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CHITOSAN-LIGNIN COMPOSITE FOR RECOVERY OF LANTHANUM (III) IONS FROM AQUEOUS SOLUTIONS

(Kitosan-Lignin Komposit untuk Perolehan Semula Lanthanum (III) Ion Dari Larutan Akueus)

Shariff Ibrahim[1]*, Nur Shuhaidah Shamsul Kamal[1], Megat Ahmad Kamal Megat Hanafiah[2],
Noorul Farhana Md Ariff[1], Sabiha Hanim Saleh[1]

[1]*School of Chemistry and Environment, Faculty of Applied Sciences,*
Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[2]*Faculty of Applied Sciences,*
Universiti Teknologi MARA, 264000 Jengka, Pahang, Malaysia

**corresponding author: sha88@uitm.edu.my*

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Abstract

A chitosan-lignin composite was prepared, characterised, and applied as an effective adsorbent to recover precious rare earth La(III) ions. The characterisation studies revealed that the chitosan-lignin composite consisted of slightly acidic groups, as both pH_{ZPC} and pH of the slurry were 6.17 and 5.47, respectively. The specific surface area of the composite was found to be 1.41 m^2 g^{-1} using Brunauer Emmett Teller (BET), which was lower than the raw chitosan surface area. The FTIR spectrum showed the disappearance of the primary amine peak of chitosan at 1648 cm^{-1} due to interaction with the benzene ring in lignin. Factors influencing La(III) adsorption behaviour include the pH of the solution, adsorbent dosage, concentration, and contact time. The maximum adsorption of La(III) was at pH 4 with an adsorbent dosage of 0.5 g L^{-1}. The Langmuir isotherm model fitted well to the experimental isotherm data, with $R^2 = 0.99$. The maximum adsorption capacity of the chitosan-lignin composite was 500 mg g^{-1} at 300 K. A competitive ion experiment revealed Ce(III) ions, another lanthanide group member, adsorbed more than La(III) when both metal ions were mixed in a binary system. Maximum desorption of 90% La(III) was noted with Na_2EDTA as the desorbing agent.

Keywords: adsorption, composite, chitosan, lignin, kinetics

Abstrak

Komposit kitosan-lignin disediakan, dicirikan, dan digunakan sebagai penjerap yang berkesan untuk pengambilan semula ion La(III) nadir bumi. Kajian pencirian menunjukkan bahawa komposit kitosan-lignin terdiri daripada kumpulan yang sedikit berasid kerana kedua-dua pH_{zpc} dan pH buburan masing-masing adalah 6.17 dan 5.47. Luas permukaan komposit yang spesifik didapati 1.41 m^2 g^{-1} menggunakan Brunauer Emmett Teller (BET), iaitu lebih rendah daripada luas permukaan kitosan mentah. Spektrum FTIR menunjukkan hilangnya puncak kitosan amina primer pada 1648 cm^{-1} kerana interaksi dengan cincin benzena di lignin. Faktor-faktor yang mempengaruhi tingkah laku penjerapan La(III) termasuk pH larutan, dos penjerap, kepekatan, dan masa sentuhan. Penjerapan maksimum La(III) berlaku pada pH 4 dengan dos penjerap 0.5 g L^{-1}. Model isoterma Langmuir sesuai dengan data isoterma eksperimen dengan pekali regresi $R^2 = 0.99$. Kapasiti penjerapan maksimum komposit kitosan-lignin ialah 500 mg g^{-1} pada 300 K. Eksperimen persaingan ion mendedahkan Ce(III), iaitu ahli kumpulan lantanida lain, dijerap lebih banyak berbanding La(III) ketika kedua-dua ion logam tersebut bercampur dalam sistem binari. Nyahjerapan maksimum La(III) mencatatkan 90% dengan Na_2EDTA sebagai agen penyahjerapan.

Kata kunci: penjerapan, komposit, kitosan, lignin, kinetik

Introduction

The extensive use of lanthanides in various high technology industries, such as chemical engineering, electronics, metallurgy, and medicine, is due to their unique properties, making them one of the most demanding metals worldwide [1]. Lanthanum (La), a member of the lanthanide group, is categorised as a much sought-after metal. It is a crucial component in making catalysts, ceramics, glass, metal products, and battery alloys. Lanthanum is found in allanite, monazite, cerite, and bastnaesite, which are rare earth compounds [2]. With increasing industrial demand for La, environmental pollution has become a significant issue, particularly water supplies. Efficient management is critical for maintaining a healthy environment, and wastewater recovery can offer a steady supply of La by optimising its use. Numerous techniques for resolving this problem have been investigated, including co-precipitation, ion exchange, and solvent extraction [3]. These techniques, however, are inefficient and expensive to operate and maintain [4]. Due to high-affinity metal adsorption and environmentally acceptable methods, adsorption seems to be the most effective technique for removing lanthanides from aqueous solutions [1].

The use of chitosan as a biosorbent medium has been extensively studied for various applications [5]. Chitosan is a biodegradable biopolymer that may be modified chemically to enhance its physicochemical characteristics [6]. It is effective in removing a variety of inorganic and organic pollutants [7]. However, the high cost of chitosan and a number of its poor characteristics, including mechanical strength, chemical strength, porosity, and surface area, restrict its performance [8, 9]. Thus, modification methods should be used to enhance chitosan's adsorptive capacity. As a result, the possibility of combining chitosan with other adsorbents, such as lignin is discussed in this section.

Apart from its accessibility, lignin has been studied for its polyphenol structure and physicochemical characteristics [10]. Lignin comprises propyl-phenolic subunits that serve as potential active sites for dye and metal adsorption [11]. Numerous investigations into the efficacy of chitosan–alkali lignin composites in removing various kinds of pollutants have been conducted [12, 13]. Researchers discovered that adding lignin to chitosan enables the use of renewable by-products while also lowering the total cost of obtaining the chitosan precursor [14, 15]. They concluded that combining chitosan and lignin may reduce the use of chitosan since lignin is considered a universal waste by-product of the paper and cellulosic bioethanol industries. This is because lignin accounts for about 15-35% of the dry biomass [16].

This article discusses the use of chitosan-lignin composites for removing rare earth metals from aqueous solutions and desorbing them from metal-loaded adsorbents. To better understand the adsorbent/desorption behaviour of the chitosan-lignin composites, they were characterised. Batch parameters, such as the influence of the pH solution, the adsorbent dosage, and the ions competition experiment, were investigated. The data was then applied to determine their fitness for various isotherm models. Desorption with several solvents examined the possible recovery of adsorbed La(III) ions from chitosan-lignin composites. Despite many works on the utilisation of chitosan lignin as an adsorbent material, to the best of our knowledge, the application for La(III) adsorption was scarce [1]. As a result, this work served as a valuable foundation for future research.

Materials and Methods

Materials

Chitosan high molecular weight (95% deacetylated), lignin alkali, and acetic acid reagent (≥99.7%) were purchased from Aldrich. The standard solution used in this work was Lanthanum nitrate hexahydrate, analytical grade ($La(NO_3)_3.6H_2O$, 96%), purchased from Merck. Deionised water was utilised throughout the adsorption experiments.

Preparation of chitosan-lignin adsorbent

The adsorbent preparation was taken from a previous study [14]. A weight of 2.0 g of chitosan was dissolved using acetic acid (2%, v/v) and left overnight. The lignin solution was set up by dissolving 2.0 g of lignin powder in 100 mL of deionised water. Finally, chitosan and lignin solutions were mixed homogeneously by an orbital shaker at 300 rpm for 3 h. The mixture was then left to dry overnight at 100°C. Lastly, the dried adsorbent was sieved to a size of <500 µm.

Characterisation of chitosan-lignin

The aqueous slurry pH was obtained by mixing 1.0 g of chitosan-lignin adsorbent into 50 mL of deionised water, stirring for 24 hours, filtering, and measuring the final pH. The pH of zero-point charge (pH_{ZPC}) was measured by mixing 0.15 g of chitosan-lignin with 50 mL (0.01 M) of NaCI solution into a series of beakers. The initial pH values of these solutions were arranged from 4 to 12, using 0.10 M of NaOH or HCl solutions and left to agitate at 150 rpm for 48 hours at room temperature before measuring the final pH of the solutions. The Fourier transform infrared (FTIR) spectra were recorded using an FTIR spectrophotometer (PerkinElmer 2000, USA). The samples were analysed in the range of 4000-450 cm^{-1}. Finally, the specific surface area and pore size were evaluated using Brunauer Emmett Teller (BET) and Barrett Joyner Halenda (BJH) methods.

Batch adsorption studies

The adsorption experiments were carried out at room temperature (300 K) using 50 mL of 100 mg L^{-1} La(III) solution with continuous stirring at 250 rpm for 45 minutes. These solutions were then eventually filtered using Whatman 42 filter paper. The filtrate was then analysed using an inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer DV5300, USA). The effect of pH was determined by adjusting the pH of La(III) solution from 2 to 6. The dosage effect was measured by varying the dosage of chitosan-lignin adsorbent from 0.5 to 2.0 g L^{-1}. For the ionic competition experiments, 0.05 g of chitosan-lignin adsorbent was added to a mixture of 50 mL (100 mg L^{-1}) La(III) and Ce(III) binary systems. The amount of La(III) and Ce(III) adsorbed, q_e (mg g^{-1}) was determined using Eq. (1). Unless stated, all the experiments were replicated, and the results are reported in mean with relative standard deviations of less than 5%.

$$q_e = \frac{C_o - C_e}{m} V \quad (1)$$

where C_o and C_e are the initial and equilibrium concentrations (mg L^{-1}) of La(III)/Ce(III), respectively; V is the volume of the La(III)/Ce(III) solution (L), and m is the weight of chitosan-lignin composite (g).

Desorption studies

La(III) loaded sorbents were put in an oven at 320 K for 2 h. These were then collected and stirred with 50 mL of deionised water, 0.01 and 0.1 M Na_2EDTA solutions, and 0.01, 0.10, and 1.0 M of NaOH, HCl, and HNO_3, respectively, for 2 h. After stirring, the mixtures were filtered and analysed using ICP-OES. The percentage of desorption can be calculated using equation 2:

$$\text{Percentage of desorption (\%)} = \frac{C_{e(des)}}{C_{e(ads)}} \times 100 \quad (2)$$

where $C_{e(des)}$ is the concentration of metal ion desorbed from the adsorbent (mg L^{-1}), and $C_{e(ads)}$ is the concentration of adsorbed metal ion (mg L^{-1}).

Results and Discussion

Characterisation of chitosan-lignin

The pH_{ZPC} was observed as 6.17, thus, reflecting the net positive charge of the surface below this pH. The pH value of chitosan-lignin at 5.47 indicates that this adsorbent carries slightly acidic groups. The surface area of the chitosan-lignin composite was 1.41 m^2 g^{-1}, lower than the surface area of raw chitosan, 2.26 m^2 g^{-1}. The finding here is consistent with the work of Sohni et al. [17]. They explained that the lignin attachment to the internal framework of raw chitosan resulted in blockage of chitosan porosities. The FTIR spectra of the functional groups of raw chitosan, raw lignin, and the chitosan-lignin composite are presented in Figure 1. The chitosan spectrum shows the presence of -OH and

-NH groups at 3000 – 3500 cm^{-1}. The wavenumbers at 1651 and 1035 cm^{-1} represent Amide I and C-O-C groups, respectively. The lignin spectrum reveals the following information: there is a broad peak from 2500 to 3500 cm^{-1}, suggesting carboxylic acid and -OH (aliphatic and aromatic) groups. The peak at 1710 cm^{-1} could be assigned to the C=O of the carboxylic group. The wavenumber from 1500 to 1600 cm^{-1} represents the C=C group in the aromatic ring. It can be observed that few significant changes occur in the spectrum of the chitosan-lignin composite compared to the spectrum of raw chitosan and raw lignin. The band of chitosan at 1651 cm^{-1} for the amide I group is shifted to 1602 cm^{-1}; meanwhile, the C-O-C stretching band assigned at 1035 cm^{-1} is shifted to 1030 cm^{-1}. Chen et al. [18] suggested that the measurable changes at these wavenumbers were due to the possible hydrogen bonding between the -OH groups of the lignin phenolic ring and the 1,4-glycoside oxygen atom of chitosan. Another possible interaction could involve the electrostatic attraction between the chitosan amino group and the carboxylic group of lignin, as indicated by the peak at 1599 cm^{-1}.

Effect of pH

The pH of the solution affects the amount of La(III) adsorption. Thus, studying the different conditions of pH solution is crucial as it can influence the properties of the adsorbent surface and the adsorbate species. According to Iftekhar et al. [19], La(III) ions are dominant in solutions with a pH below 6, while in solutions with a pH above 6, $La(OH)_3$ precipitation would form. Therefore, adsorption was conducted at pH solutions below 6. In Figure 2, the amount of La(III) adsorbed was almost constant from pH 2 to 6. A slight decrease in adsorption at pH 2 was probably due to the competition between the La^{3+} and H^+ ions for the adsorption sites [20]. Upon increasing pH to 4, the adsorption of La(III) shows a slight improvement with the highest adsorption capacity of 84.2 mg g^{-1}. Overall, good replicate data was observed, as the standard deviation was below 0.43.

Effect of dosage

It is widely known that the increased percentage of adsorption with increasing dosage was attributable to the existence of more active sites. However, a decreasing quantity of adsorbed La(III) was observed when the dosage was raised in Figure 3. At constant metal concentrations, increasing the dosage of the chitosan-lignin composite increased the number of unsaturated active sites and particulate interaction, such as aggregation, from a small quantity of dosage. Oyewo et al. [21] found a similar effect of aggregation, in which the adsorbent's surface area decreased, and the diffusion route length increased. Yanfei et al. [22] hypothesised that particle contact might desorb certain adsorbates that are only weakly and reversibly attached to the adsorbent surface. In general, excellent replication data was obtained, with a standard deviation of less than 1.54.

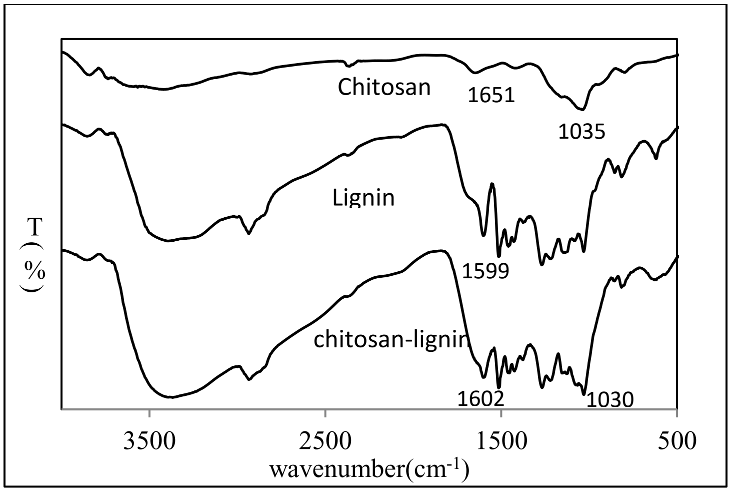

Figure 1. FTIR spectra of chitosan, lignin and Chitosan-lignin

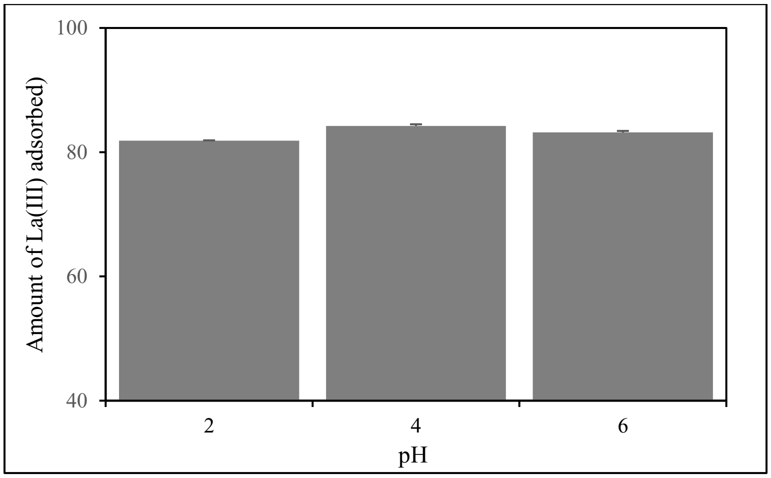

Figure 2. Effect of initial pH on adsorption of La(III) on chitosan-lignin composite

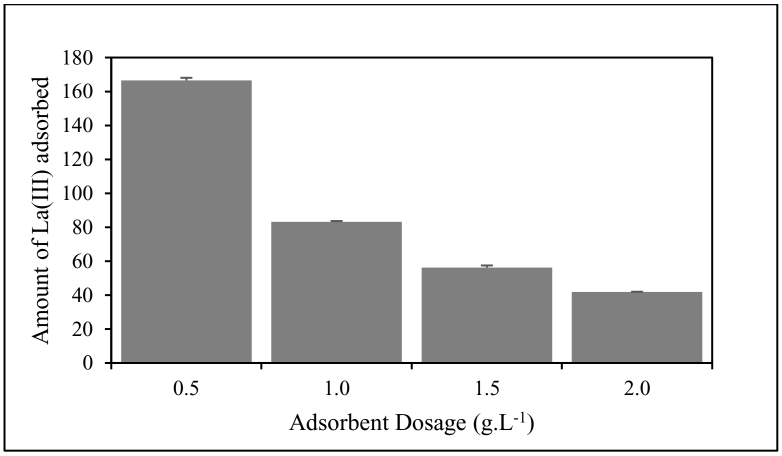

Figure 3. Effect of adsorbent dosage on adsorption of La(III) on chitosan-lignin composite

Adsorption isotherms

The linearised Langmuir equation [23] and Freundlich equation [24] are given in Equations 4 and 5, respectively:

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m} \quad (4)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where, in the Langmuir equation, C_e is the equilibrium La(III) concentration (mg L^{-1}), q_e is the sum of La(III) adsorbed at equilibrium (mg g^{-1}), q_m is the highest adsorption capacity (mg g^{-1}), and K_L is a constant (L mg^{-1}). The value of K_L mirrors the bonding strength between La(III) and chitosan-lignin surfaces. As for the Freundlich model, K_F addresses the Freundlich constant (mg g^{-1}), and n is thought of as the heterogeneity of the adsorbent outer layer and its affection for the adsorbate.

The plot for Langmuir and Freundlich isotherm models for La(III) adsorption onto the chitosan-lignin are presented in Figures 4 and 5, respectively. Table 1 tabulated data for both models of the isotherm model. Both models showed R^2 values > 0.99, with the Langmuir model recording a maximum adsorption capacity of 500 mg g^{-1}. The value of n above 1 in Table 1 reflects the favourable adsorption. Table 2 compares the adsorption capacity of chitosan-lignin in adsorbing La(III) with other adsorbents. It can be concluded that the chitosan-lignin composite is a promising adsorbent for use in industries for the recovery of La(III) ions.

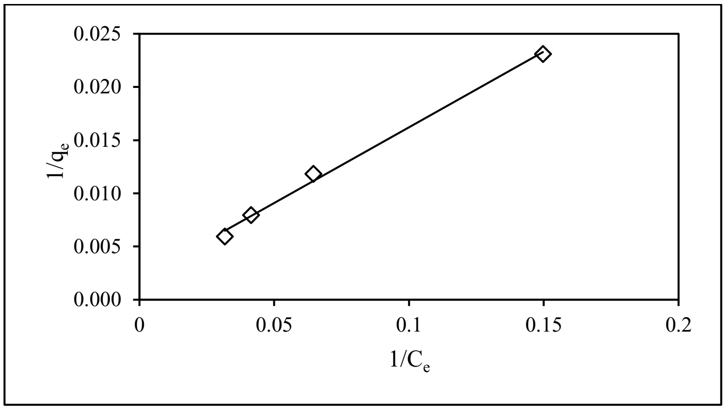

Figure 4. Langmuir isotherm for adsorption of La(III) on chitosan-lignin composite

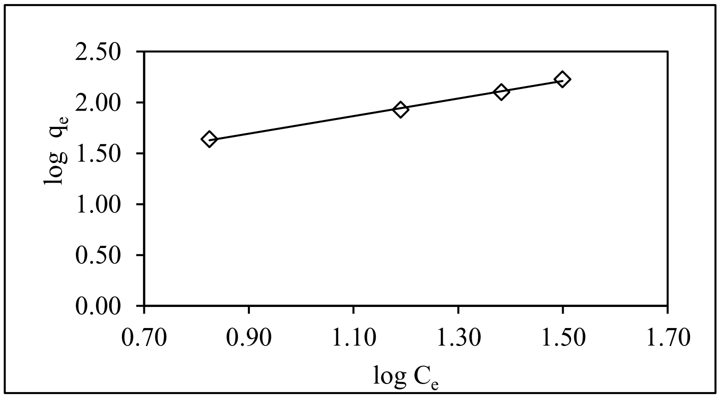

Figure 5. Freundlich isotherm for adsorption of La(III) on chitosan-lignin composite

Table 1. Langmuir and Freundlich parameters for adsorption of La(III) on chitosan-lignin composite

Langmuir			**Freundlich**		
q_m (mg g^{-1})	**K_L (L mg^{-1})**	**R^2**	**K_F (mg g^{-1})**	**n**	**R^2**
500	0.014	0.995	8.228	1.15	0.96

Table 2. Comparison of maximum adsorption capacity (q_m) values for adsorption of La(III) onto various types of adsorbents

Adsorbents	q_m (mg g^{-1})	References
Chitosan-lignin composite	**500.00**	**This study**
Ammonium citrate-modified biochar	362.32	[26]
Poly(vinyl alcohol) & mercaptopropyltrimethoxysilane modified chitosan	460.94	[27]
MgFe-LDH-Cyanex272	480.80	[28]
Pseudomonas sp.	950.00	[29]

Competition between ions

The adsorption effect among lanthanide ions was obtained using a binary system consisting of La(III) and Ce(III) ions. The understanding of competition between ions is essential as one should consider the multi-case component for industrial practice. In binary systems, adsorption consists of light rare earth elements (LREEs) and heavy rare earth elements (HREEs), favouring HREEs. However, in the same group of REEs of the metal system, the system favours higher than lower atomic numbers [25]. As shown in Figure 6, Ce(III) ions were more adsorbed than La(III). Higher Ce(III) sorption was due to Ce(III) having a higher atomic number (58) compared to La(III) (57) as described by Ogata et al. [25]. In this case, both lanthanide ions are competing to occupy the same binding sites on the adsorbent surface, as explained by Vijayaraghavan et al. [26]. Overall, good replicate data was observed, as the standard deviation was low at below 0.25.

Desorption studies

The ideal adsorbent is the one that has high efficiency in adsorption and efficient desorption behaviour [27]. The ability to desorb La(III) ions from the chitosan-lignin composite surface was evaluated using different desorbing agents with varying concentrations, namely distilled water, NaOH, HCl, HNO_3 and Na_2EDTA solutions. Distilled water is reported to have the ability to desorb La(III) ions, which are not strongly bonded to the adsorbent surface, or adsorption occurs via physisorption [28]. This is due to some small portion of La(III), superficially adsorbed to the adsorbent surface, most likely physical adsorption, thus explaining the low desorption amount. Anastopoulos et al. [28] observed the same phenomena in their desorption study of Pb^{2+} and Ni^{2+} from renewable lignocellulosic materials. They concluded that some physisorbed metals are easily released into the aqueous solution.

In Figure 7, only 4.26% of La(III) ions were desorbed by distilled water, explaining why La(III) ions were bonded by a strong chemical bond such as chemisorption. The NaOH desorbing agent failed to desorb La(III) due to the stability of La(III) ions in a basic solution [28]. In an acidic solution of HCl and HNO_3, La(III) ions were observed to be desorbed at a low percentage, ranging from 3.41 to 9.74% for HCl and 3.10 to 4.16% for HNO_3, respectively. In general, a much higher concentration of acid (1.0 M) used would introduce more protons (H^+) into the solution than at lower acid concentrations. Therefore, more adsorbates were desorbed from the adsorbent surface by an ion-exchange mechanism [29]. The highest desorption percentage was observed using Na_2EDTA, as it desorbs about 90% of La(III) ions. The ability of EDTA to desorb a large quantity of La(III) ions from the surface of chitosan-lignin proves that desorption of La(III) happens by complexation [30]. However, further increasing the concentration of EDTA results in a lower desorption percentage due to precipitation caused by the formation of La(III)-EDTA complexes, as suggested by Awwad, et al. [31]. The desorption study using Na_2EDTA concentration of 1.0 M was not conducted, as Na_2EDTA was difficult to dissolve at this concentration.

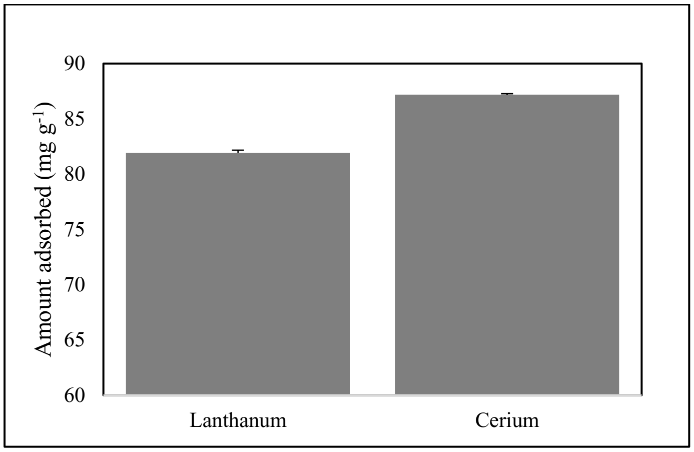

Figure 6. Adsorption of La(III) on chitosan-lignin composite in a binary system

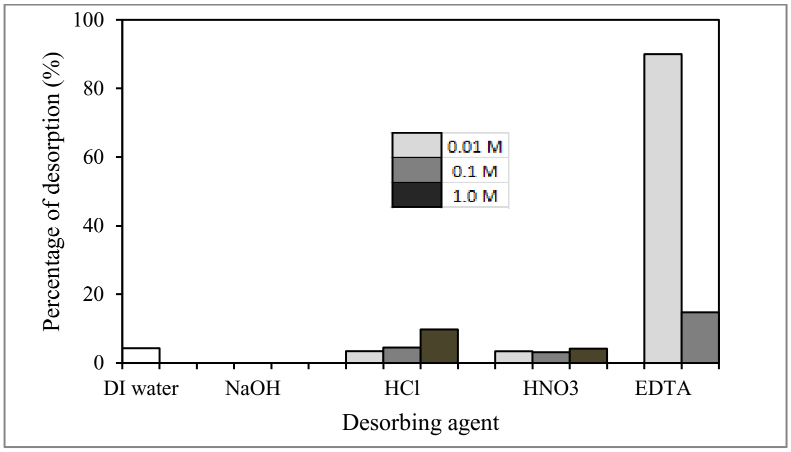

Figure 7. Desorption percentage of La(III) from chitosan-lignin composite using different desorbing agents

Conclusion

The present study demonstrated that the chitosan-lignin composite is a promising–adsorbent for recovering La(III) ions from aqueous solutions. Characterisation experiments reveal that the prepared adsorbent was acidic with a pH of 5.47. BET surface area at 1.41 $m^2 g^{-1}$ indicates reduced surface area compared to raw chitosan at 2.26$m^2 g^{-1}$. FTIR spectra showed successful integration between chitosan and lignin. The experiments indicate that adsorption was affected by adsorbent dosage and La(III) concentration. However, the amount of La(III) adsorbed was slightly affected by pH, with the highest amount of 84.2 mg g^{-1} observed at pH 4. The Langmuir isotherm recorded a maximum adsorption capacity of 500 mg g^{-1}. Na_2EDTA was the best desorbing agent to strip La(III) ions from the chitosan-lignin composite surface. In ionic competition studies, the higher atomic number of rare earth elements would favour their adsorption.

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