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Removal of thorium (IV) from aqueous solutions by deoiled karanja seed cake: Optimization using Taguchi method, equilibrium, kinetic and thermodynamic studies

Sayanasree Varala[a,b], Alka Kumari[a], B. Dharanija[c], Suresh K Bhargava[d], R. Parthasarathy[b], B. Satyavathi[a,*]

[a] Chemical Engineering Division, CSIR-IICT, Hyderabad, India
[b] School of Civil, Environmental & Chemical Engg, RMIT University, Australia
[c] University College of Technology, Osmania University, Tarnaka, Hyderabad, India
[d] School of Science, Engineering & Health office, RMIT University, Australia

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ABSTRACT

In the present study, an attempt has been made to select a new biosorbent, de-oiled karanja seed cake (DKSC) an agro-industrial wastes and explored the potentiality of the same for the removal of Th(IV) metal from aqueous solutions. Taguchi (L_{16}) orthogonal design with three factors (4^3) namely initial metal concentration, pH and biosorbent loading were employed for the multivariate optimization in biosorption studies for Th(IV). An appropriate larger-is-better criterion was adopted to maximize the biosorption capacity and bioremoval efficiency along with S/Nratio, ANOVA and desirability approach. Additionally the DKSC was characterized by FTIR, SEM and other standard methods. The equilibrium studies revealed that the data fitted best to Langmuir model. The kinetic and thermodynamic studies revealed that the biosorption process was well suited with pseudo-second order kinetic model with spontaneous and endothermic in nature. The research proved that DKSC exhibited high efficiency for the biosorption studies of thorium showing a novel application as biosorbent.

1. Introduction

Thorium is a naturally occurring radionuclide with nuclear significance. This radionuclide is toxic in nature and is widely found in various industrial effluents and is a strong gamma-emitting by-product of nuclear reactor operations [1,2]. The effluents containing Th(IV) are known to cause acute toxicological effects and harmful diseases [3]. The separation/pre-concentration of thorium from aqueous streams is therefore a significant study that would help not only in the environmental control but also for the treatment in hazardous and nuclear waste management. Numerous physico-chemical methods like chemical precipitation, chemical oxidation or reduction, electro coagulation, electrochemical treatment, evaporative recovery, filtration, ion exchange and membrane technologies have been widely used for removal of metal ions. These processes generally necessitate use of expensive chemicals in a few methods or/and accompanied by disposal problems. Also, the above mentioned methods are ineffective in the treatment of effluents containing very low concentration of metals ($<$100 mg/L), that are toxic and hazardous to human beings. With increase in environmental awareness and governmental regulations, there is prominence on the development of eco-friendly customs to decontaminate wastes using low-cost methods and materials [1].

Biosorption is a very cost-effective and efficient treatment method for the removal of contaminants from effluents due to property of the biomass to bind and concentrate metals from even very dilute aqueous solutions [2]. Biosorption may occur by either physical bonding or chemisorption. It is dictated by the type of functional groups that are present on the surface of the biomass, the nature of the metal being adsorbed. The biosorption of metals and radionuclide's has received attention because of its uniqueness and advantages such as low operating cost, high efficiency in detoxifying very dilute effluents and a minimal amount of disposable sludge, representing an important breakthrough. Literature suggests that extensive investigations have been carried out to discover suitable and relatively cheap biosorbents proficient in removing significant quantities of metal ions [1].

* Corresponding author. Fax: +040 27193626.
E-mail address: drsatyavathib@gmail.com (B. Satyavathi).

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Recently agricultural by-products and plant wastes such as rice bran, wheat bran, tree leaves [4], tea and coffee grounds [3,5], paper mulberry leaf powder [6], rice husk [7], olive stones [8] and citrus wastes have been identified as important and economic sources to be used as biosorbents. De-oiled karanja seed cake (DKSC) is an agro-industrial waste that can be used as biosorbent as it is available cheap, reusable and offers a simple pre-treatment process for removing metal ions from contaminated sites.

Milletiapinnata is a species of tree in pea family, fabaceae, resident of tropical and temperate Asia, Australia and Pacific Islands, regularly known by the synonym *Pongamiapinnata* and commonly called as *karanja* in India. It is one of the few nitrogen fixing trees to produce bean-like brownish-red seeds about 1 .5–2.5 cm long with a brittle, oily coat containing 30–40% oil. In India, the oil, apart from being the main source for biodiesel, has many other applications in the fields of pharmacy (as an herbal medicine for the treatment of human and animal skin diseases) and industry (in soap making and tanning industries). Statistics show that for every ton of oil extracted two tons of cake is generated. The generated seed cake is toxic with little or no economic value and therefore can be used as a biosorbent to combat the menace of metal pollution. The authors have not come across any reports wherein DKSC has been utilized for the removal of thorium from aqueous streams.

In the present study, the potentiality of DKSC as a biosorbent for the removal of Th(IV) from aqueous solution was investigated. A simple pre-treatment method was adopted to enhance the ability of the biomass to be used as a biosorbent. Parameters like initial metal concentration, pH of the initial solution and biosorbent loading influence the biosorption process. Hence, optimization of the biosorption process is essential. Taguchi robust design approach was adopted to find the optimum operational parameters for achieving high Th(IV) removal from aqueous solution using DKSC as biosorbent. An orthogonal array experiment design ($L_{16}(4^3)$) with three factors having four levels each was employed. Multivariate optimization technique was used to investigate the biosorption capacity (q_e) and bioremoval efficiency($B\%$) to come up with optimal factor settings for biosorption process. Furthermore equilibrium isotherm modeling, kinetic and thermodynamic studies for Th(IV) biosorption were also investigated.

2. Materials and methods

2.1. Chemicals and reagents

All the chemicals used in the experiments were of analytical grade. Thorium AAS standard 1000 μg/μl (Inorganic ventures, USA), acetate Buffer pH 4.6 (Sigma–Aldrich) was used in complexometric analysis for the generation of calibration curve. A stock solution of thorium (1000 mg/l) was prepared by dissolving exactly 2.459 g of $Th(NO_3)_4{\cdot}5H_2O$ (Finar chemicals) in demineralized water and acidified with 1 ml of concentrated HNO_3 to prevent hydrolysis. Thorium solutions of different concentrations were prepared by serial dilution of stock solution with demineralized water. Xylenol orange solution (10^{-3} M) was prepared by taking 0.7606 g of xylenol orange tetra-sodium salt dry powder ($C_{31}H_{28}N_2O_{13}SNa_4$) and dissolved in 50% ethanol, procured from Sd Fine chemicals. The reagent was always prepared fresh. Acetate Buffer of 6 ($\pm$0.2) pH was prepared by mixing appropriate portions of 0.01 M glacial acetic acid and 0.01 M sodium acetate.

2.2. Analytical method

A spectrophotometric analysis based on the complex formation of thorium with xylenol orange was carried out [9]. The sample aliquots containing <10 mg of thorium were mixed with 10 ml of acetate buffer, 5 ml of xylenol orange solution and allowed to stand for approximately 3 h and absorbance was measured at 575 nm using 1 cm cell quartz cuvettes against reagent blank. The standard calibration curve was generated by considering standard solutions of 2–15 mg in the same procedure as mentioned above. The correlation coefficient obtained for calibration curve was 0.9989. The concentrations of thorium present in the unknown samples were calculated from this standard curve.

2.3. Instrumentation

Thorium concentrations in the samples were determined using Lab India 3000$^+$ Model UV/Vis Spectrophotometer. The biosorption studies were done using Cintex orbital shaker Model CIC-8. The pH of the solution was measured using a Sartorious PB-11 pH meter. Radleys- RR98072 magnetic stirrer was used in the pre-treatment method of biomass and lab oven (Tempo instruments and equipments (I) Ltd) was used for drying the biomass. A high precision citizon balance with accuracy of $\pm$0.0001 g was used for weighing the biomass. Lab Companion RW-2025GA refrigerated and heating bath circulator was used for maintaining a constant temperature of the solution and Heidolph RZR 2021overhead stirrer was used for the kinetic studies that were carried out in a 250 ml glass jacketed reactor. PerkinElmer Spectrum 100 FTIR spectrometer and Hitachi S-3000N Scanning electron microscope were used for the characterization of biomass.

2.4. Collection and Preparation of biosorbent

The DKSC was obtained from local market in Hyderabad, India and washed with distilled water multiple times to remove dirt and other watersoluble impurities using a magnetic stirrer at ambient conditions. The washed biomass was oven dried at 150 °C for approximately 4 h to remove excess moisture. The dried biomass was then grinded using mortar and pestle and sieved in Taylor norms to increase the surface area. The average particle size found was <325 μm. The sieved biomass was again oven dried at 150 °C to remove bound moisture and stored in a sealed polyethylene bag to prevent moisture attack from environment. All the experiments were carried out using this biomass as biosorbent.

2.5. Experimental design–Taguchi orthogonal array

The main operational parameters to influence the biosorption process were identified as the initial Th(IV) concentration, initial pH of the solution and the DKSC loading and therefore the influence of these factors were studied. In the present study, Taguchi (L_{16}) orthogonal array experimental design consisting of three factors having four levels each was employed and is presented in Table 1. The design suggested that 16 experiments were to be conducted for the selected factors with their corresponding levels as presented in Table 2 along with the experimental results obtained. A pH exceeding 6 leads to precipitation of thorium as thorium hydroxide ($Th(OH)_4$), therefore the pH range selected was 2–5. Metal ion concentration

Table 1
L_{16} factors and levels which were studied by Taguchi method.

Factor	Level			
	1	2	3	4
(X_1) Initial metal concentration (mg/L)	15	40	85	130
(X_2) pH	2	3	4	5
(X_3) DKSC loading (g/L)	0.25	0.5	0.75	1.00