Recovery of Dysprosium Ions by Biosorption-desorption onto Organic Plants Wastes

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The recovery process of dysprosium from sewage by biosorption-desorption has been evaluated using low-cost biosorbents. Both dried and 450°C carbonized mandarin-orange peels and ginkgo leaves were selected as biosorbents and used to evaluate the recovery process of dysprosium ions. Evaluating the effect of pH with respect to contact time indicated a rapid biosorption of dysprosium ions onto the surfaces of the biosorbents. Equilibrium was reached within 10 min of contact, with the best biosorption capacity of 25.64 mg/g obtained with carbonized ginkgo leaves. The recovery process of adsorbed dysprosium was studied using hydrochloric acid, nitric acid, sulfuric acid and hot water. High recovery rates were obtained with acids but not with hot water. Hot water did not desorb dysprosium. Maximum recovery rates of 86.06% and 100% were obtained for dried ginkgo leaves and mandarin-orange peels, respectively, whereas 86.40% and 96.88% were obtained for 450°C carbonized ginkgo leaves and mandarin-orange peels, respectively. This suggests that carbonization treatment has little influence on the desorption capacity of mandarin-orange peels but significantly improves the biosorption performance of ginkgo leaves and mandarin-orange peels.

Key Words: Rare Earth, organic plants wastes, carbonization, dysprosium, biosorption

1 INTRODUCTION

The rare earth elements (REEs) are becoming increasingly important due to their essential role in green technology such as electronic devices, automobiles, national security applications, wind power generation, hybrid engines and permanent magnets etc [1-2]. China presently produces more than 90% of the global REE output and its increasingly tight export quota [2]. Countries or companies like Toyota, whose manufacturing or technology base depends on imported metals have started looking for alternative sources, by secure their control of mines in Australia, South Africa and Greenland [3]. Dysprosium, an element of lanthanide family, classify as heavy REE is currently for more than 99% mined in China [4]. Dysprosium is considered as one of the most critical REEs in the short term [4-5]. Due to the increasing price of REEs this few years, new technologies need to be improved to recover or recycle dysprosium from waste water and others sludge. Several expensive methods exist to recover REEs from ores such as pyrometallurgy, hydrometallurgy processes in case of REEs rich ores. Thus, find a low-cost and efficient technology for the concentration and recovery of REEs led to the choice of biosorption. Some biomasses have been tested and found efficient for the recovery of Dy(III), Sc(III), La(III) etc [3,6]. However, due to the large number of candidate biomasses, biosorption of REEs need to be deepened and more biomasses need to be tested. In this work, we propose the use of dried and 450°C carbonized mandarin-orange peels and ginkgo leaves (ginkgo biloba) as efficient biosorbents for the removal and recovery of dysprosium ions from aqueous solutions. The mechanism of the processes biosorption-desorption is also examined.

2 MATERIALS AND METHODS

2.1 Equipments

Thermo Gravimetric/Differential Thermal Analysis (Thermo plus EVO TG 8120/Rigaku) was carried out under Nitrogen condition. The carbonization of mandarin orange peels and ginkgo leaves was performed using electric furnace (HPM-0G/AS ONE). The specific surface area and pore diameter were measured using Pore Size Analyzer (NOVA 2200 e/TFII) by adsorption-desorption process with N₂. A reciprocal shaking bath (FTB-01/AS ONE) was used for the batch experiment processes. The pH of the solution was measured with a prior calibrated pH meter (HM-25R/TDA DK). The dysprosium content in treated solution was analyzed using ICP-OES (Inductively Coupled Plasma-Optimal Emission Spectrometer/Perkin Elmer/ Optima 5300).

2.2 Biosorbents preparation

Mandarin-orange peels and ginkgo leaves were thoroughly washed with distilled water and then dried at 80°C for at least 48 hours to remove the adherent moisture. After drying, the samples were heated in an electric furnace, for 30 min under N₂ atmosphere (gas flow: 15 L/min) to avoid any oxidation during the carbonization process. Then the samples were desiccated until completely cooled. Carbonization temperature was set at 450°C.
in order to obtain a carbon-rich material. The samples were then sieved to obtain a fraction of fine particles all passing 0.6 mm.

2.3 Batch adsorption studies

Batch studies were conducted to investigate the effect of parametric factors such as pH, solution temperature and contact time. Except where noted, a stock solution containing 1000 mg/L of dysprosium was diluted with deionized water to adjust the concentration of Dy to 10 mg/L. The pH of the solution was then adjusted using 1 mol/L of HCl or 1 mol/L of ammonia aqueous solution. Next, the biosorbent was mixed with dysprosium solution, resulting in a dosage of 1 g/L. The mixture was then shaken in a bath at 20°C and 150 rpm. The sample was then filtered with 0.2 μm filter and the filtrate was analyzed in terms of the remaining dysprosium concentration. The amount of Dy(III) ions adsorbed \( q \) (mg/g) was calculated using the following equation

\[
q = \frac{V(C_{\text{init}} - C_{\text{fin}})}{M}
\]

where

- \( M \) represents the amount of dysprosium ions adsorbed per gram of biosorbent. The percentage of removed Dy(III) ions was expressed as:

\[
\text{Removal ratio} = \frac{C_{\text{init}} - C_{\text{fin}}}{C_{\text{init}}}
\]

\( V \) Volume of the solution (L)
\( M \) Mass of the biosorbent used (g)
\( C_{\text{init}} \) Initial Dy ions concentration (mg/L)
\( C_{\text{fin}} \) Final concentration of Dy ions in solution (mg/L)

Samples for desorption experiments were prepared by putting biosorbents and adsorbate into contact for an hour, in order to saturate the available biosorbent sites with dysprosium ions. Then the samples were dried on the oven at 80°C for 72 hours. 0.02 g of the prepared sample was mixed with 20 mL aqua regia (high concentrated acidic solution composed of mixed HCl and HNO₃ at a volume ratio 3:1) and shaken at 20°C for an hour. The solution obtained was analyzed using ICP-OES and the results obtained were considered as the maximum concentration of dysprosium on the surface of the biosorbent (This result was very close to the supposed concentration of dysprosium on the surface of the biosorbent). Equation (1) was used to determine the maximum desorption capacity \( q_{\text{o}} \) for the selected biosorbents. Similarly, 0.02 g of the prepared sample was mixed with 1 mol/L of HCl, HNO₃, H₂SO₄ or 70°C of H₂O and the desorbed dysprosium concentration was determined in terms of total dysprosium capacity \( q(x) \) using the above solutions. Here, \( X \) represents HCl, HNO₃, H₂SO₄ or 70°C of H₂O. The desorbed amount of dysprosium using solution \( X \) (Desorbed % (\( X \))) was expressed as Eq.(3). All the investigations were done at least in triplicate to avoid any discrepancy in experimental data.

\[
\text{Desorbed % (}X\text{)} = \frac{q(X)}{q_{\text{o}}} \times 100
\]

3 RESULTS AND DISCUSSION

3.1 Thermal decomposition of raw mandarin-orange peels and ginkgo leaves

The weight loss measurement of mandarin-orange peels and ginkgo leaves can be well understood by considering the elementary amount of raw material transformed at a temperature compared to the total amount transformed during the whole carbonization process (Eq.(4))

\[
a = \frac{W_{\text{i}}}{W_{\text{s}}}
\]

Figure 1 Thermal decomposition of ginkgo leaves and mandarin-orange peels under nitrogen flow: decomposition rate 10°C/min
where $W_0$, $W_f$ are respectively the weight of solid (dried) burned at temperature $T$ and the total weight of solid burned during the pyrolysis process. In other words, $\alpha$ represents the rate of volatile matter release from the raw material with increasing decomposition temperature.

$\alpha$ was calculated from the weight loss data obtained with TG-DTA. Figure 1 shows the experimental results of the weight loss rate $\alpha$ vs. $T$ for mandarin-orange peels and ginkgo leaves and the heat flow named differential thermal analysis (DTA) versus $T$. It should be noted that, due to TG-DTA machine program setting, the biomass suggested to analysis is burn and re-burn at similar temperature. Then, the highest curve represents the raw data obtain after the first burning and the lowest deals with the data obtained by re-burning the same material. From Figure 1, it can be observed that $\alpha$ of ginkgo leaves increases to its peak at around 300°C and then decreases (albeit with kinks) with increasing temperature to reach equilibrium at 700°C. Contrarily, the profile for mandarin-orange peels displays two main peaks at 200°C and 300°C, after which $\alpha$ decreases with temperature to reach equilibrium at 550°C. Peaks correspond to the temperature at which large amount of volatile matter is released from the raw material [7]. Thus, for both, mandarin-orange peels and ginkgo leaves, decomposition of macromolecules may have occurred between 150°C and 300°C. Beyond 300°C, however, the weight loss rate decreased progressively, implying that carbon-rich material may have formed in the range of 300-500°C, albeit with a slow rate of gasification [8]. Hence, there seems to be an optimal decomposition temperature at which carbon rich materials is formed. Consequently, 450°C (At 450°C, a carbon-rich material should be obtained) was selected as carbonization temperature for both mandarin peels and ginkgo leaves. We obtained four kinds of biosorbents: dried mandarin-orange peels (MP); dried ginkgo leaves (GL); 450°C carbonized mandarin-orange peels (MP450) and 450°C carbonized ginkgo leaves (GL450). The physical characteristics of the biosorbents are shown in Table 1.

### Table 1 Specific characteristics of the selected biosorbents

<table>
<thead>
<tr>
<th>Biosorbents</th>
<th>BET surface area (m²/g)</th>
<th>Average pore diameter (nm)</th>
<th>Total pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GL</td>
<td>193.92</td>
<td>3.62</td>
<td>0.76</td>
</tr>
<tr>
<td>GL450</td>
<td>247.75</td>
<td>4.31</td>
<td>0.27</td>
</tr>
<tr>
<td>MP</td>
<td>141.78</td>
<td>3.75</td>
<td>0.13</td>
</tr>
<tr>
<td>MP450</td>
<td>237.92</td>
<td>31.50</td>
<td>1.87</td>
</tr>
</tbody>
</table>

3.2 Effect of pH on dysprosium ions removal

pH is one of the most important and predominant factors to be considered when assessing the sorption capacity of a biosorbent for dysprosium by sequestering from an aqueous solution. The pH of the system controls the sorption capacity due to its influence on the surface properties and metal speciation [9]. The sorption experiments were carried out in the pH range 1-5 while keeping other parameters constant. Precipitation is observed for pH beyond 5 due to the formation of hydroxide form of REE. The biosorption of MP, MP450, GL, GL450 (Figure 2) were inhibited at high acidic pH (pH 1-2). From pH 2, rapid uptake reaching the optimum pH 5 is observed for carbonized biosorbents whereas dried biosorbents indicate a kind of saturation from pH 3 to 5 and the removal percentage reaches 100%. Thus pH=5 was chosen for other experiments regarding MP, MP450 and pH=3 for GL, GL450. For both, dried and carbonized biosorbents, a low uptake is observed in the pH range of 1-2. This may be due to the competition of hydronium ions with Dy³⁺. This results are similar to the one reported by Karavaiko et al. [10] As pH increases, hydronium ions concentration decreases and then an electrostatic interactions occurs between Dy³⁺ and biosorbents charges resulted in the high uptake observed for carbonized biosorbents.

3.3 Effect of contact time

Dysprosium uptake onto MP, MP450, GL and GL450 was investigated with respect to contact time over the time range 0-60 min, while keeping other parameters constant. Figure 3 shows the effect of contact time for selected biosorbents at above mentioned pH, keeping the biosorbent dosage to 1 mg/L. For all the biosorbents, a rapid uptake of dysprosium ions was observed during the first 5 min followed by a slight variation of uptake rate over 5 min, suggesting that the equilibrium was attained within 10 min. The carbonized materials show the best biosorption capacity compared with dried ones. These results indicate that carbonization enhanced the sorption capacity of the material.

![Figure 2](image)

**Figure 2** Effect of pH on removal of dysprosium. Dy initial concentration 10 mg/L; Biosorbent dosage: 1 g/L; pH range 1-5; Solution temperature 20°C.

![Figure 3](image)

**Figure 3** Effect of contact time. Dy initial concentration: 10 mg/L; biosorbent dosage 1g/L; initial pH: (GL, GL450)=3, (MP, MP450)=5; solution temperature 20°C.
3.4 Adsorption isotherms

Sorption capacity of MP, MP450, GL and GL450 as a function of initial dysprosium concentration was investigated over a concentration range of 1-50 mg/L while keeping biosorbent dosage constant at 0.2 g/L. The amount of adsorbed dysprosium ions increased with increasing initial dysprosium concentration, emphasizing the dependency of sorption capacity of the system on the initial concentration.

In order to describe the interactive relationship between biosorbent and adsorbate and design the sorption system, Langmuir model was examined using Eq.(5)

\[
C_e = \frac{1}{b\cdot q_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]

where:
- \(C_e\) is the Dy concentration in solution at equilibrium (mg/L)
- \(q_e\) is the amount adsorbed per gram of the biosorbent at equilibrium (mg/g)
- \(b\) is the Langmuir constant (L/mg)
- \(q_{\text{max}}\) is the maximum adsorption capacity (mg/g)

Langmuir isotherms Eq.(5) deal with monolayer coverage formed by adsorbed molecules [11]. As can be seen in Table 2, Langmuir isotherm model fitted well the experimental data and the best densities were observed with carbonized materials demonstrating the importance of carbonization.

3.5 Kinetics

Adsorption kinetics describes the solute uptake rate as a function of residence time of adsorbate at the solid-liquid phase including the diffusion process [7]. The kinetic rate of Dy(III) ions were investigated using the pseudo first-order and second-order kinetic models. The agreement between experimental data and models as depicted by the values of their correlation coefficients \(R^2\) are summarized in Table 3. The pseudo first-order kinetic model is described by Eq.(6)

\[
\log\left(q_e - q_t\right) = \log q_e - \frac{t}{k_1/2.303}
\]

The pseudo second-order kinetic model is expressed as Eq.(7):

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]

where:
- \(K_1\) is the pseudo first-order kinetic equilibrium rate constant (mg/g/min)
- \(K_2\) is the pseudo second-order kinetic equilibrium rate constant (mg/g/min)
- \(q_e\) is the amount adsorbed per gram of the biosorbent at equilibrium (mg/g)
- \(q_t\) is the amount adsorbed per gram of the biosorbent at time \(t\) (mg/g)
- \(t\) is the contact time (min).

Figure 4 represents the plots \(t/q\) vs. \(t\) for the selected biosorbents at the indicated experimental conditions. Table 3 shows the values of the kinetics. The correlation coefficients for the pseudo second-order kinetic model shows a much better fit compared with the coefficients derived from the pseudo first-order kinetic model, suggesting that the biosorption of Dy(III) ions onto GL, GL450, MP and MP450 follow the pseudo second-order kinetic model.

3.6 Biosorption activation energy and enthalpy of activation

The Arrhenius equation for calculating activation energy is known as Eq.(8) and the enthalpy knows as Eq.(9)

\[
k_2 = k_\text{exp} \left(\frac{-E_a}{RT}\right)
\]

\[
\Delta H^\circ = E_a - RT
\]

where:
- \(k\) is the pre-exponential factor (g/mg/min)
- \(E_a\) is the activation energy of sorption (J/mol)
- \(R\) is the gas constant (8.314 (J/mol.k)
- \(T\) is the solution temperature (K)

Arrhenius equation parameters were evaluated using the pseudo second-order kinetic constant obtained based on temperature controlled data (30°C, 50°C, 70°C). Results obtained by variation of solution temperature are shown in Figure 5.

The value of activation energy is obtained by using the pseudo second-order kinetic equilibrium rate constant \(k_2\) obtained at each temperature. A plot of \(\ln k_2\) vs. \(1/T\) yields a straight line with a slope \(-E_a/RT\). Generally, the value of activation energy is used to distinguish between physical and chemical sorption. Physical sorption is characterized by low energy whereas chemical sorption involves stronger forces needed for the formation of external bonding [7]. In the present study the values of activation energy shown in Table 4 suggested that Dy (III) ions were chemically adsorbed onto all the selected biosorbents. The high value of \(E_a\) for MP450 may be due to the forces involved in the formation of bonds during the chemisorption process. The positive values of the enthalpy of activation \(\Delta H^\circ\) indicated the endothermic aspect of the.
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3.7 Recovery of dysprosium

The recovery of adsorbed dysprosium is an important step to obtain the transition metal in its pure form. More the recovery rate is high more the process is efficient. The results for the desorption rate of dysprosium using HCl, HNO₃, H₂SO₄ or 70°C of H₂O are shown in Table 5. All the tested acid solutions indicated high rate of desorption. Hot water was found to be a poor desorbents. The high desorption rate obtained demonstrates the good efficiency of the method and since low-cost biosorbents are used, the process is low-cost and can be employed to recover dysprosium from ores or sewage.

3.8 Possible mechanism

The functional groups of the biosorbents have been analyzed (Table 6) on Fourier transformed infrared spectrometer (FT-IR). The presence of C=O groups provided from carbonyl and amide group as well as aromatic ring are noted on GL, MP and MP450.

Table 4 Thermodynamics parameters

<table>
<thead>
<tr>
<th>Thermodynamic parameters</th>
<th>GL</th>
<th>GL450</th>
<th>MP</th>
<th>MP450</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy Ea (kJ/mol)</td>
<td>21.86</td>
<td>11.84</td>
<td>21.03</td>
<td>97.09</td>
</tr>
<tr>
<td>(\Delta H^*) (kJ/mol) (At 20°C)</td>
<td>19.43</td>
<td>9.40</td>
<td>18.59</td>
<td>94.66</td>
</tr>
</tbody>
</table>

Table 5 Recovery rate of dysprosium using different kinds of acid:

<table>
<thead>
<tr>
<th>Species</th>
<th>Recovery rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GL</td>
<td>86.06</td>
</tr>
<tr>
<td>MP</td>
<td>100.00</td>
</tr>
<tr>
<td>GL450</td>
<td>86.39</td>
</tr>
<tr>
<td>MP450</td>
<td>96.88</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acid concentration</th>
<th>HNO₃</th>
<th>H₂SO₄</th>
<th>HCl</th>
<th>H₂O(70°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GL</td>
<td>86.06</td>
<td>89.92</td>
<td>81.99</td>
<td>31.55</td>
</tr>
<tr>
<td>MP</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>0.00</td>
</tr>
<tr>
<td>GL450</td>
<td>86.39</td>
<td>79.80</td>
<td>85.71</td>
<td>0.00</td>
</tr>
<tr>
<td>MP450</td>
<td>96.88</td>
<td>93.50</td>
<td>97.59</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 6 FT-IR results of dried and carbonized mandarin-orange peels and ginkgo leaves

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>GL</th>
<th>GL450</th>
<th>MP</th>
<th>MP450</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonyl C=O</td>
<td>1748.16</td>
<td>x</td>
<td>1734.66</td>
<td>1733.69</td>
</tr>
<tr>
<td>Amide C=O</td>
<td>x</td>
<td>1652.70</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>Aromatic C=C</td>
<td>1508.06</td>
<td>x</td>
<td>1560.13</td>
<td>1508.06</td>
</tr>
<tr>
<td>Alkyne C≡C</td>
<td>2179.17</td>
<td>x</td>
<td>2243.77</td>
<td>x</td>
</tr>
<tr>
<td>Amine C-N</td>
<td>1264.11</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Alkyl halide C-Cl</td>
<td>685.57</td>
<td>799.35</td>
<td>x</td>
<td>753.07</td>
</tr>
<tr>
<td>Alkane C-H</td>
<td>x</td>
<td>x</td>
<td>2899.45</td>
<td>x</td>
</tr>
</tbody>
</table>

Figure 5 Effect of temperature on Dy removal


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With the thermal decomposition of ginkgo leaves, the aromatic and C=O groups decomposed totally. We can conclude that at 450°C, all the macromolecules decomposed totally and only the carbon reacts in the biosorption process of GL450. Except the electrostatic interaction characterizing any biosorption process, biosorption onto C=O functional group should be also pointed out with MP, MP450 and GL. Oxygen is more electronegative than carbon and then is apt to react with Dy³⁺ in the solution. The desorption process is just the reverse process in which oxygen is protonated leading to the release of Dy³⁺ from biosorbents.

4 CONCLUSIONS

In the present work, both carbonized and dried mandarin-orange peels and ginkgo leaves have been examined as possible sources of low-cost biosorbents to remove dysprosium ores and recover the metal for further use. High biosorption density of 25.64mg/g was obtained for carbonized ginkgo leaves and the recovery rate of 86.40% proved the efficiency of the process named low-cost process.

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