Synthesis and Characteristics of Al(III)-Imprinted Silica Gel Sorbent

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In this study, a new Al(III)-imprinted silica gel sorbent was synthesized by a surface imprinting technique for selective extraction or preconcentration of Al(III). Compared with non-imprinted polymer particles, the aluminium ion-imprinted silica gel (Al-IIIISG) had higher selectivity and adsorption capacity for Al(III). The maximum static adsorption capacity of the aluminium ion-imprinted silica gel for Al(III) was 12.79 mg/g. Results suggested that aluminium ion-imprinted silica gel was a material of efficient, low-cost for Al(III) separation and concentration.

Key Words: Imprinted silica gel sorbent, Static adsorption capacity, Separation and concentration.

INTRODUCTION

Molecular imprinting technology is an efficient method to produce functionalized materials that so far there are a lot of metal ions imprinted polymers have been prepared, including Cu(II)¹, Hg(II)², UO₂(VI)³, Ni(II)⁴, Pa(II)⁵, Pd(III)⁶, Zn(II)⁷, Cd(II)⁸ and Cs(I)⁹ imprinted polymers. A new method using Al(III)-imprinted sorbent for preconcentration trace aluminium in solution samples prior to its determination by flame atomic absorption spectrometry was established. This method presented high selectivity and adsorption capacity for Al(III) and possessed simple, convenient and accurate characteristics.

EXPERIMENTAL

Reagents of analytical and spectral purity were used for all experiments and doubly distilled deionized water was used throughout. Standard stock solutions of Al(III) was prepared by dissolving analysis pure-grade Al₂(SO₄)₃·18H₂O (Chengdu Lianhe Chemical Company, Chengdu, China). Silica gel (60-100 mesh, Chemical Company of National Medicine, China) and γ-aminopropyltrimethoxy silane (APS, Nanjing Liangui Chemical Company, China) were used to prepare the ion-imprinted and non-imprinted functional silica gel sorbent.

The silica gel surfaces were activated by refluxing silica (60-100 mesh) with 1:1 hydrochloric acid under stirring for 4 h, then the activated silica gel was filtered and washed with doubly distilled water to neutral and dried under vacuum at 80 °C for 12 h. Al₂(SO₄)₃·18H₂O was dissolved in 80 mL methanol under stirring and heating, then 4 mL γ-aminopropyltrimethoxy silane was added into the mixture. The solution was stirred

and refluxed for 2 h, then 4 mL TEOS was added into the mixture and the solution was stirred and heated for 24 h. The product was washed by ethanol to remove the reactionless γ-aminopropyltrimethoxy silane and TEOS. Then 1:1 hydrochloric acid was added to remove metal ions from the polymer. The final product was filtered, washed with doubly distilled water to neutral and dried under vacuum at 68 °C for 16 h.

Flame atomic absorption spectrometry measurements were carried out on a Zeenit 700 p spectrometer (Analytik jena, Germany) with an air/acetylene flame. The instrumental parameters were optimized in order to obtain maximum signal-to-noise ratio. Infrared spectra of the imprinted and non-imprinted absorbent were performed with a Fourier transform infrared (FT-IR) spectrometer (Nicolet6700, American). Chemical bonding information was obtained by Raman spectrometer. The Raman spectrometer (Nicolet DXR, American).

RESULTS AND DISCUSSION

Adsorption experiments and selectivity studies: The adsorption capacity of Al(III) on ion-imprinted and non-imprinted silica gel sorbent were investigated by static adsorption study. It was performed by mix 0.1 g absorbents (imprinted and non-imprinted) with Al(III) ion solution in the concentration range 10-200 mg/L (pH-6) for 0.5 h. The pH of solution was adjusted to desired values by adding hydrochloric acid as buffer. At the end of predetermined time intervals the polymers was separated by centrifugation. The selected metal ions Cr(III) was added to solutions to prove the competitive adsorption. Under the conditions of optimum initial concen-

tration of Al(III), 0.1 g each of individual inorganic species were added to solutions and the absorbed amount of these elements were ascertained by flame atomic absorption spectrometry.

The adsorption capacity, distribution ratio, selectivity factor of Al(III) with respect to Cr(III) and relative selectivity factor were calculated using following equations:

$$Q_e = \frac{(C_o - C_e)V}{W}$$

$$D = \frac{Q_e}{C_e}$$

$$S = \frac{D_{Al}}{D_M}$$

$$S_r = \frac{S_i}{S_n}$$

$$E = (C_o - C_e) / C_o \times 100\%$$

where, Q_e represents the adsorption capacity (mg/g), C_o and C_e the initial and equilibrium concentrations of Al(III) (mg/L), W the mass of polymer (g), V the volume of methods ion solutions (L), D the distribution ratio (L/g), S the selectivity factor, D_{Al} and D_m represent the distribution ratio of Al(III) and Cr(III), S_i the relative selectivity factor, D_i , D_n and S_i , S_n represent the distribution ratios and selectivity factors of imprinted and non-imprinted silica gel sorbent, respectively.

IR analysis: To ascertain the presence of useful chemical bond in Al(III)-imprinted chloride-functionalized silica gel sorbent, FT-IR spectra were obtained from non-imprinted, imprinted and adsorptive silica gel sorbents. As showed in Fig. 1, the observed features around 1090 cm^{-1} and 958 cm^{-1} indicated Si-O-Si and Si-O-H stretching vibration, respectively. The presence of adsorption water was reflected by $\nu(\text{OH})$ vibration at 3429 cm^{-1} and 1636 cm^{-1} . The bands around 800 cm^{-1} and 472 cm^{-1} resulted from Si-O symmetrical and anisomerous vibrations. Imprinted and non-imprinted sorbent showed a very similar location and appearance of the major bands.

Raman spectra: The structural and chemical properties of the ion-imprinted and non-imprinted functional silica gel sorbent was probed by means of Raman studies. Fig. 2 shows the Raman spectra of ion-imprinted and non-imprinted functional silica gel sorbent samples. The absence of sharp and well-defined peaks suggests local structural disorder of the prepared films.

Adsorption capacity of Al(III)-imprinted sorbent for Al(III): The adsorption capacity is an important factor to evaluate the Al(III)-imprinted sorbent. In order to investigate the adsorption capacity of Al(III) on imprinted and non-imprinted polymer particles, 0.1 g of polymer particles was introduced into a solution of Al(III). As showed in Fig. 3, the adsorption capacity of imprinted silica gel sorbents increases with the increased initial concentration and the highest adsorption capacity could achieve 12.79 mg/g with saturation state, when the non-imprinted silica gel sorbents could only reach 4.21 mg/g around. The adsorption capacity for imprinted particles is higher than for non-imprinted particles at all initial concentrations of aluminium because in imprinted particles the cavities created after removal of template is complementary to the imprinted ion in size and coordination geometries, whereas in non-imprinted particles there is a random distribution of ligand functionalities.

Fig. 1. FT-IR spectra of the non-imprinted, imprinted and adsorptive silica gel sorbents

Effect of coexisting ions: The effects of coexisting ions on the adsorption of Al(III) in imprinted sorbent were investigated. The results of competitive adsorption of Cr(III)/Al(III) were showed in Table-1. The tolerance of the coexisting ions, defined as the largest amount making the recovery of the studied elements less than 90 %. Results showed that up to mg/L of Zn(III), mg/L of Ni(III) had no significant interference on

TABLE-I
DISTRIBUTION RATIOS, SELECTIVITY FACTOR AND SELECTIVITY COEFFICIENT OF IMPRINTED SILICA GEL SORBENTS

Sorbents	Initial Concentration		Adsorption Rate		Adsorption capacity		Sr	
	Al(III)	Cr(III)	Al(III)	Cr(III)	Al(III)	Cr(III)	Al(III)	Cr(III)
Imprinted	1	0	99.9	-	1.665	-	-	-
	1	1	99.6	65.4	1.593	0.627	21.5	6.72
Non-imprinted	1	0	98.7	-	1.645	-	-	-
	1	1	95.3	86.4	1.588	1.434	3.2	-

Fig. 2. Raman spectra of the activated, imprinted and non-imprinted silica gel sorbents

Fig. 3. Effect of concentration on the adsorption of Al(III) on imprinted silica gel sorbents

determination under the Selectivity conditions, which shows that Al(III)-imprinted silica gel sorbent has a good selectivity for Al(III).

Conclusion

In this work, a selective and sensitive method for determination of copper was used by a new type of Al(III)-imprinted silica gel sorbent. The preparation of was relatively simple and rapid. The ion-imprinted sorbent had high adsorption capacity and selectivity for Al(III). The maximum adsorption capacity of Al(III) on ion-imprinted silica gel sorbent was 12.79 mg/g. Competitive adsorption studies showed that Al(III)-imprinted silica gel sorbent offer the advantage of selectivity towards Al(III) ion in the presence of Cr(III) ions.

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REFERENCES

1. L.-L. Ding, S.-Q. Long, Y.-H. Zhou and Y. Deng, *Asian J. Chem.*, **24**, 10 (2012).
2. I. Dakova, I. Karadjova, V. Georgieva and G. Georgiev, *Talanta*, **78**, 523 (2009).
3. D.K. Singh and S. Mishra, *Anal. Chim. Acta*, **644**, 42 (2009).
4. A. Ersoz, R. Say and A. Denizli, *Anal. Chim. Acta*, **502**, 91 (2004).
5. C. Esen, M.E. Andac, N. Bereli, R. Say, E. Henden and A. Denizli, *J. Mater. Sci. Eng. C*, **29**, 2464 (2009).
6. B. Godlewska-zykiewicz, B. Lesniewska and I. Wawreniuk, *Talanta*, **83**, 596 (2010).
7. J.C. Zhao, B. Han, Y.F. Zhang and D.D. Wang, *Anal. Chim. Acta*, **603**, 87 (2007).
8. D.K. Singh and S. Mishra, *J. Hazard. Mater.*, **164**, 1547 (2009).
9. Z.L. Zhang, X.H. Xu and Y.S. Yan, *Desalination*, **263**, 97 (2010).