

Adsorption of rare earth elements using bio-based sorbents

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Abstract. Rare earth elements (REEs) have recently received significant attention due to their irreplaceable industrial application for the number of crucial advanced technologies in production of permanent magnets, batteries, luminescence lamps, lasers and other electronic and electrical goods. These technologies have been strongly affecting present consumption of REEs as well as looking for alternative sources, that would guarantee their sufficient supply for the future demand. This study investigates one of the possible and widely employed techniques for the efficient and at the same time, environmentally friendly recovery of REEs by adsorption using bio-based adsorbents. Overall, three bio-sorbents with different composition (residual biomass originated from agriculture and bio-refineries) were examined to study removal efficiency of the 7 most commonly used REEs in mixed aqueous solution. Batch adsorption experiments were carried out at the room temperature, varying the pH value (pH=1,54; 4,24) and different initial concentration of REEs to determine optimum condition for their recovery. Results revealed that removal efficiency for most of the REEs was much higher at pH=4,24 and reached 70-100% for the minimal concentrations and 30-40 % at maximal initial concentrations respectively. Adsorbent containing residual biomass and chitosan showed to be the most effective bio-sorbent for recovery of most of the REEs. In order to describe and fit the obtained data Langmuir and Freundlich isotherms models were employed.

1 Introduction

Rare earth elements are a group of 17 metals that have similar chemical and physical properties that make them valuable and irreplaceable for production of various technological devices. REEs include three elements of 3B group of the periodic table, Scandium, Yttrium and Lanthanum and lanthanides, and 14 elements from the 3A group. Their unique properties can be explained by electron configuration that allows REEs to keep their exceptional magnetic properties. All REE cations (from Ce³⁺ to Yb³⁺) without full electron shells are

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known to be strongly paramagnetic [1]. Paramagnetism provides one of the most common industrial uses of REEs such as high performance magnets.

According to U.S. Department of Energy, Nd, Eu, Dy and Y are included in their medium-term criticality matrix [2]. It is expected that demand for Dy and Nd will reach 2600% and 700% respectively as these two metals are included in matrix phase of most common permanent magnets. Phosphors contain Y and Eu. Ce and Y are employed in the production of LEDs that is sharply increasing [3].

With rising demand and consumption of REEs the problem of stable supply has become considerable especially with increase in prices. Nowadays, China is a dominant country that holds global reserves and resources and provides around 95% of the world's supply of rare earth elements [4]. Thus, this fact makes other countries and companies totally dependent on the imports from China that enhances the issues of REEs prices security of supply on the international market.

Besides, less than 1% of end-of-life residues containing REEs were recycled in 2011 [5]. This can mostly be explained by challenges in technologies, inefficient collection and separation of valuable elements from the main product and lack of motivation [3, 6]. Moreover, excessive amounts of REEs are being industrially produced and discharged from mining and mineral processing plants. Effluents from industrial processes that use REEs enter wastewater treatment plants, which might lead to their greater occurrence in the soil and aquatic systems, introducing public and ecological health risks [7]. Hence, the establishment of recycling and recovery of REEs is an urgent task and has to be developed.

Among conventional techniques for the metal removal from aqueous solutions adsorption is proven to be economical and an effective method. Biosorption is a promising technique of adsorbing metals using various low-cost natural biomaterials: biomass from algae, bacteria, fungi, yeast, as well as industrial and agricultural wastes. Recently, more research is done in biosorption of heavy metals rather than of REEs. However, there are several studies investigating marine brown algae [8] and marine biomass (seaweed and shell) [9] for the biosorption of REEs. According to the literature, biomass from green algae has been used as an effective biosorbent for the recovery of precious metals [10, 11, 12] as well as of neodymium obtained from hard disk drive magnets [13]. Chitosan is considered to be effective for uptake of metals as amino groups of chitosan chains work as coordination spots. It is also the second abundant polymer in nature after cellulose [14]. Agricultural by-products as millet husk have been widely studied as biosorbents for removal of heavy metals because it is broadly available, very cheap and is almost pure cellulose, natural polymer, which advantages as adsorbent were discussed above. After its carbonization millet husk becomes effective adsorbent with well developed porous structure and good adsorptive properties. Thermally expanded graphite was used as an industrial waste. It is known that thermally expanded graphite has high adsorptive properties, thus wastes from its production would possess the same properties as the primary materials.

The purpose of this study is to evaluate biosorption of REEs from aqueous solutions on bio-based adsorbents originated from residual biomass and chitosan and various additives from agricultural waste and bio-refineries (such as millet husk and graphically expended graphite). The influence of parameters effecting adsorption process and removal efficiency such as, pH and initial metal concentration were examined. Obtained data was compared and fit using Langmuir and Freundlich models.

2 Materials and methods

2.1 Adsorbents

Adsorbents used in this study were prepared and provided by the research group from Peter the Great St. Petersburg Polytechnic University. The information on adsorbent composition is presented in Table 1.

Table 1. Composition of analyzed adsorbents

Adsorbent	Composition
1	Residual microalgae biomass + chitosan + thermally expanded graphite
2	Residual microalgae biomass + chitosan
3	Residual microalgae biomass + chitosan + millet husk

Residual microalgae biomass of *Chlorella sorokiniana* was obtained after extraction of lipids and fatty acids.

Chitosan is originated from industrial processing by-products of crustaceans, namely shell of walking limbs of the Kamchatka crab (*Paralithodes camtschaticus*).

Thermally expanded graphite was obtained while electrochemical oxidation of graphite with subsequent hydrolysis and thermal treatment at 900 °C.

Millet husk was carbonized by thermal treatment at 300 °C during 20 minutes. At such temperature parching takes place due to which the formation of porous structure with pore size from 0.8 – 4 nm develops. Then the millet husk was ground to dispersion of 0.5±0.1 mm and mixed with residual biomass and 6% chitosan solution dissolved in the 3% acetic acid. The resulting mixture was mixed until homogeneous for 1 hour, then poured through syringe into 5% NaOH solution, where were kept for 24 hours. Afterwards granules were washed with water to reach pH of 7.0 – 7.5. Drying of granules was carried out at room temperature for 24 hours. The same principle for the preparation of other adsorbents was implemented.

2.2 Preparation of aqueous REEs solutions

Artificial aqueous solutions of REEs were prepared from the standards solutions with the concentration of 10000 mg/L and 1000 mg/L in 3 % HNO₃. All solutions have a purity grade of 99.995-99.997 % and are suitable for ICP-MS and ICP-OES analyses. Matrix solution was prepared by dilution of standards of each element by deionized water until reaching the desired concentrations that are presented in Table 2.

Table 2. Initial concentrations of metals in matrix solution

Element	Concentration, mg/L
Dy	10
Eu	10
Al	50
La	100
Y	100
Ce	100
Nd	200

2.3 Batch adsorption experiments

Experiments were carried out in 250 ml Erlenmeyer flasks containing adsorbent dosage of 0.1 g of each adsorbent and 50 ml of stock solution. The initial and maximum metal

concentrations are presented in Table 2. Furthermore, stock solution was gradually diluted in parallel by deionized water, so that solutions with minimum metal concentrations had a dilution of 1:32. The pH values of 1.54 and 4.24 were adjusted by 1 M and 0.5 M NaOH solutions. Following preparation of solutions with desired concentration from 200 mg/L to 6.25 mg/L (example for Nd) and pH adjustment, aliquots of prepared solutions were taken and diluted to 10 mL to determine initial metal in matrix solution.

REEs adsorption from obtained solutions was conducted in batch mode with contentious mixing at 760 ± 5 rpm for 60 minutes at the room temperature.

After equilibrium was reached, the adsorbents were removed and aliquots of solutions were taken, adjusted to 10 mL to detect equilibrium metal concentrations. The measurement of metal concentrations was carried out using Coupled Plasma-Optical Emission Spectroscopy (Agilent 5100 ICP-OES).

A calibration curve for quantitative assessment of REEs and Al was prepared from standard multicalibration solution with initial concentration of 5 mg/L. For each element at least 4 different specific wavelengths were used. All experiments were carried out in triplicates.

2.4 Isotherm Models

In this study, Langmuir and Freundlich isotherms were plotted to predict and feasibly describe the performance of analyzed adsorbents. Isotherms typically illustrate the equilibrium relationship between the adsorbate adsorbed on the surface and the amount of adsorbate in the solution. Linear regression was used to determine which isotherm is best fitted; the correlation coefficients R^2 were compared for practicality evaluation of isotherm equations.

The Langmuir isotherm assumes monolayer adsorption on the surface that has specific number of identical homogeneous sites where adsorption may take place. Once the site is occupied by one adsorbed atom, no further adsorption can take place at the site, so adsorption is localized. The linear form of Langmuir isotherm equation can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}, \quad (1)$$

where q_{max} – maximum adsorption capacity (mg/g)

K_L – Langmuir constant related to the rate of adsorption (L/mg)

C_e – equilibrium concentration in the solution (mg/L)

q_e – amount of metal ion adsorbed per unit of weight of adsorbent (mg/g)

Values of K_L and q_m were obtained from the intercept and slop of the linear plot graphs (C_e/q_e was plotted vs C_e) [15].

The Freundlich isotherm is an empirical equation that describes adsorption of organic and inorganic compounds on various adsorbents as well as biosorbents. The linear form of the Freundlich equation has following form

$$\log q_e = \log K_F + \frac{1}{n} * \log C_e, \quad (2)$$

where K_F – Freundlich constant, related to the bonding energy

n – heterogeneity factor, $1/n$ is related to adsorption intensity

C_e – equilibrium concentration in the solution (mg/L)

q_e – amount of metal ion adsorbed per unit of weight of adsorbent (mg/g)

The plot of $\log q_e$ vs $\log C_e$ gives the slop $1/n$ and intercept K_f [16].

3 Results and discussion

The Langmuir and Freundlich isotherms were fitted to the obtained data. The parameters of isotherms as well as their correlation coefficients (R^2) are represented in Table 3. q_{max} is presented as the average value for the triplicate experiments ($p < 0.05$).

Table 3. Isotherm best-fit constants and correlation factors

Elements	Adsorbent	pH	Langmuir		Freundlich		
			q_{max} (mg/g)	R^2	1/n	K_F	R^2
Al	1	1.54	1.24	0.847	0.25	0.60	0.676
	2		2.54	0.997	0.59	0.75	0.975
	3		1.03	0.999	0.30	0.59	0.903
	1	4.24	1.95	0.993	0.07	1.43	0.890
	2		2.38	0.999	0.11	1.68	0.901
	3		2.66	0.992	0.14	1.39	0.985
Ce	1	1.54	10.49	0.918	0.70	0.43	0.986
	2		6.64	0.979	0.43	1.18	0.955
	3		5.94	0.997	0.47	0.93	0.981
	1	4.24	3.80	0.984	0.24	1.43	0.679
	2		4.41	0.996	0.22	1.76	0.939
	3		6.98	0.618	1.00	1.00	1
Dy	1	1.54	1.43	0.925	0.62	0.57	0.898
	2		1.20	0.989	0.32	0.84	0.865
	3		0.80	0.968	0.43	0.44	0.751
	1	4.24	1.20	0.857	0.33	0.41	0.902
	2		1.33	0.996	0.35	0.72	0.840
	3		1.71	0.602	0.53	0.39	0.916
Eu	1	1.54	1.56	0.663	0.40	0.69	0.901
	2		1.45	0.951	0.44	0.82	0.990
	3		1.48	0.861	0.48	0.60	0.965
	1	4.24	0.96	0.991	0.14	0.65	0.961
	2		1.74	0.991	0.33	0.94	0.920
	3		1.07	0.930	0.21	0.59	0.890
La	1	1.54	3.39	0.999	0.26	1.26	0.899
	2		4.57	0.994	0.40	1.09	0.797
	3		3.24	0.999	0.24	1.29	0.820
	1	4.24	4.61	1	0.33	1.71	0.946
	2		5.02	0.999	0.31	2.03	0.928
	3		4.28	0.999	0.27	1.93	0.966
Y	1	1.54	4.89	0.999	0.24	1.93	0.894
	2		5.01	0.998	0.19	2.34	0.854
	3		4.68	0.998	0.21	1.98	0.853
	1	4.24	5.20	0.999	0.38	1.17	0.908
	2		4.85	0.999	0.30	1.74	0.880
	3		4.39	0.999	0.36	1.18	0.931
Nd	1	1.54	11.36	0.993	0.45	1.69	0.912
	2		10.82	0.998	0.29	3.28	0.947

	3	4.24	9.01	0.999	0.28	2.85	0.846
	1		11.44	0.999	0.24	3.81	0.921
	2		12.18	0.997	0.27	3.41	0.875
	3		13.44	0.986	0.38	1.79	0.972

Comparison of obtained data reveals that correlation coefficients R^2 for both isotherm models were rather high. However, for the most of the elements in the matrix solution the R^2 values for the Langmuir isotherm compared to those for the Freundlich isotherm, Langmuir adsorption model is well suited for the prediction of maximum metal uptake rate values. Exception was only Eu, for which the correlation coefficients R^2 of Freundlich isotherm were higher (at the pH value of 1.54), while for pH value of 4.24 Langmuir isotherm was fit better. At the same time, values of $1/n$ that indicate the strength of adsorption, were 0.4, 0.44 and 0.48 for adsorbents 1, 2 and 3 respectively, suggesting that process of biosorption is beneficial. As $1/n$ values between 0.1 and 1 imply for successful adsorption [17]. Overall, for most of the metals results indicate that REEs biosorption on the analyzed adsorbents is following monolayer adsorption on the surface of the adsorbents.

The total metal biosorption capacities of adsorbents were calculated and reported in Table 4.

Table 4. Total maximum metal capacities for analyzed adsorbents

Adsorbents	pH=1.54	pH=4.24
	Calculated $\sum q_{max}$ (mg/g)	Calculated $\sum q_{max}$ (mg/g)
1	34.36	29.16
2	32.23	31.91
3	26.18	34.53

In Figures 1-6 the removal efficiency of each of the analyzed metals at their minimum and maximum initial concentrations on three bio-based sorbents can be seen.

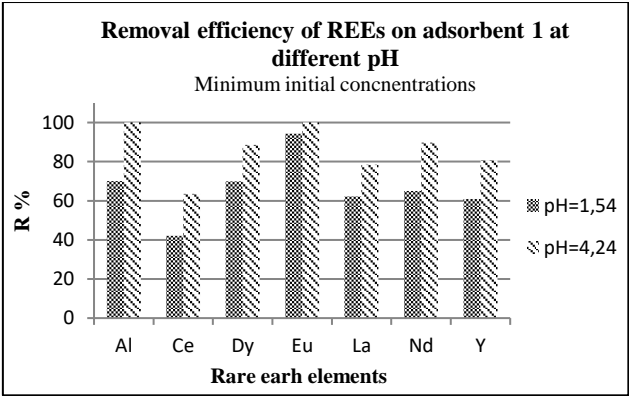


Fig. 1. Comparison of removal efficiency at various pH at min C_{in}

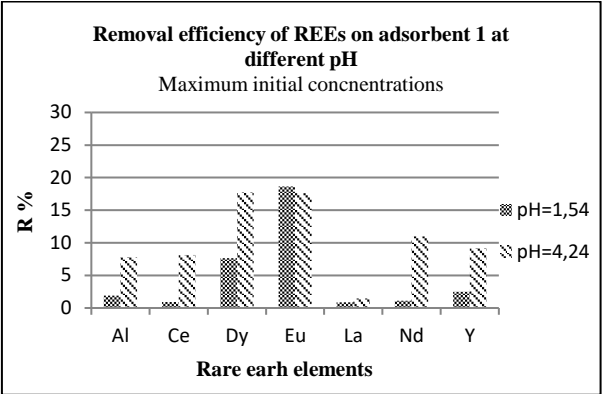


Fig. 2. Comparison of removal efficiency at various pH at max Cin

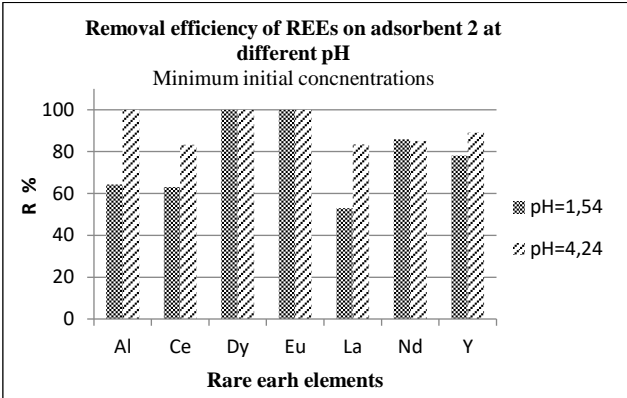


Fig. 3. Comparison of removal efficiency at various pH at min Cin

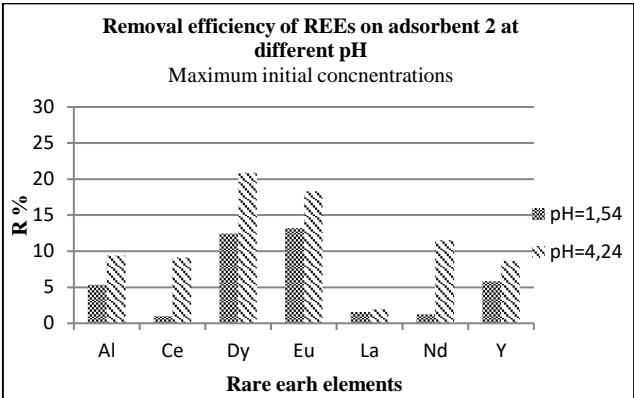


Fig. 4. Comparison of removal efficiency at various pH at max Cin

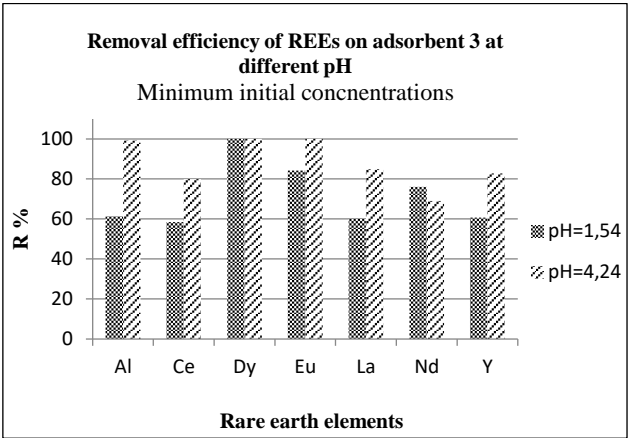


Fig. 5. Comparison of removal efficiency at various pH at min Cin

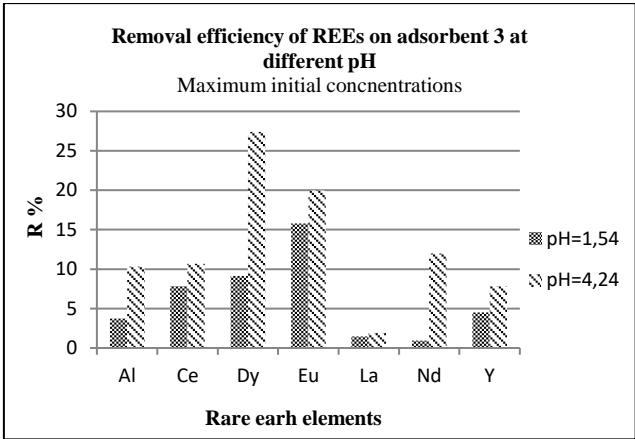


Fig. 6. Comparison of removal efficiency at various pH at max Cin

The important factors that usually affect the process of adsorption include pH, initial metal concentration, temperature and the adsorbent dosage. In order to evaluate the biosorption potential of analyzed REEs and Al, first two factors were taken into consideration while performing batch experiments.

pH is a very important parameter influencing hydrolysis, complexation and redox reactions during metal recovery [18]. pH dependence of analyzed metals is reported in this study. For the adsorbents, the removal efficiency for all the metals was higher at a higher pH value of 4.24. It can be explained by the fact that pH effects the dissociation of the carboxyl groups, present in biomass and plays a significant role in metal biosorption. With increase of pH the extent of carboxyl group dissociation is rising as well, leading to more available sites for metal biosorption, thus to the higher values of removal efficiency.

The effect of initial metal concentration on the adsorption of analyzed metals was studied as well. The biosorption efficiency was decreasing as the initial concentrations of metal ions were increasing. At high initial metal concentrations the available sites for adsorption became fewer, thus strongly affecting the removal percentage of analyzed elements. For most of the metals the removal efficiency at lower initial metal concentrations was in the range of 60-100%. While for higher initial metal concentrations percentage removal reached up max 20-25% for Dy and Eu due to their low initial concentration in matrix solution (10 mg/L). For

other analyzed metals, which concentration was in the range of 50-200 mg/L the percentage removal reached 10-15 %.

However, higher removal at quite low metal concentrations might be beneficial for industrial applications, for example in waste water treatment plants where effluents have relatively low REEs concentrations.

4 Conclusions

The purpose of this study was to investigate the feasibility of adsorption of REEs on bio-based adsorbents containing residual microalgae biomass, chitosan and additives originated from industrial and agricultural by-products. Adsorption of rare earth metals and aluminium was carried out using batch equilibrium experiments. Obtained results demonstrated that adsorption is depended on the initial metal concentration and the pH value. The percentage removal of analyzed metals reaches 80-100 % at the pH value of 4.24, however, decreases with the increase of initial metal concentrations.

Equilibrium adsorption data revealed that for the most metals the data fitted well the Langmuir isotherm model with the calculated values of total maximum sorption capacity (q_{\max}) 29.16, 31.91 and 34.53 mg/g at the pH of 4.24 for adsorbents 1, 2 and 3 respectively.

Ultimately, this study demonstrates that among analyzed biosorbents better performance was achieved by the adsorbent 2 and 3 with optimum value of pH 4.24 and the percentage removal for most of the metals was more than 80 %.

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