DESORPTION STUDIES FOR THE RECOVERY OF THORIUM FROM LOADED BIOSORBENT (DKSC): PARAMETER OPTIMIZATION AND EQUILIBRIUM MODELLING

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Abstract- The aim of this work was to verify the reversibility of sorption process for metal recovery and thus the possibility of the desorption process through batch mode. The present study intended for the desorption of thorium from loaded biomass, deoiled karanja seed cake (DKSC) an agro-industrial waste resulted after expelling oil from the seeds. DKSC has been reported to be one of the most efficient biomass with high metal uptake capacity in the biosorption of thorium and the loaded DKSC at optimum conditions in the thorium biosorption studies was chosen as the raw material for desorption studies and was treated with HCl and HNO_3 to recover the sorbed thorium and an effective desorptive solution was identified based on the desorption rate (D%). The operational parameters like L/S ratio and desorptive solution concentration were optimized for maximum desorption rate. A maximum of 96% for desorption rate was attained for 1M HCl with L/S ratio 7.The equilibrium studies were performed at optimal conditions and validated with Langmuir and Freundlich isotherm models and the data fitted well with Langmuir model with highest R^2 of 0.99.

I. INTRODUCTION

Thorium is a naturally occurring radionuclide with ample nuclear importance due to its application as an alternative fuel by converting it into ^{233}U. It is majorly resulted as a strong gamma-emitting by-product during nuclear reactor operations and is found in various industrial effluents. Even at trace levels nuclear fuel reprocessing concentrate this element in the environment and the effluents containing Th (IV) are known to show acute toxological effects in humans. Thorium agglomeration in living cells damages spleen and marrow, and results in liver, pancreatic and lung cancer. Therefore, the removal and recovery of this radionuclide from industrial discharge is appreciable and helpful in hazardous and nuclear waste management and environmental pollution control [1,2].

Biosorption is substantially most attractive process for the treatment of industrial streams containing radionuclides using biological materials owing to its unique process characteristics. However, the application of this method as an effluent treatment process necessitates further steps including recovery of bound metal and subsequent recycling of biosorbent which can be attained via desorption process. Desorption involves elution of sorbed metal ion from loaded biomass using an appropriate eluting/desorbing medium and is metal selective, economically feasible and ensures efficient recovery of bound metals in the eluate which can be reused for further process applications. It also provides reutilization of biomass in multiple adsorption-desorption cycles which reduces waste generation and discarding problems. Desorption studies have provided an evidence on the reversibility of the metal sorption process and the mechanism is similar to that of biosorption with probable contribution of ion exchange and the studies reported in the literature have mentioned that desorption can be accomplished by proton exchangers [3,4].

Deoiled karanja seed cake(DKSC) is derived from karanja plant, a native plant of India and is suitable as biosorbent due to its nonedible and toxic nature. It is proven to be one of the most potential biosorbents available for the removal of thorium ions from aqueous streams [5]. The present study showed keen interest in the recovery of thorium from loaded biomass, De-oiled karanja seed cake (DKSC) through batch desorption method using HCl and HNO_3 as desorbing solutions and to optimize the operational parameters that affect the desorption process for maximum desorption rate (D%).

II. MATERIALS AND METHODS

Thorium loaded DKSC (Th-DKSC) obtained from thorium biosorption studies at optimum process conditions was secured and is used as raw material in the present study. Desorption studies were performed in batch mode using a shaking incubator (Daihan Labtech India Pvt Ltd.,). Th-DKSC was added to different volumes of eluting agents in conical flasks to attain required L/S ratio and the mixture was agitated at 25°C, 200 rpm for 5 hrs to attain equilibrium. Later, the soli-liquid mixture was filtered using Whatmann filter paper no.40. The equilibrium time was determined based on the preliminary studies. The concentration of thorium in eluate was determined spectrophotometrically using UV-VIS spectrophotometer (Lab India 3000+ model) and was ascertained as C_{des} (mg/L).

The results were expressed in terms of desorption rate, D%

$$D\% = \frac{q_{des}}{q_{bio}} X\ 100 \qquad (1)$$

$$q_{des} = \frac{C_{des}\ X\ V}{m} \qquad (2)$$

where q_{des} being desorption capacity, C_{des} is the concentration of thorium in the eluate after desorption, V is volume of desorptive solution and m is the mass of the loaded biosorbent.

Table 1: The Linear And Non-Linear Forms Of The Isotherm Models

Isotherms Models	Non-Linear form	Linear form
Langmuir	$q_{des} = \frac{Q_o K_L C_{des}}{1 + K_L C_{des}}$	$\frac{1}{q_{des}} = \frac{1}{Q_o} + \frac{1}{Q_o K_L C_{des}}$
C_{des}-equilibrium concentration of adsorbate (mg/L), q_{des}- desorption capacity at equilibrium (mg/g), Q_0-maximum desorption capacity (mg/g), K_L-Langmuir isotherm constant related energy of adsorption (L/mg)		
Freundlich	$Q_{des} = K_f C_{des}^{\frac{1}{n}}$	$\log Q_{des} = \log K_f + \frac{1}{n} \log C_{des}$
K_f - freundlich isotherm constant (mg/g), approximate indicator of desorption capacity, n- desorption intensity/heterogeneity parameter, C_{des} - the equilibrium concentration of adsorbate (mg/L), Q_{des} - the amount of metal desorbed per gram of the adsorbent at equilibrium (mg/g)		

III. RESULTS AND DISCUSSIONS

3.1 Effect of Contact time (preliminary studies): Preliminary studies were performed to assess the efficient contact time for the desorption process. Th-DKSC was agitated firmly in 0.1M HCl with L/S ratio 1 for 6 hours in a 250 ml jacketed reactor at 25°C and 200 rpm. Sample aliquots were withdrawn at regular intervals and were analysed for the concentration of thorium accordingly. The results obtained were shown in Fig. 1. From the graph it can be said that the desorption of thorium from loaded biomass is a slow process and occurred in three stages. The initial stage (I) was rapid and increased linearly with time (until 120 minutes), followed by a slow and steady step during stage II (up to 210 minutes) and finally an equilibrium stage (III) occurred at 300 minutes (5 hours). Thus 5 hours was confirmed as efficient contact time and the same was provided in all the subsequent desorption experiments.

3.2 Effect of process parameters: The main agenda of this study was to verify the effect of process parameters towards desorption rate (D%) and were varied as, desorptive solution: HCl, HNO_3; Concentration: 0.01, 0.1 and 1M; L/S ratio: 3,5,7,8 and 10. The results obtained were presented Figure 2. As seen from the bar graph, D% increased progressively for the increase in concentration of desorptive solution for both HCl and HNO_3 and attained a maximum of 96 % for HCl (Fig. 2 (a)) and 93% for HNO_3 (Fig. 2 (b)). This can be attributed to the fact that increase in acid concentration lead to the build-up of H^+ ions in the solution, thus increasing the concentration gradient and driving force for ion-exchange, favouring the desorption process. The results obtained were in accordance with several reports in the literature [2,6]. Hence it can be confirmed that 1M HCl with L/S ratio 7 was the most optimal operating process parameters for the thorium desorption from loaded DKSC.

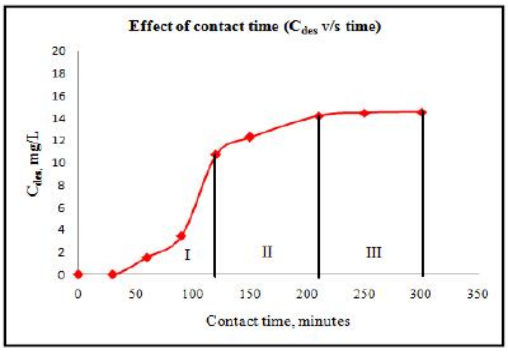

Figure 1: Effect of Contact time for determination of equilibrium time

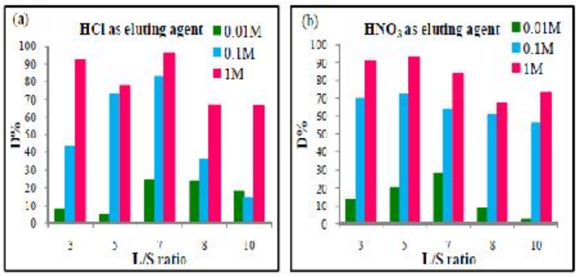

Figure 2: Effect of eluting agent and concentration along with L/S ratio (a) HCl, (b) HNO_3

Equilibrium modelling: Equilibrium studies were conducted for the desorption process at optimal conditions (1M HCl at L/S ratio 7) and the results obtained were validated with non-linear Langmuir and Freundlich models (Table 1). The model parameters evaluated were shown in Table 2 along with regression coefficients (R^2). As seen from the table, Langmuir model obtained highest R^2 value of 0.998 stating that the equilibrium data fitted the best with the model. Equilibrium data for thorium biosorption using DKSC also fitted very well with the Langmuir model [5]. Fig. 3 shows the predicted values using non-linear Langmuir model (dashed line) and the experimental equilibrium data (blue dots) suggesting that the model best fits with the experimental data.

Table 2: Parameters for equilibrium models

Langmuir model			Freundlich model		
q_{max}	K_L	R^2	n	K_F	R^2
62.50	5.333	**0.998**	33.333	55.4625	0.188

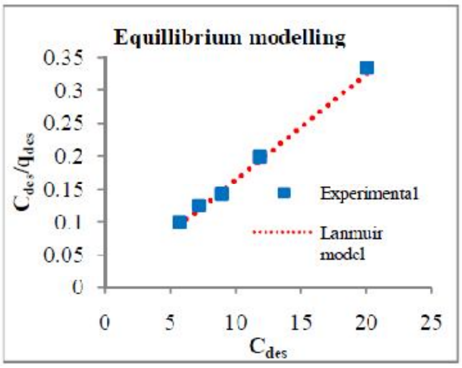

Figure 3: Equilibrium modelling

CONCLUSIONS

The present work aimed in the recovery of thorium, a radioactive element through desorption process from loaded biomass. DKSC is an agro-industrial based non-edible biomass resulted after expelling oil from karanja seeds and has proven and reported to be one of the most efficient biosorbent with high metal uptake capacity in the biosorption studies of thorium. Thorium loaded DKSC at optimum conditions in the thorium biosorption studies was chosen as the raw material for desorption studies. Loaded DKSC was treated with proton exchangers (HCl and HNO_3) to recover the sorbed thorium and an effective desorptive solution was identified based on the desorption rate (D%) and the operational parameters L/S ratio, Concentration of desorptive solution were optimized for maximum desorption rate. Desorption of thorium from loaded DKSC has been investigated as a function of contact time in the range 15-300 minutes and preliminary investigation discovered that 300 minutes was sufficient for the effective desorption, therefore fixed for all the desorption experiments. 1M HCl with L/S ratio 7 was evaluated to be the optimal process parameters for effective desorption of thorium from loaded DKSC with maximum desorption rate obtained as 96%. The desorption equilibrium data fitted the best with Langmuir isotherm model with highest R^2 value of 0.998.

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