2.3. Apparatus

At the end of the each biosorption experiment, Pb^{2+} concentration in the aqueous phase was determined by an atomic absorption spectrophotometer (AAS) (Unicam 929). The surface charges of the sorbent material were measured by a zeta potential analyzer (Malvern zeta sizer). The functional groups on the sorbent structure were analyzed using an Infrared Spectrophotometer (Bruker Tensor 27) within the range of 4000–400 cm^{-1}. The surface microstructure of the sorbent material was characterized using scanning electron microscope (JEOL 560 LV) coupled with energy dispersive X-ray (EDX) analysis. Prior to analyze, sorbent samples were sputter coated in a Polaron SC-7620 Sputter Coater using a gold–palladium target to improve electron conductivity and image quality.

3. Results and discussion

3.1. Influence of the pH on Pb^{2+} biosorption

The batch biosorption studies were carried out at different initial pH values ranging from 1.0 to 6.0 in order to determine the