

Study on the Adsorption of La(III) by Green Tea

JING-MEI LI, QING-ZHOU ZHAI* and JU-LIANG WANG

Research Center for Nanotechnology, Changchun University of Science and Technology, Changchun 130022, 7186 Weixing Road, P.R. China

*Corresponding author: Fax: +86 431 85383815; Tel: +86 431 85583118; E-mail: zhaiqingzhou@163.com; zhaiqingzhou@hotmail.com

(Received: 22 October 2010;

Accepted: 28 February 2011)

AJC-9659

The adsorption properties of green tea for La(III) in aqueous phase were studied. The results showed that the adsorption effect of the green tea on lanthanum(III) was better over the range of pH 5-7. At 40 °C, saturation adsorption quantity of the green tea for La³⁺ was 40.18 mg/g and the adsorption accorded with Langmuir isothermal equation. The desorption studies showed when 0.1 mol/L hydrogen chloride was used as adsorbent and the desorptive time was 3 h, desorptive ratio achieved 87.02 %. The good effect of desorption was attained.

Key Words: La(III), Green tea, Adsorption.

INTRODUCTION

Tea is one of the three large drinks in the world. In recent year, the most popular drink has got to be green tea. In tea, more than 500 kinds of substances such as protein, vitamin, amino acid, organic acid, carbohydrates, mineral substance and aroma material such as polyphenol kind, *etc.*, are contained. Among them, many kinds of compound are the ones that the tea specially has, having nutrient and pharmacological actions¹. Green tea is called no ferment tea, whose components have tea polyphenol, caffeine, lipopolysaccharide, carbohydrates, protein, enzyme kind, vitamin and mineral substance. Tea polyphenol is the collectivity of polyphenol kind compound, consisting more than 30 kinds of polyphenol substances that mainly include tea phenol, flavone, anthocyanidin, phenolic acid, *etc.* Among them, catechol content is most. Many important efficacies of tea, all are related to tea polyphenols. The specific surface area of tea is very large and there are many pores inside tea as well as tea has complicated network structures. Also, tea is rich in containing many kinds of active groups such as the active groups containing nitrogen, phosphorus, oxygen, sulfur, *etc.* Thus, tea can be used as a kind of sorbent to apply to the aspects of adsorption and separation of metal ions. Tea has already used in the studies of adsorbing heavy metal ions *viz.*, Cu(II), Pb(II), Zn(II), Cr(III), Ni(II), Co(II)² and Cd(II), Pb(II)³, Pb(II), Hg(II)⁴, Ag(I)⁵, U(VI), Th(IV)⁶ in water. This paper concerns the adsorption performance of tea to rare earth element lanthanum(III) and explores and studies a new method of extraction of lanthanum. This paper used green tea as a sorbent to make the adsorption study of La(III). The results showed that the speed of adsorption of La(III) was fast, the

adsorption ratio was high and the effect of temperature was small. The desorption studies found that the desorption effect of La³⁺ by 0.1 mol/L HCl solution was better. When the desorption time was 3 h, the desorption ratio attained 87.02 % and lanthanum could be effectively desorbed.

EXPERIMENTAL

A HJ-6A digital display magnetic constant temperature agitator (Jiangsu Jintan Ronghua Apparatus Manufacture Co., Ltd., China); Measurements of the pH were made using a PHS-3C fine pH meter (Shanghai Fine Scientific Instrumentation Co., Ltd, China); A 722S spectrophotometer (Shanghai Lingguang Technique Co., Ltd., China) with 1 cm cells was used for determination of the content of lanthanum.

A La³⁺ standard stock solution of 1.000 mg/mL was prepared by using 0.1173 g of La₂O₃ (spectral purity) to dissolve 5.0 mL of 5.0 mol/L HCl solution and dilute to 100 mL with water. A 10.0 µg/mL of La³⁺ working solution was obtained by properly diluting the stock solution. The tea used in the experiment was the green tea produced in Fuding city, Fujian province, China. The raw tea was placed in a warm water of 60 °C to dip in for 20 min, taken out to be washed by water and then placed in an oven at 60 °C for 10 h. The drying tea was cut up to a granularity of 0.5 mm and the sample was loaded in a sample bag and placed in a desiccator and kept for use. A 0.05 % (w/v) of DBC-arsenazo (DBC-ASA) solution was prepared by dissolving 0.0500 g of DBC-ASA in 100 mL of water. A pH 2.2 of HCl-KCl buffer solution was obtained by mixing 92.48 mL of 0.20 mol/L of KCl solution and 7.52 mL of 0.20 mol/L HCl solution. NaOH solution (0.10 mol/L), HCl solution (0.10 mol/L), EDTA (ethylenediaminetetraacetic

acid) solution (0.10 mol/L), $\text{H}_2\text{C}_2\text{O}_4$ (0.10 mol/L) were used. Unless specially stated, all the reagents used were of analytical-grade. The water used was deionized distilled water.

Procedure for the adsorption of green tea on La^{3+} in solution: In a 100 mL conical flask, 50 mL of 10.0 $\mu\text{g}/\text{mL}$ La^{3+} solution was added and the pH value of the system was adjusted by using 0.10 mol/L HCl and 0.10 mol/L NaOH. A 0.1000 g of green tea was added and stirred for 3 h on the magnetic stirrer at a room temperature. The solution in the conical flask was filtrated and 1 mL of the filtrate was taken and determined by DBC-arsenazo spectrophotometry⁷ for La^{3+} concentration.

Procedure for the determination of La^{3+} concentration in filtrate solution by DBC-arsenazo spectrophotometry: An aliquot of standard or sample solution containing 0-10.0 μg of lanthanum(III) was transferred to 10 mL calibrated flask. Then, 1.0 mL of 0.050 % (w/v) DBC-arsenazo solution and 1.0 mL of HCl-KCl buffer solution at pH 2.2 were successively added and diluted to the mark with water. After 20 min, the absorbance was measured at 632 nm in a 1 cm cell against a reagent blank prepared in the same manner, omitting DBC-arsenazo⁷. Beer's law was followed over the range of 0-1.0 $\mu\text{g}/\text{mL}$ of La^{3+} concentration. According to the obtained data, a linear regression equation was calculated out and the La^{3+} concentration in the determined solution was calculated.

Procedure for the desorption of La^{3+} : The tea for which an adsorption equilibrium was achieved under the optimum experimental conditions, was filtrated, transferred to a 100 mL conical flask. A 50 mL of 0.10 mol/L HCl or EDTA or $\text{H}_2\text{C}_2\text{O}_4$ solution was respectively added to the tea and stirred for 2 h on the magnetic stirrer. The La^{3+} concentration in the desorbed solution was determined and the desorption ratio was calculated. The strippant for which desorption effect is better was chosen to desorb the green tea for 10 h. Every other 1 h the La^{3+} concentration in the desorbed solution was determined and desorption ratio was calculated.

RESULTS AND DISCUSSION

Adsorptive study

Effect of pH: A 50 mL of 10.0 $\mu\text{g}/\text{mL}$ La^{3+} solution was popped, placed in a 100 mL conical flask and adjusted to different pH value by using 0.10 mol HCl and 0.10 mol NaOH solutions to make adsorptive experiments and calculate adsorptive ratio. The results are shown in Fig. 1. The standard solution used in the experiments was LaCl_3 solution in which the pH of La^{3+} hydrolysis for the formation of $\text{La}(\text{OH})_3$ is 8.03, thus the adsorptive effect of the green tea was discussed over the range of pH 2-7 in this paper. The effect of pH on adsorption was obvious. Over the range of pH 5-7, the adsorptive effect of La^{3+} by the green tea was good. When pH is less than 5, the adsorptive effect was worse. Its reason consists that under the condition of $\text{pH} < 5$, the hydroxyl group present in the tea and the H^+ come from the solution formed the positive charge active center that formed a competitive reaction with La^{3+} . Therefore, the adsorptive ratio of La^{3+} was lower. Under the conditions of pH 5-7, between the H^+ in the hydroxyl groups contained in the green tea and La^{3+} , ion exchange reaction easily occurred. Thus, the adsorptive ratio was higher.

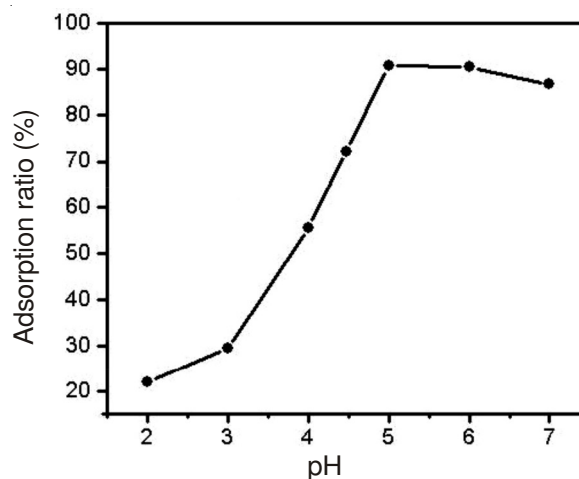


Fig. 1. Effect of pH on La^{3+} adsorptive ratio

Effect of temperature: A 50 mL of 10.0 $\mu\text{g}/\text{mL}$ La^{3+} solution was popped, placed in a 100 mL conical flask and adjusted to pH 5. According to the experimental procedure, the adsorptive ratio of La^{3+} in the solution by tea was determined at different temperature and the results are shown in Fig. 2. The adsorptive effect of La^{3+} by the green tea was optimum at 40 °C. Increase in the temperature was not advantageous to La^{3+} adsorption, but the effect of temperature on the adsorptive effect of the green tea was not much significant. Over the range of the selected temperature, the difference of the best and worst adsorptions was 3.64 %. When temperature was lower, the intensity of adsorptive bond was large and the bond energy distribution was wider. Thus, adsorptive active points were more and the adsorptive quantity was larger.

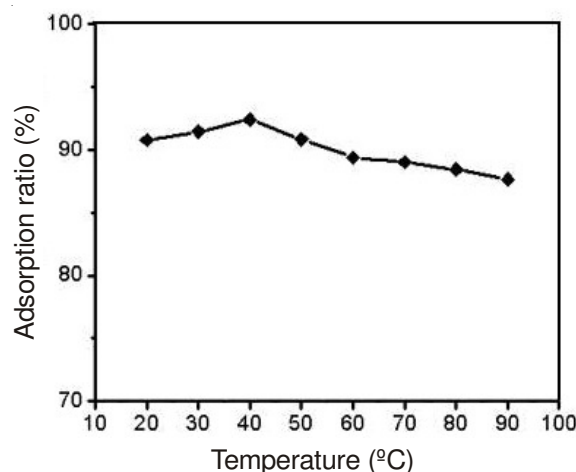


Fig. 2. Effect of temperature on La^{3+} adsorptive ratio

Effect of adsorptive time: A 50 mL of 10.0 $\mu\text{g}/\text{mL}$ La^{3+} solution was popped and placed in a 100 mL conical flask. 0.1000 g of the green tea was added and adjusted pH to 5. At different time the adsorptive ratio of La^{3+} by the green tea was determined. The adsorptive kinetic curve obtained showed (Fig. 3) that before 1 h the adsorptive ratio of La^{3+} by the green tea and time presented a linear rise relationship and the adsorptive ratio achieved 81.14 %. At 2 h, adsorption attained an equilibrium and the adsorptive ratio of La^{3+} achieved 90.03 %. Above 80 % of adsorptive total amount of La^{3+} was

accomplished within 1 h and the process belonged to a fast adsorption. As the tea polyphenol and phenol type derivatives in green tea have complexing effects on La³⁺, so in this process fast complexation and adsorption should be included. The reaction mechanism of the adsorption of tea is complicated. Some phenol type derivatives in tea has the precipitation effect on La³⁺ and thereby this process should also include some fast precipitation of La³⁺ and La³⁺ was adsorbed due to this.

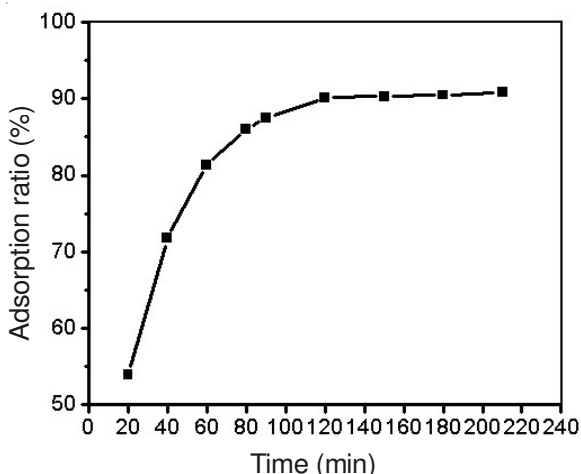


Fig. 3. Kinetic curves of the adsorption of La³⁺

Adsorption isothermal curve: When the initial concentration of La³⁺ was in the range of 0-210 µg/mL at pH 5 and the temperature of 20, 40, 60 °C, adsorption experiments were respectively made to calculate adsorptive capacity. The results showed (Fig. 4) that the adsorptive quantity increased as the initial concentration of the ion increased. The adsorption of La³⁺ by green tea reached an equilibrium at the concentration of about 160 mg/L in the solution. At different temperature the maximum adsorption quantities of adsorption of La³⁺ were 38.74, 40.18, 36.06 mg/g, respectively. When the concentration of La³⁺ was in the range of 0-140 mg/L in the solution, the adsorption was major in single molecular layer and accorded with Langmuir isothermal equation.

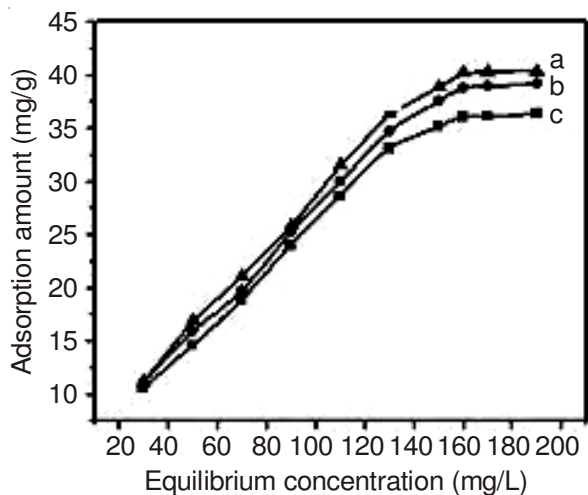


Fig. 4. Isothermal adsorptive curves of La³⁺ (a) 60 °C; (b) 20 °C; (c) 40 °C

Langmuir equation described the relationship of the metal ions concentration and the amount of adsorbed metal ion under the equilibrium state at a definite temperature:

$$C/q = C/q_m + 1/(q_m \cdot b)$$

In the formula: q - represents green adsorption amount at equilibrium; q_m - represents saturation adsorption quantity constant; b - represents affinity constant; C - represents equilibrium concentration.

Table-1 shows the constants q_m and b of the adsorption of La³⁺ by the tea calculated from Langmuir equation. The dynamic principle of adsorption of the tea is similar with Langmuir isothermal adsorptive curves. The surface of tea is lacunaris, network structure, and the surface area is large. All these create good conditions for the adsorption of tea. Also, it is essential that as equilibrium concentration increases, adsorption quantity increases and adsorption ratio decreases. The decrease of adsorption may be that the adsorption process of tea could make the tea surface interspace be gradually filled by the adsorbed ions and the network of the tea was destroyed.

| TABLE-1 PARAMETERS OF LANGMUIR ADSORPTION ISOTHERM | | |
|---|-----------------------|--------------------------------------|
| Temperature (°C) | q _m (mg/g) | b (dm ³ g ⁻¹) |
| 20 | 38.74 | 0.0597 |
| 40 | 40.18 | 0.0647 |
| 60 | 36.06 | 0.0604 |

Desorptive study: Hydrogen chloride, EDTA, H₂C₂O₄, which are cheap and common reagents, were used to study the adsorption performance of green tea. The results showed that 0.1 mol/L HCl solution was used to desorb La³⁺ for 3 h, the desorptive ratio was 89.02 % (Fig. 5) and lanthanum can be effectively recovered. The reason is that the electrical density of La³⁺ excessively centralizes and in the outer layer there is vacant d orbit. The complexes, which were formed between La³⁺ and the hydroxyl, carboxide, etc, in the green tea, were not stable. Under the condition that the acidity was stronger, the complexes were destroyed as the H⁺ in the solution competed with the metal. When 0.1 mol/L EDTA solution was used to desorb La³⁺ and the desorption time was 4 h, the desorption

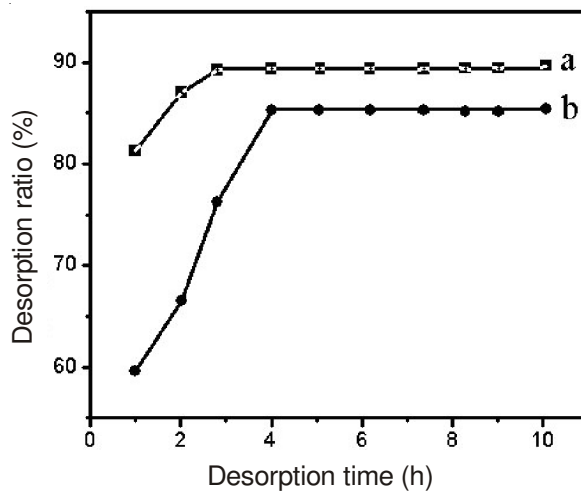


Fig. 5. Effect of desorptive time on desorption of lanthanum (a) HCl desorptive system; (b) EDTA desorptive system

effect was also more obvious and the desorptive ratio achieved 84.81 %. This mainly is as EDTA as an organic complexant can make strong complexing action with most of metal cationic ions to form stable complexes and the complexes formed by La^{3+} and the hydroxyl, carboxylic groups, etc., in the green tea were not stable. Thus, La^{3+} was easily desorbed. The effect of the third desorptive solution $\text{H}_2\text{C}_2\text{O}_4$ was not good and the desorptive ratio was of 23.46 %. This is because the acidity of $\text{H}_2\text{C}_2\text{O}_4$ is not enough strong and $\text{C}_2\text{O}_4^{2-}$ can precipitate with La^{3+} , which is disadvantageous to desorption and desorption effect could not achieved.

Conclusion

(1) The adsorption studies of the adsorption of green tea on La(III) showed that under the optimum conditions the adsorptive ratio was at 90.03 %. Hence, the green tea has strong adsorptive ability to La(III).

(2) The equilibrium time of adsorption La(III) by green tea was 2 h, the optimum pH 5 and the optimum adsorption temperature was 40 °C. However, the effect of the variation of

temperature on its adsorption was not significant. At the same temperature, the adsorptive quantity increased as the equilibrium solution concentration increased and the adsorptive ratio increased with decreasing in the concentration.

(3) The studies of desorptive conditions found that 0.1 mol/L HCl solution was used and the desorptive effect of La^{3+} was better. When the desorption was 3 h, the desorptive ratio achieved 89.02 %. When 0.1 mol/L EDTA solution was used in desorption for 4 h, the desorptive ratio attained 84.81 % and lanthanum could be effectively recovered.

REFERENCES

1. J.Y. Du, L. Bai and B.Z. Bai, *Agric. Technol.*, **23**, 53 (2003).
2. F.S. Zhao, S.H. Li and X.P. Luo, *Ion Exch. Adsorp.*, **6**, 117 (1990).
3. G.Z. Li, Y.M. Liu and G.Z. Li, *Spectros. Spectr. Anal.*, **24**, 1444 (2004).
4. Y.Y. Chen, F. Liu and J.H. Song, *J. Leshan Teacher's College*, **20**, 41 (2005).
5. Z.G. Yang, C.F. Yang and G.N. Mu, *Chin. J. Appl. Chem.*, **11**, 80 (1994).
6. F.L. Zhou, X.F. Xie, H. Tang and Z.Y. Tan, *Chin. J. Anal. Chem.*, **30**, 355 (2002).
7. H. Yu, Q.Z. Zhai, X.X. Zhang and J. Sun, *Chin. Rare Earths*, **29**, 41 (2008).