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Removal of Aluminum from Synthetic Rare Earth Leach Solution by Selective Complexation and Turbidity Point Extraction

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Abstract: During the leaching process of ion-adsorbed rare earth ores, large amounts of non-rare earth impurities such as aluminum and iron will be generated. This study selected glutamic acid as a complex agent to selectively calculate aluminum ions; then, added non-ionic surfactants and extract and separate aluminum ions from a rare earth solution using the cloud point extraction method. The effects of solution pH, reaction temperature, equilibration time, amount of glutamic acid, reaction time, and amount of Triton X-114 on aluminum extraction were investigated. The results showed that with a M_{glu}:M_{Al} ratio of 3:1, a solution pH of 4.5, a constant temperature of 40 °C, and the addition of 10 mL Triton X-114 after 10 min of reaction time, the single extraction efficiency of aluminum ions reached 78.01%, and the extraction efficiency of rare earths was only 5.09% after 10 min of equilibration time. The reaction equation of glutamic acid with aluminum ions was determined, and the lowest extraction concentration of aluminum ions in the glutamic acid complexation extraction solution was found to be $c_{Al} = 0.045 \pm 0.003$ g/L, with a separation coefficient of $\beta(Al/RE) = 66.15$. This result indicated that the aluminum ions in the mixed solution could be effectively separated from the rare earth ions when using glutamic acid as a complexing agent in combination with the turbidity point extraction method.

Keywords: rare earths; aluminum removal; turbidity point extraction; selective complexation; glutamic acid

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1. Introduction

Rare earth elements (REEs) are the collective name for a total of 17 elements, including scandium and yttrium, of the lanthanides in the periodic table of elements. REEs are known as “all-purpose earths” and “industrial vitamins” due to their special properties and wide range of applications. They are widely used in rare earth permanent magnetic materials, rare earth phosphors, rare earth chemical catalysts, alloys, and glass ceramic industries [1–5]. The leaching of ore causes ion impurities (such as iron, aluminum, etc.) to leach into the leaching solution [6–8]. The presence of these impurity ions affects the quality of rare earth products during rare earth precipitation and separation and increases the cost due to the need for impurity elimination. Among them, the coexistence and similar nature of aluminum ions and rare earth ions leads to a low purity of the obtained rare earth leachate [9]. Therefore, rare earth dealumination is a top priority. Zeng Zhiyuan et al. developed a new highly selective 1-butyl-3-(3,3-dimethyl-2-oxobutyl)-imidazol-3-ium bis(2-ethylhexyl) glycinate for the removal of aluminum from ion-adsorbed rare earth ore leachates. Under optimized extraction conditions, the removal rate of aluminum is greater than 95%, and the recovery rate of rare earth is greater than 96% [10]. Wu Guolong et al.

used 3- (bis (2-ethylhexyloxy) phosphoryl) -3-phenylpropionic acid as the extractant to remove Al^{3+} through cascade extraction. Although the concentration of aluminum ions has decreased from 304.5 mg/L to 4.35 mg/L, and the rare earth recovery rate is 95.6%, this method has expensive extractants and complex production processes [11]. Hu Kaibo et al. studied the removal of aluminum from gadolinium chloride using three pyridinium-based ionic liquids as liquid–liquid extraction solvents. By adjusting the pH of the water phase, the separation factor β for Al^{3+}/Gd^{3+} was as high as 340, the removal rate of Al^{3+} was 97.1%, but the recovery rate of Gd^{3+} was only 85.6% [12]. Ni Shuainan et al. proposed a new method based on a hydrophobic deep eutectic solvent for separating Al^{3+} and Gd^{3+}, which has a good purification effect on single component rare earth gadolinium chloride [13]. Li Wentao et al. prepared aluminum ion imprinted polymer using a surface imprinting method, and used adsorption to remove aluminum. Aluminum ions have good selectivity at low concentrations, but no selectivity at high concentrations [14]. Yu Gaoshan et al. developed 4-octyloxybenzoic acid (POOA) as a solvent for the extraction and separation of aluminum from rare earths. The results showed that POOA had better phase separation performance than naphthenic acid, which was easy to emulsify [15]. The traditional aluminum removal process using ammonium bicarbonate as a precipitant is often accompanied by high rare earth loss and ammonia nitrogen pollution. Zhou Hepeng et al. found that decadecylglucoside (dG) is an environmentally friendly and effective precipitant, which can achieve a low rare earth loss rate and high aluminum removal rate [16]. Li Jinhui et al. proposed a 5-sulfosalicylic acid selective complexation-D290 resin adsorption process for the extraction of aluminum, which exhibited good adsorption and extraction with regards to aluminum but provided poor treatment efficiency [17]. Wang Yudong et al. proposed the selective complexation process of 8-hydroxyquinoline to remove aluminum, the product of which (8-hydroxyquinoline aluminum) is an important organic optoelectronic material. The economy and practicality of this method are high, but the separated solution still contains a large amount of aluminum ions [18]. Wang Yabing et al. [19] proposed octylphenoxy isopropionic acid saponification followed by extraction separation to remove aluminum, and the purity of rare earths after aluminum removal is high, but it is only applicable to rare earth stock solutions with high aluminum contents.

The literature research has revealed that the turbidity point extraction technique has been applied to the detection and analysis of trace metal elements. Turbidity point extraction is an environmentally friendly liquid–liquid extraction technique, also known as micellar-mediated extraction [20–22] and liquid coalescence extraction. The cloud point extraction method, developed from the cloud point phenomenon of a non-ionic surfactant, is a method of extracting metal complexes into non-ionic surfactant phases for separation and enrichment by temperature-triggered phase separation. The turbidity point extraction involves extracting metal complexes into non-ionic surfactant phases for separation and enrichment, and then triggering phase separation by adjusting the temperature. In this study, the aluminum ions in the rare earth solution are complexed by glutamic acid. The turbidity point extraction of the non-ionic surfactant Triton X-114 was selected for extracting metal aluminum complexes. This method is simple, efficient, and scientifically interesting, and it can achieve the extraction and separation of rare earth ions and aluminum ions in solution.

2. Experimental Materials and Methods

2.1. Experimental Materials

The simulated rare earth leaching solution used for the experimental study process was a rare earth solution configured with yttrium as the main component. The concentration of Y^{3+} in the solution was 5 g/L, and the Al^{3+} content was adjusted according to the experimental study.

The experimental configuration of the 75 g/L rare earth leach solution is the acid leach solution of the medium yttrium europium-rich rare earth concentrate, whose main chemical composition is as follows (Table 1).

Table 1. The main chemical composition of rare earth concentrate.

Element	Al_2O_3	Fe_2O_3	Y_2O_3	La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	Gd_2O_3	**Else**
Content/%	0.14	0.089	25.63	13.85	1.95	16.78	15.23	4.43	21.901

2.2. Analytical Test Instruments

The main equipment used for the experiments was a UV-visible spectrophotometer (UVf-6300 type, Shanghai Meproda Instruments Co., Ltd., Shanghai, China), magnetic stirring thermostatic water bath (HH-6S, Jiangsu Jintan Yitong Electronics Co., Ltd., Changzhou, China), electronic balance (AR223CN, OHAUS Instruments (Shanghai) Co., Ltd., Shanghai, China), and a benchtop pH meter (PH6175, Shanghai Ren's Electronics Co., Ltd., Shanghai, China).

2.3. Experimental Methods

A certain mass of glutamic acid was added to the leaching solution, and the mixed solution was placed onto a constant temperature magnetic stirring table. The pH of the solution was adjusted, and an appropriate amount of Triton X-114 was added after a certain time. The solution was heated to a certain temperature for a period of time, and aluminum ions were extracted to separate the aluminum and rare earth ions in the solution. The experimental flow chart is shown in Figure 1.

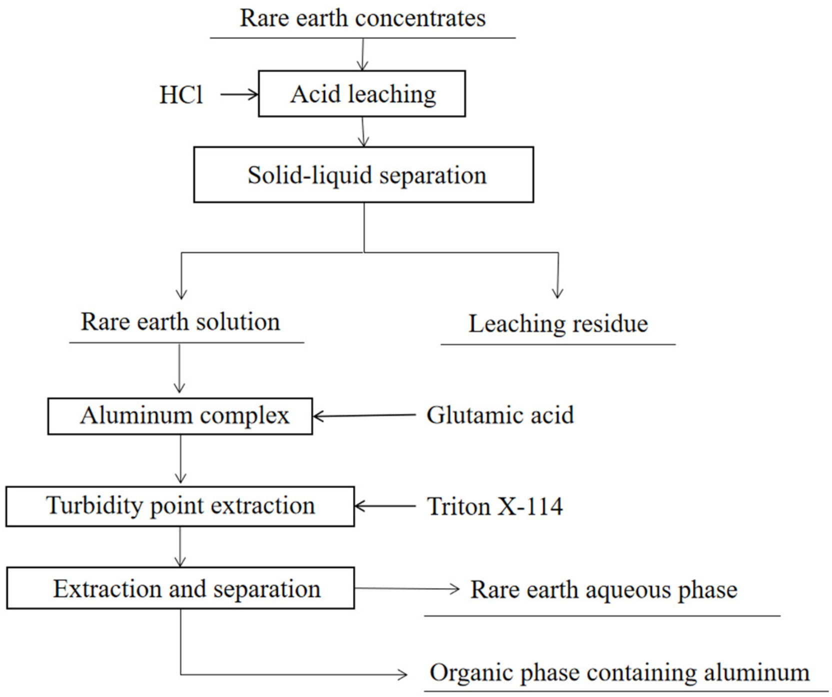


Figure 1. Flow diagram of experiment.

2.4. Experimental Factors

pH. The complex reaction of glutamic acid with aluminum ions presupposes the dissociation of hydrogen ions from the amino groups and carboxyl. Therefore, the pH has a great influence on the coordination ability of glutamic acid and aluminum ions. Under conditions with a low pH, the free hydrogen ions of glutamic acid are inhibited, thereby affecting the effectiveness of glutamic acid in removing aluminum ions. However, aluminum ions will be precipitate under the high pH conditions. It is vital to find the appropriate pH.

Reaction Temperature and other factors: balance time (extraction time of the extractant and the complex), glutamic acid dosage, reaction time (reaction time of the complexation agent with the aluminum ions), and Triton X-114 (a non-ionic surfactant associated) dosage.

2.5. Detection of Rare Earth Elements and Aluminum Content in the Solution

The content of rare earth was determined by the EDTA titration method, and the content of Al^{3+} was determined by chrome-azurin S colorimetry [23].

3. Results and Discussion

3.1. Effect of pH and Reaction Temperature and Balance Time on the Efficiency of Aluminum Extraction

The effect of adjusting pH, reaction temperature, and balance time on aluminum removal efficiency is described. As shown in Figure 2, in the pH 2.5–3.5 range, the extraction rate of aluminum ions does not increase significantly with an increasing pH. The degree of protonation/charge of glutamic acid $pk_1 = 2.16$, $pk_2 = 4.27$, indicates that the amino and carboxyl hydrogen ions on glutamic acid are not completely removed when the pH of the solution is low, and only a small amount of glutamic acid reacts with the aluminum ions. When the pH = 4, the extraction rate of aluminum ions from the rare earth solution is 58.79%, and the extraction rate of the rare earth is 4.86%. As the pH is increased to 4.5, the extraction rate of the aluminum ions is 74.88%, and the extraction efficiency of the rare earth ions is 6.67%.

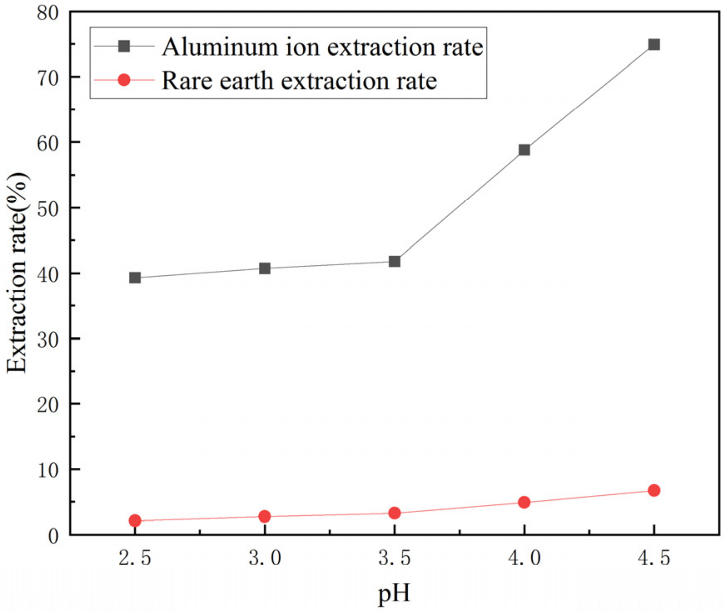


Figure 2. The effect of pH on the extraction rate of aluminum ions and rare earth ions. (n (Al^{3+}): n (glutamic acid) = 1:3, volume ratio of rare earth to Triton X-114 is 5:1, T = 40 °C, the reaction time is 20 min).

As shown in Figure 3, the extraction rate of rare earth ions increases with the increase of temperature. The temperature has little effect on the extraction rate of aluminum ions. With an increase in temperature, the excess glutamic acid in the solution starts to combine with rare earth ions; the complexation of rare earth ions with glutamic acid requires higher temperatures. Therefore, the extraction of rare earth ions is easier at high temperatures. The high reaction temperature therefore affects the coordinating ability of the glutamic acid complexation reaction, further increasing energy consumption and costs. A reaction temperature of 40 °C appears to be the most suitable.

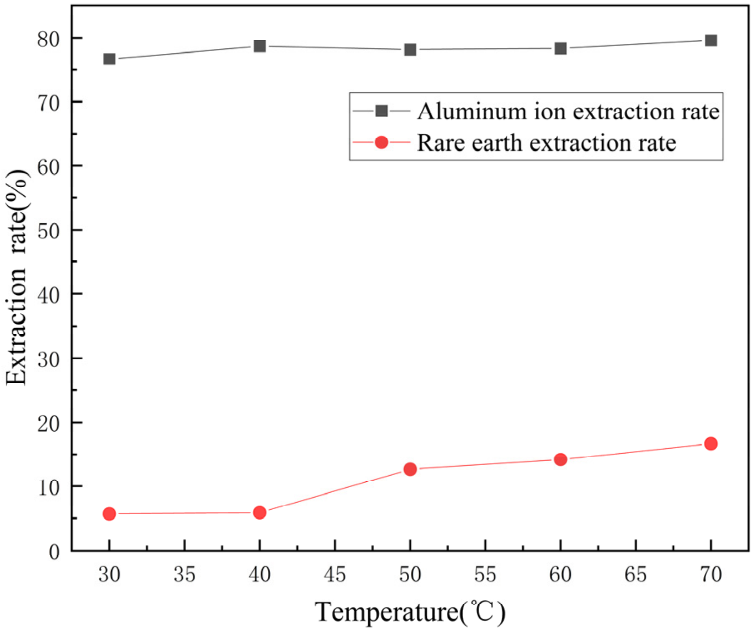


Figure 3. The effect of temperature on the extraction rate of aluminum ions and rare earth ions. (n (Al^{3+}): n (glutamic acid) = 1:3, volume ratio of rare earth to Triton X-114 is 5:1, pH = 4.5, the reaction time is 20 min).

As shown in Figure 4, after 10 min of equilibration, the extraction rate of rare earth ions and aluminum ions in the solution is 5.88% and 78.85%. This shows that a balance time of 10 min can better remove the aluminum ions in the rare earth material solution. As the balance time continues to increase, the extraction rates of aluminum ions and rare earth ions did not change with the change of balance time. Therefore, choose a balance time of 10 min.

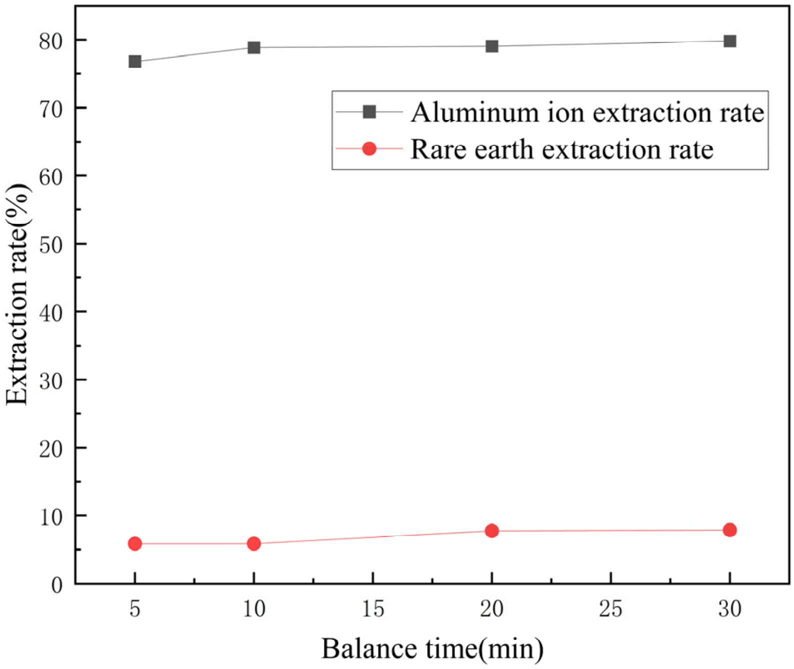


Figure 4. The effect of balance time on the extraction rate of aluminum ions and rare earth ions. (n (Al^{3+}): n (glutamic acid) = 1:3, volume ratio of rare earth to Triton X-114 is 5:1, T = 40 °C, pH = 4.5).

3.2. Effect of the Amount of Glutamic Acid and Triton X-114 and Reaction Time on the Efficiency of Aluminum Extraction

Several 50 mL rare earth stock solutions were prepared, and glutamic acid was added to each solution. The relationship between the amount of glutamate and the extraction efficiency of aluminum was discussed, and the results were shown in Figure 5.

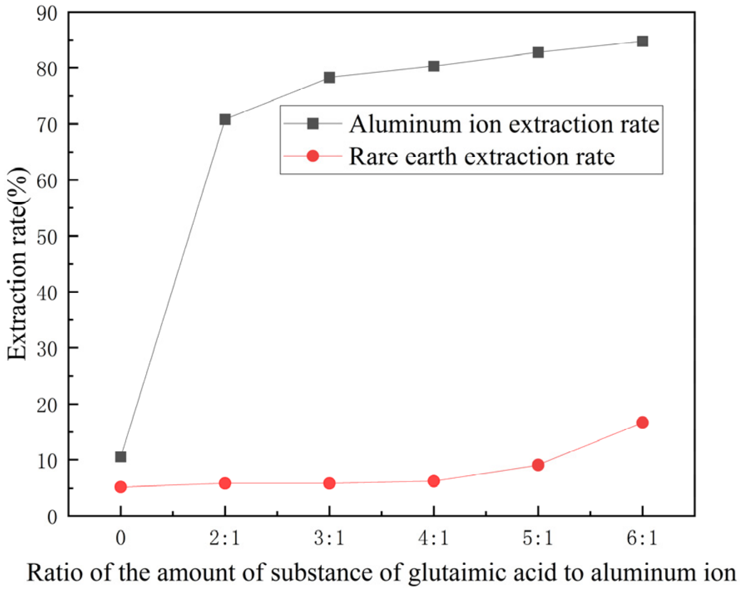


Figure 5. The effect of glutamic acid dosage on the extraction rate of aluminum ions and rare earth ions. (Volume ratio of rare earth to Triton X-114 is 5:1, T = 40 °C, pH = 4.5, the reaction time is 20 min).

Only the amount of glutamic acid and Triton X-114 and reaction time were changed to change the effect on aluminum removal efficiency. As shown in Figure 5, when no glutamic acid was added to the solution, very few aluminum ions were removed; the addition of glutamic acid to the solution resulted in the extraction rate of aluminum ions from the rare earth solution increasing from 70.83% to 83.79%. Following the addition of glutamic acid in an amount five times greater than the molar amount of aluminum ions, the extraction rate of rare earth ions starts to increase significantly from 6.25% to 16.67%. The reason for this is that the presence of excess glutamic acid in the leachate starts to react with the rare earth ions. Comparing the ratios of M_{glu}:M_{Al} = 3:1 and M_{glu}:M_{Al} = 4:1, the increase in the aluminum ion extraction rate was not obvious after doubling the amount of added glutamic acid. In consideration of cost, a 3:1 molar ratio of glutamic acid to aluminum ions is most suitable.

As seen from Figure 6, when the constant temperature reaction is carried out over 10 min, the extraction rate of aluminum ions in rare earth solutions can reach 78.56%, while the extraction rate of rare earth ions is only 4.45%. Thus, the use of a constant temperature over a 10 min reaction time can remove the aluminum ions in the rare earth solution most effectively. As the reaction time increases, there is no significant change in the extraction rate of aluminum ions and rare earth ions, which indicates that the rate of glutamic acid and aluminum ion complexation is high and that a controlled reaction time of 10 min is suitable for this operation.

As shown in Figure 7, when the amount of Triton X-114 was increased from 5 mL to 10 mL, the extraction rate of aluminum ions increased from 72.95% to 78.01%, while the extraction rate of rare earth ions remained stable. As the volume of Triton X-114 in the solution increases further, the extraction rate of Al^{3+} in the mixed solution remains approximately the same, but the extraction rate of rare earth ions starts to rise. This is because the extraction rate of Triton X-114 for aluminum glutamate has reached its saturation point, and as more Triton X-114 is added, glutamate rare earths are extracted, improving the ability of rare earth ions to be extracted. In summary, it is most appropriate to set the amount of Triton X-114 to 10 mL.

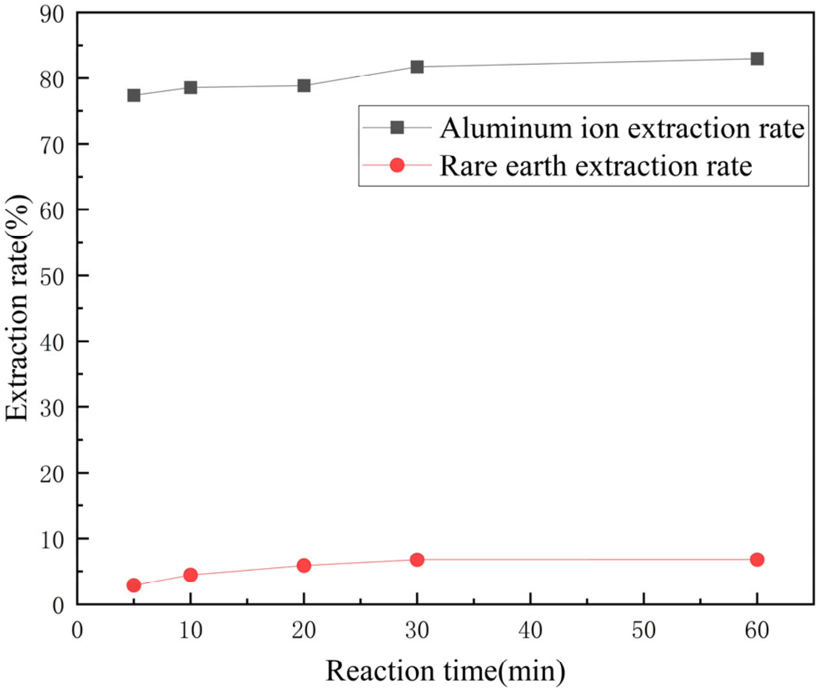


Figure 6. The effect of reaction time on the extraction rate of aluminum ions and rare earth ions. (n (Al^{3+}): n (glutamic acid) = 1:3, volume ratio of rare earth to Triton X-114 is 5:1, T = 40 °C, pH = 4.5).

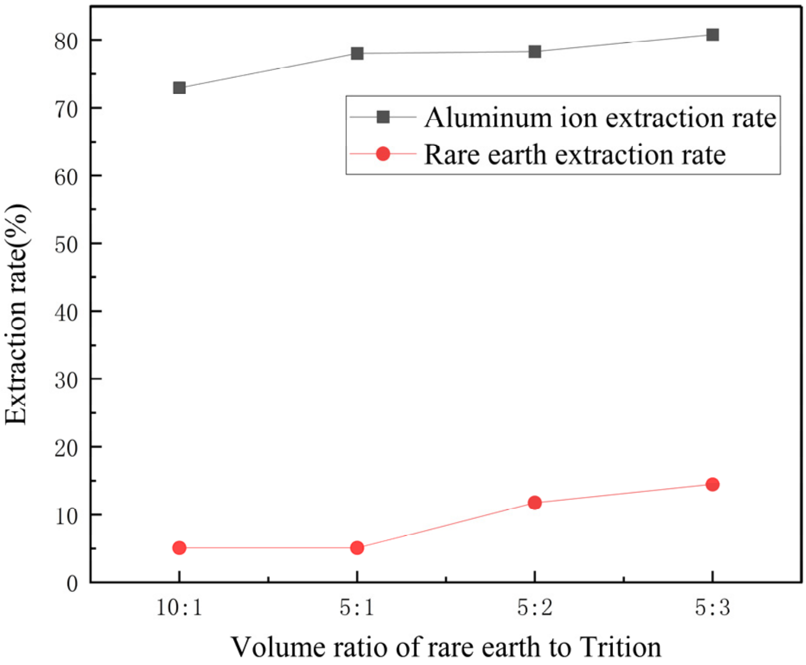


Figure 7. The effect of Triton X-114 dosage on the extraction rate of aluminum ions and rare earth ions. (n (Al^{3+}): n (glutamic acid) = 1:3, the reaction time is 20 min, T = 40 °C, pH = 4.5).

3.3. Al Extraction Efficiency of Glutamic Acid in Mixed Solutions with High Rare Earth Concentration

To investigate the extraction efficiency of glutamic acid in high-concentration mixed rare earth solutions, the solution with a rare earth concentration of 75 g/L and an Al^{3+} concentration of 4 g/L was analyzed. For M_{glu}:M_{Al} = 3:1, the solution pH = 4.5 remains unchanged, the temperature was held constant at 40 °C, 10 mL Triton X-114 was added, and the balance time was 10 min. In this case, the single extraction rate of aluminum ions was 69% and the extraction rate of rare earths was 26% when glutamic acid is used as the complexing agent. This indicates that the process is effective in extracting and removing aluminum in mixed solutions with high rare earth concentrations.

3.4. Effect of Hydrochloric Acid Concentration on the Reverse Extraction Efficiency

An amount of 20 mL of the extracted organic phase was taken, O/A = 1:5, 40 °C, the balance time was 10 min, and hydrochloric acid concentration was a variable. The effect of hydrochloric acid acidity on the extraction efficiency of Triton X-114 is shown in Figure 8.

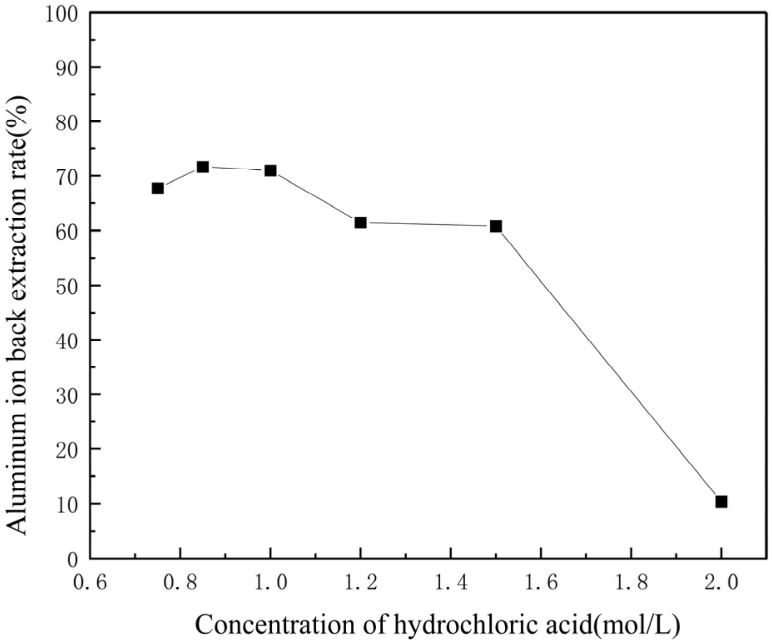


Figure 8. The effect of hydrochloric acid concentration on the back extraction rate of aluminum ions.

As shown in Figure 8, the initial concentration of hydrochloric acid was too high, resulting in almost no back-extraction of aluminum ions from the organic phase. Hydrochloric acid dissolves most of the organic phase, making phase separation difficult. The acidity of hydrochloric acid decreases, and the reverse extraction rate of aluminum ions increases. When the added hydrochloric acid is 1.0 mol/L hydrochloric acid, 72% of the aluminum ions in the system are reverse extracted. Therefore, the use of 1.0 mol/L hydrochloric acid as the reverse extraction is most beneficial to the process.

3.5. Effect of Organic to Aqueous Phase Ratio on the Reverse Extraction Efficiency

Experimentally, 20 mL of the extracted organic phase was taken, 1 mol/L hydrochloric acid was used, and the solution was left to equilibrate for 10 min. The effect of the O/A phase ratio on the reverse extraction efficiency of Triton X-114 was investigated, and the results are shown in Figure 9.

As shown in Figure 9, the volume of the organic phase remained unchanged, and the reverse extraction rate of the aluminum ion in the organic phase increased with the increase of the O/A ratio, and there was no further change after 1:7. This is because as the O/A ratio decreases, the contact area between the organic phase and the aqueous phase also increases, making the efficiency of the reverse extraction more pronounced. When O/A = 1:7, the back extraction rate of aluminum ions in the organic phase can reach 90.42%, and past this point, the back extraction rate of aluminum ions remains basically unchanged. Therefore, O/A = 1:7 is a suitable volume ratio.

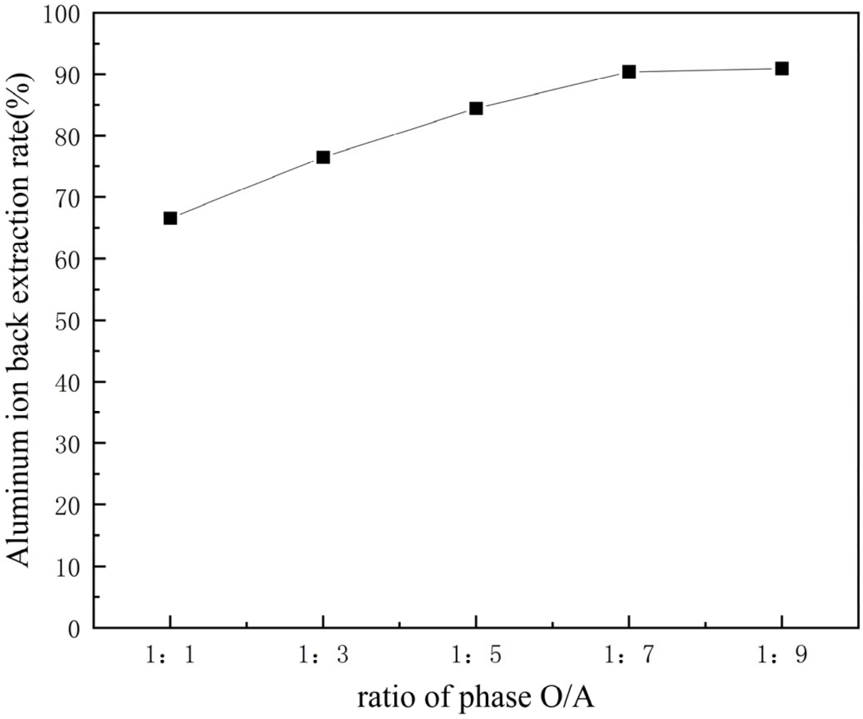


Figure 9. The effect of the O/A phase ratio on the back extraction rate of aluminum ions.

3.6. Effect of Reaction Temperature on Reverse Extraction Efficiency

An amount of 20 mL of the extracted organic phase was taken, and 1 mol/L hydrochloric acid was added. The O/A ratio was 1:7. The purpose of changing the reverse extraction temperature was to investigate the relationship between the reverse extraction temperature and the reverse extraction efficiency of Triton X-114. The results are shown in Figure 10.

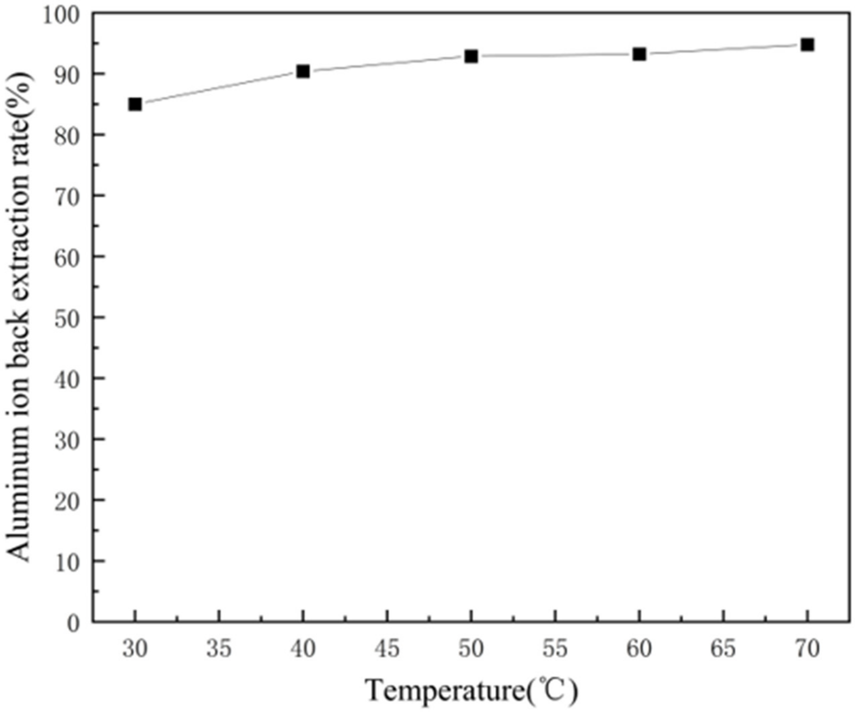


Figure 10. The effect of temperature on the back extraction rate of aluminum ions.

As shown in Figure 10, the reverse extraction rate of aluminum ions in the organic phase remains essentially unchanged as the temperature increases. This is due to the lower temperature requirement of the reverse extraction process. When the temperature is 40 °C, the reverse extraction rate of aluminum ions in the organic phase reaches 90.56%. Beyond this temperature, the reverse extraction rate of aluminum ions remains basically unchanged, and higher temperatures only further increase energy consumption and costs. Therefore, choosing a reaction temperature of 40 °C is the most suitable.

3.7. The Effect of Balance Time on the Reverse Extraction Efficiency

An amount of 20 mL of the extracted organic phase was taken, 1 mol/L hydrochloric acid was added, the O/A ratio was set to 1:7, and the balance time was varied to investigate its influence on the reverse extraction efficiency of Triton X-114. The results are shown in Figure 11.

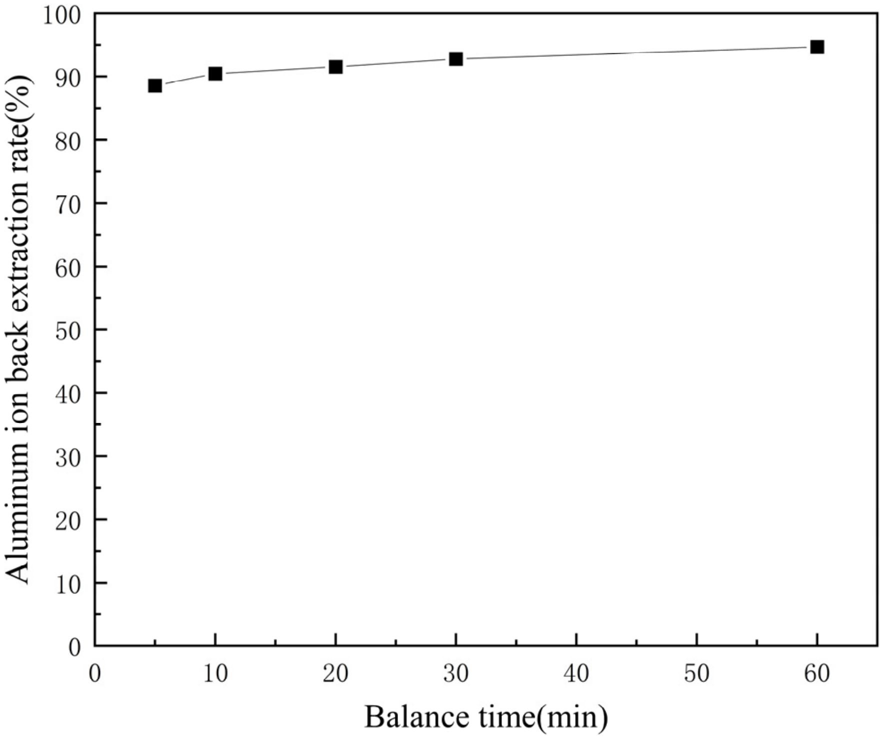


Figure 11. The effect of balance time on the back extraction rate of aluminum ions.

It can be seen from Figure 11 that reaction time has little influence on the back extraction rate of aluminum ions in organic phase. This indicates that the length of the equilibration time has a negligible effect on the reverse extraction experiment. After 10 min of equilibration, the reverse extraction rate of aluminum ions in the organic phase reaches 90.46%; therefore, a balance time of 10 min was chosen as the most appropriate.

3.8. UV Spectrophotometric Study on the Complexation Reaction of Glutamic Acid with Aluminum

Glutamic acid molecules show absorption peaks in the UV-visible spectral band, so the reaction between glutamic acid and aluminum ions can be studied by UV-vis spectrophotometry. The experiment used glutamic acid aqueous solution as the reference. A mixture consisting of equal concentrations of glutamic acid and aluminum ions was prepared for UV-vis scanning detection, and the results are shown in Figure 12.

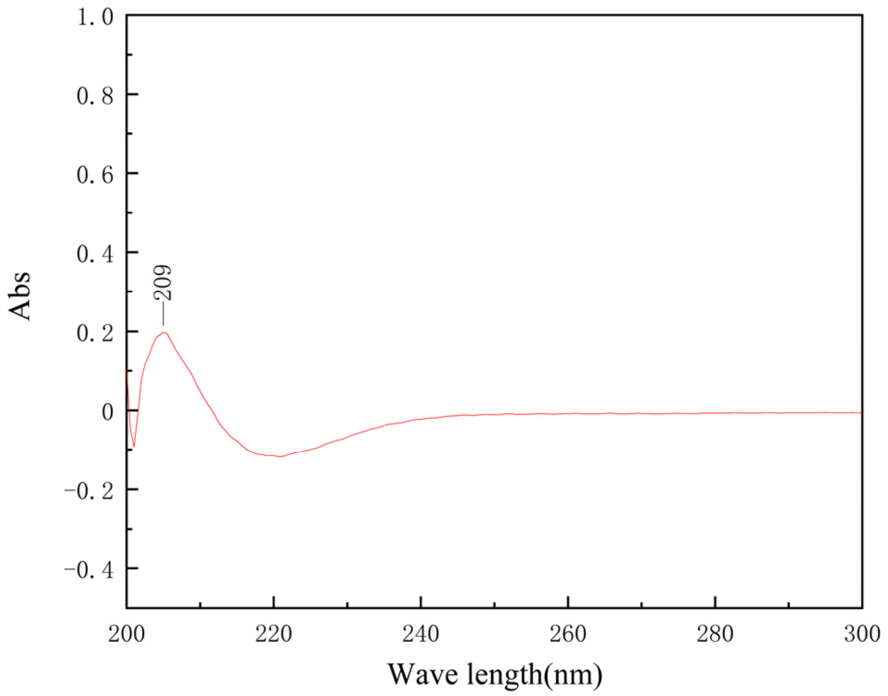
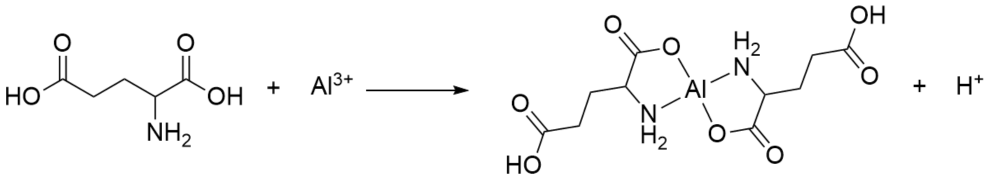


Figure 12. UV−visible spectral analysis on a mixture consisting of equal concentrations of glutamic acid and aluminum ions.

As shown in Figure 12, a stable absorption peak at 209 nm was observed for a reaction solution of glutamic acid and aluminum ions. This indicates that a glutamic acid aluminum complex is produced in the mixed solution.

A search of the literature reveals that the amino and carboxyl ends of amino acids can form cyclic products with metal ions at certain ratios. Amino acid complexes use metal cations to form coordination bonds with the amino and carboxyl ends of amino acids and form five- or six-membered rings [24,25]. The equation for the reaction of glutamic acid with aluminum ions is shown in Scheme 1.



Scheme 1. The reaction mechanism of glutamic acid with aluminum ions.

3.9. Study on the Mechanism of Aluminum Extraction by Turbidity Point Extraction of Glutamic Acid

Glutamic acid can form complexes with rare earth ions or aluminum ions in rare earth liquid. The experimental results show that glutamic acid preferentially reacts with aluminum ions and that the aluminum ions are extracted in the subsequent operation so that they can be separated from the rare earth ions in the rare earth liquor. In this experiment, glutamic acid was added to a solution containing only aluminum ions. After the reaction was complete, Triton X-114 was added in the turbidity point extraction process to observe its effect on the extraction rate of aluminum ions, the results of which are shown in Figure 13.

As shown in Figure 13, in the aqueous solution with an Al^{3+} concentration of 2.89 g/L, the aluminum ion extraction efficiency is 62.85% when 5 mL Triton X-114 is added, and the concentration of extracted Al^{3+} in the organic phase is 1.861 g/L. When the Triton X-114 is increased in volume, the extraction rate of Al^{3+} also increases gradually. When 20 mL of Triton X-114 was added, the extraction rate of aluminum ions reached 76.09%, and the concentration of extracted aluminum ions in the organic phase was 2.198 g/L. The amount of Triton X-114 was further increased to 30 mL, at which point the extraction rate of aluminum ions was 77.85%, whereas the concentration of extracted aluminum ions in the organic phase was 2.249 g/L. This indicates that beyond a certain addition level of Triton X-114, the extraction rate of Al^{3+} in the solution remains basically unchanged.

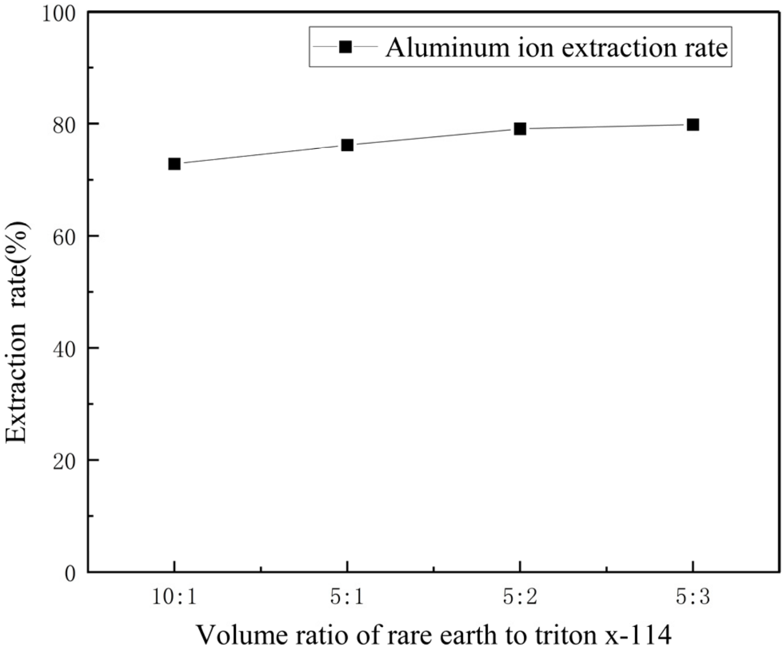


Figure 13. The effect of Triton X-114 dosage on the extraction rate of aluminum ions.

The effect of Triton X-114 on the extraction rate of rare earth was further investigated. Glutamic acid was added to the solution containing only Y^{3+} for complexation, and after the reaction was complete, Triton X-114 was added to conduct the turbidity point extraction process. The effect on the extraction rate of rare earth ions are shown in Figure 14.

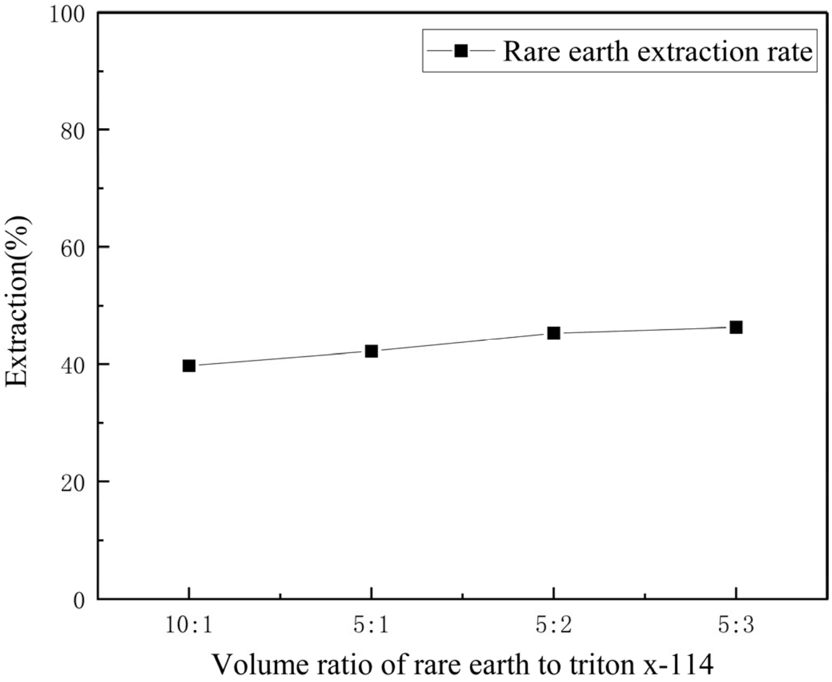


Figure 14. The effect of Triton X-114 dosage on the extraction rate of rare earth ions.

As shown in Figure 14, in the aqueous solution with a Y^{3+} concentration of 5 g/L, when 5 mL of Triton X-114 was added, the Y^{3+} extraction rate was 39.74%, and the concentration of extracted yttrium ions in the organic phase was 1.987 g/L. As the amount of Triton X-114 was increased, the extraction rate of yttrium ions also gradually increased. When 20 mL of Triton X-114 was added, the extraction rate of yttrium ions reached 45.34%, and the concentration of extracted yttrium ions in the organic phase was 2.267 g/L. With 30 mL Triton X-114, the extraction rate of yttrium ions was 46.34% and the concentration of yttrium ions extracted from the organic phase was 2.317 g/L. As the amount of Triton X-114 was further increased, the extraction rate of yttrium ions reached an equilibrium.

From Figures 13 and 14, it can be seen that when Triton X-114 5 mL was added, the concentration of extracted aluminum ions in the organic phase was 1.861 g/L, and the concentration of extracted yttrium ions was 1.987 g/L. For the solutions containing solely Al^{3+} and Y^{3+}, Triton X-114 had the same extraction capacity for both ions. Further experiments were conducted to investigate the effect of Triton X-114 in mixed solutions of Y^{3+} and Al^{3+}. Experimentally, glutamic acid was added to the mixed rare earth solution, and Triton X-114 was added after a certain time to perform turbidity point extraction. Its effect on the extraction rate of Al^{3+} and Y^{3+} are shown in Figure 7.

From Figure 7 and comparing Figures 13 and 14, it can be seen that when the solution contains both rare earth ions and Al^{3+}, the extraction rate of aluminum ions from the mixed solution is essentially the same as that of the solution containing only Al^{3+}. The extraction rate of rare earth ions from the mixed solution is much lower than that of the single rare earth solution. This indicates that when the solution contains both aluminum ions and rare earth ions, the addition of a quantitative extractant will result in the preferential extraction of the aluminum ion complex.

To further prove that Triton X-114 can extract aluminum glutamate from the rare earth solution, UV spectroscopy was conducted on the organic phase after the extraction of aluminum glutamate. Triton X-114 was used as the blank solution, and the extracted organic phase was taken as the test solution. The UV absorption spectrum obtained is shown in Figure 15.

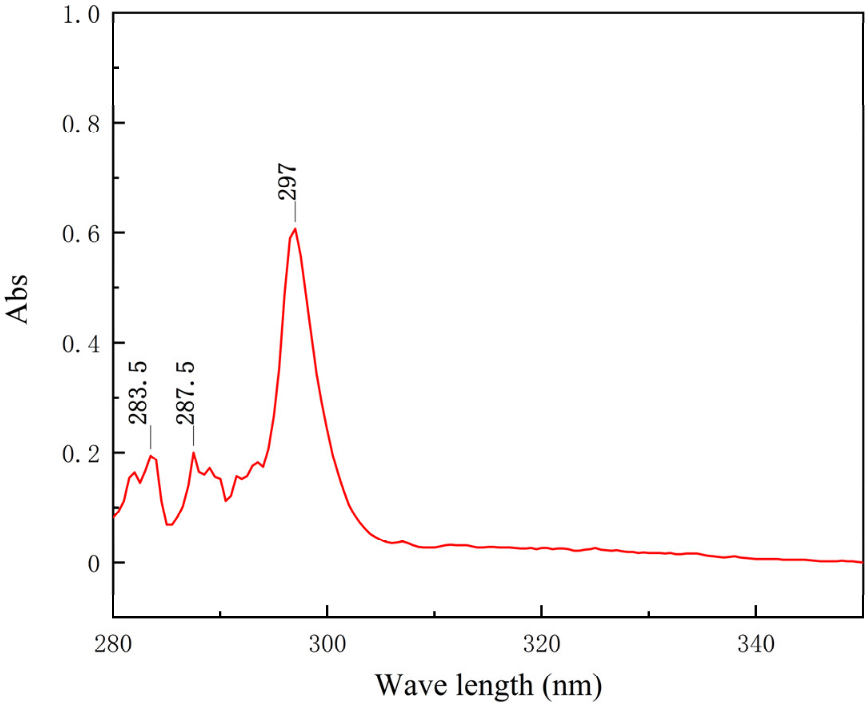


Figure 15. UV spectral analysis on the organic phase after the extraction of aluminum glutamate.

As shown in Figure 15, a new absorption peak at 297 nm appeared in the organic phase, indicating that aluminum glutamate was indeed extracted into the organic phase.

3.10. Extraction Capacity and Extraction Separation Factor

Since the extraction rate of aluminum ions is not only affected by the number of extractions, the most important factor is the amount of complexing agent added. Therefore, the same amount of new glutamic acid and Triton X-114 were added to the extracted residue after each extraction. This process involves multiple extractions, and when the concentration of aluminum ions in the aqueous phase was similar before and after extraction, the operation was stopped. The concentration of aluminum ions in the extracted residue after each extraction and the extraction rate of aluminum ions and rare earths after each extraction relative to the previous level of extraction were calculated. The results are shown in Figures 16 and 17.

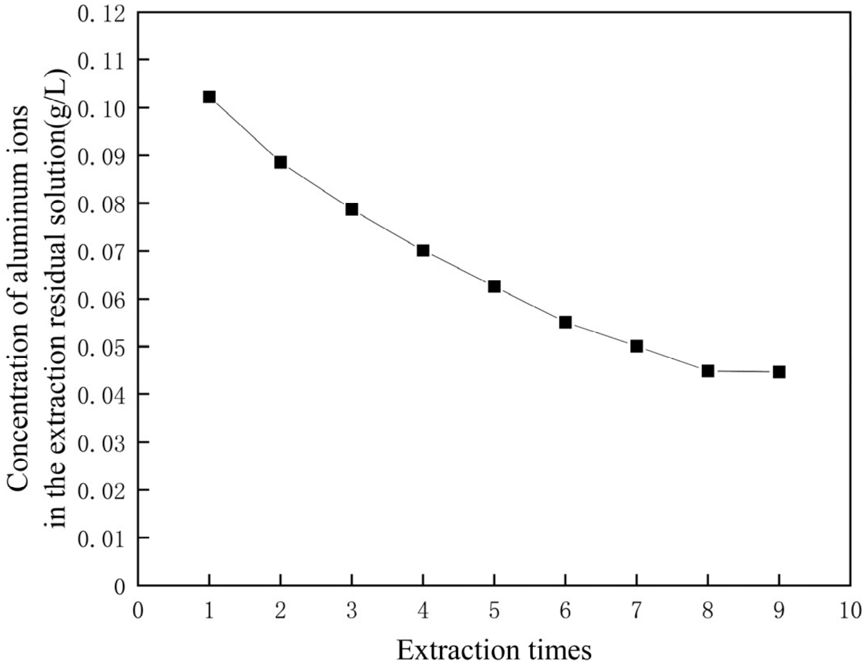


Figure 16. The relationship between the number of extraction times and concentration of aluminum ions concentration in the extraction residual solution.

As shown in Figure 16, the content of aluminum ions in the extracted residue gradually decreased with an increase in the number of extractions; the extracted residue was extracted with the fresh organic phase several times. The concentration of aluminum ions in the extracted residue remained mostly unchanged after eight extractions. When $c_{Al} = 0.045 \pm 0.003$ g/L, Figure 17 shows that as the number of extractions increases, the content of Al^{3+} in the solution gradually decreases. The newly added complexing agent begins to react with a large number of rare earth ions, leading to the extraction of a large number of rare earth ions. The separation coefficients of Al and RE in solution were investigated, and the results were as follows, reaching an extraction minimum:

$$\beta(\mathrm{Al/RE}) = \frac{Concentration\ of\ aluminum\ in\ two\ phases}{Concentration\ of\ rare\ earths\ in\ two\ phases} = 66.15 \quad (1)$$

The greater the separation coefficient deviation is from 1, the easier it is to separate; $\beta(\mathrm{Al/RE}) = 66.15$ indicates that the aluminum ions in the mixed solution can be separated well from the rare earth ions.

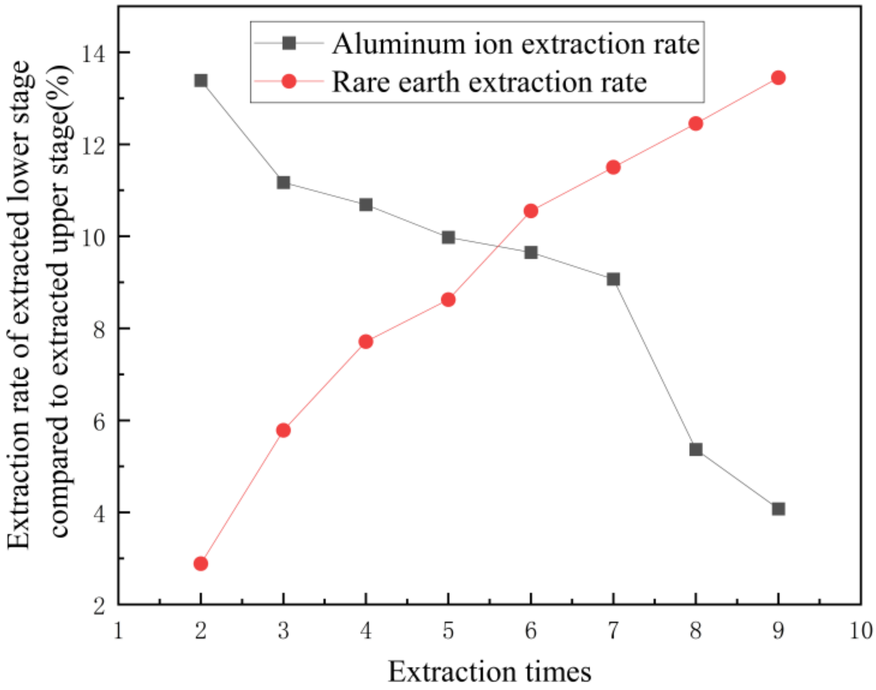


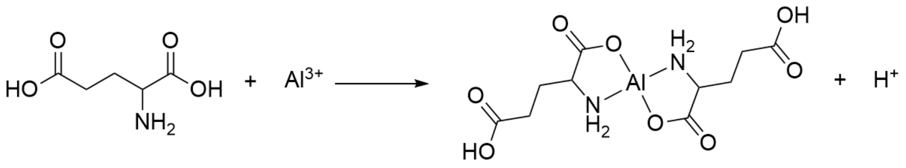
Figure 17. The relationship between the number of extraction times and extraction rate of extracted lower stage compared to extracted upper stage.

4. Conclusions

Glutamic acid was used as a complexing agent to selectively complex aluminum ions, and then Triton X-114 was added to extract and separate the aluminum ion complexes from the rare earth solution using turbidity point extraction. The experimental results show that the extraction rate of aluminum ions reaches 78.01%, which is much higher than the extraction rate of rare earth ions at 5.09%, at M_{glu}:M_{Al} = 3:1, a solution pH of 4.5, and a constant reaction temperature of 40 °C for 10 min before adding 10 mL of Triton X-114 non-ionic surfactant with an equilibration time of 10 min. The efficiency of aluminum extraction in mixed solutions with high rare earth concentrations was investigated under the optimal reaction conditions. It was found that the single extraction rate of aluminum ions was 69% and the extraction rate of rare earths was 26% when glutamic acid was used as the complexing agent. This indicates that the process still allows for the good single extraction of aluminum in mixed solutions with high rare earth concentrations. The results of the reverse extraction of the loaded organic phase showed that when a 1 + 11 volume fraction of hydrochloric acid was used as the reverse extractant, the extraction rate of aluminum ions was 90.46% at a temperature of 40 °C, O/A = 1:7, and an equilibration time of 10 min. During this time, most of the aluminum ions in the organic phase had been reverse-extracted, and the Triton X-114 non-ionic surfactant could be reused as an extractant.

The generation of aluminum glutamate was demonstrated using UV spectrophotometry and verified experimentally with respect to the sequence of extraction and the extraction of aluminum.

The reaction mechanism for the complexation of glutamic acid with Al^{3+} is (Scheme 2):



Scheme 2. The reaction mechanism for the complexation of glutamic acid with aluminum ions.

This experimental study showed that when the mixed solution contains both aluminum ions and rare earth ions, the aluminum ions can be separated from the solution preferentially by using the turbidity point extraction method. The minimum extraction concentration of aluminum ions (c_{Al} = 0.0447 ± 0.003 g/L) was studied by employing multiple extractions, and the calculated $\beta_{(Al/RE)}$ = 66.15 indicates that the aluminum ions in the mixed solution can be separated well from the rare earth ions. This study provides a process for the removal of aluminum from rare earth solutions, and in our next work, the contents of rare earth elements in different parts of the world will be compared for further comprehensive studies using the methods used in this study.

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Data Availability Statement: Data is available based on request.

Conflicts of Interest: Author Yang Gao was employed by the company Ganzhou Achteck Tool Technology Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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