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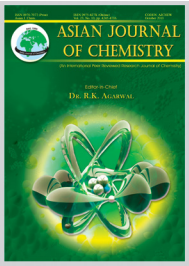

Synthesis and Characteristics of Cu(II)-Imprinted Silica Gel Sorbent

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In this study, a new Cu(II)-imprinted silica gel sorbent was synthesized by a surface imprinting technique for selective extraction or preconcentration of Cu(II). Compared with non-imprinted polymer particles, the Cu(II) ion-imprinted silica gel had higher selectivity and for Cu(II). The maximum static adsorption capacity of the Cu(II)-ion-imprinted silica gel for Cu(II) was 25.679 mg/g. Results suggested that Cu(II)-ion-imprinted polymers was a material of efficient, low-cost for Cu(II) separation and concentration.

Key Words: Copper imprinted silica gel sorbent, Adsorption capacity, Surface imprinting technique.

INTRODUCTION

Molecular imprinting technology is an efficient method to produce functionalized materials. So far there are a number of metal ions imprinted polymers have been prepared, including Fe(III)[1], Hg(II)[2], uranyl ion[3], Ni(II)[4], Pa(II)[5], Pd(II)[6], Zn(II)[7], Cd(II)[8], Cs(I)[9] imprinted polymers. A new method using Cu(II)-imprinted sorbent for preconcentration of trace copper in solution samples prior to its determination by flame atomic absorption spectrometry was established. This method presented high selectivity and adsorption capacity for Cu(II) 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 Cu(II) was prepared by dissolving analysis pure-grade $CuCl_2 \cdot 2H_2O$ (Chongqing ChuanDong Chemical Company, Chongqing, China). Silica gel (60-100 mesh, Chemical Company of National Medicine, China) and 3-chloropropyl-trimethoxy silane (CPS, Aladdin 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 8 h, then the activated silica gel was filtered and washed with doubly distilled water to neutral and dried under vacuum at 70 ºC for 8 h. To prepare the Cu(II)-imprinted chloride-functionalized silica gel sorbent, 6 g silica gel was dissolved in 50 mL toluene, then 5 mL of 3-chloropropyl-trimethoxy silane was added into the mixture. And the solution was stirred for 16 h and dried under vacuum at 60 ºC for 8 h. 2.2 g $CuCl_2 \cdot 2H_2O$ was dissolved in 45 mL methanol under stirring and heating, then 5 mL of DETA was added into the mixture. The solution was stirred and refluxed for 1 h, to which of upwards. The product was washed with methanol then dried under vacuum at 68 ºC for 8 h. 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 ºC for 16 h. The non-imprinted functionalized silica gel sorbent was also prepared using and identical procedure without adding $CuCl_2 \cdot 2H_2O$.

Flame atomic absorption spectrometry (FAAS) measurements were carried out on a Zeenit 700 p spectrometer (Analytik jena, Germany) wit 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 (Nicolet DXR, American).

RESULTS AND DISCUSSION

Adsorption experiments and selectivity studies: The adsorption capacity of Cu(II) on ion-imprinted and non-imprinted silica gel sorbent were investigated by static adsorption study. It was performed by mixing 0.1 g absorbents (imprinted and non-imprinted) with Cu(II) 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 Zn(II) and Ni(II) were added to solutions to prove the competitive adsorption. Under the conditions of optimum initial concentration of Cu(II), 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 Cu(II) with respect to Zn(II) and Ni(II), and relative selectivity factor were calculated using following equations:

$$Qe = \frac{(Co - Ce)V}{W}$$

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

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

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

$$E = \frac{(C_o - C_e)}{C_o} \times 100\%$$

where, Qe represents the adsorption capacity (mg/g), Co and Ce the initial and equilibrium concentrations of Cu(II) (mg/L), W the mass of polymer(g), V the volume of ion solutions (L), D the distribution ratio (L/g), S the selectivity factor, D_{Cu} and D_m represent the distribution ratio of Cu(II), Zn(II) and Ni(II), S_r 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 Cu(II)-imprinted chloride-functionalized silica gel sorbent, FT-IR spectra were obtained from activated, imprinted and non-imprinted silica gel sorbents. As showed in Fig. 1, the observed features aroud 1084.02 cm^{-1} and 963.78 cm^{-1} indicated Si-O-Si and Si-O-H stretching vibration, respectively. The presence of adsorption water was reflected by ν(OH) vibration at 3471.57 cm^{-1} and 1642.16 cm^{-1}. The bands around 799.55 cm^{-1} and 459.87 cm^{-1} resulted from Si-O symmetrical and anisomerous vibrations. The ν(CH) band was around 2962.17 cm^{-1}. Imprinted and non-imprinted sorbent showed a similar location and appearance of the major bands.

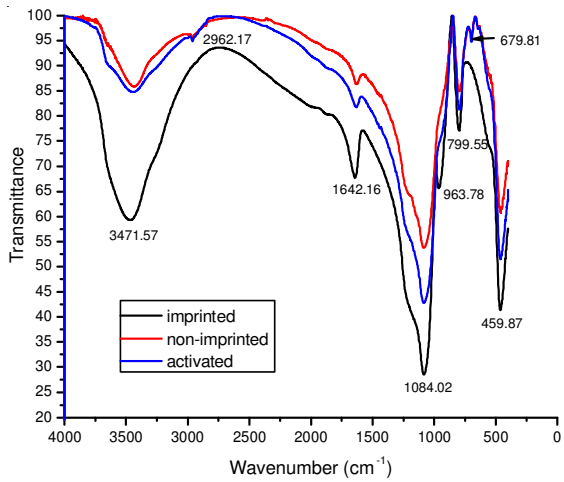

Fig. 1. FT-IR spectra of the activated, imprinted and non-imprinted silica gel sorbents

Characteristics of the Raman spectra: The structural and chemical properties of the ion-imprinted and non-imprinted functional silica gel sorbent was probed by means of Raman spectra. 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.

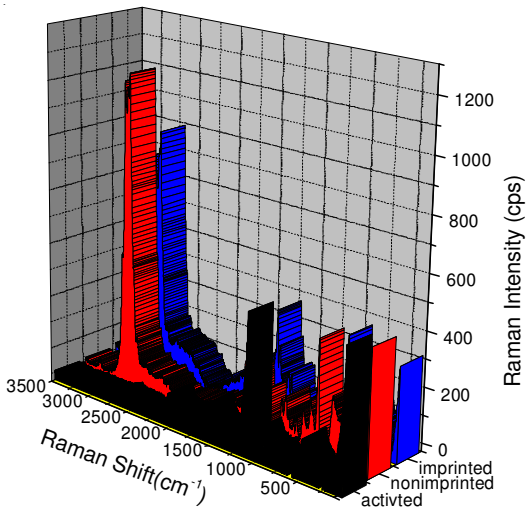

Fig. 2. Raman spectra of the activated, imprinted and non-imprinted silica gel sorbents

Adsorption capacity of Cu(II)-imprinted sorbent for Cu(II): The adsorption capacity is an important factor to evaluate the ion-imprinted polymers. In order to investigate the adsorption capacity of Cu(II) on imprinted and non-imprinted polymer particles, 0.1 g of polymer particles was introduced into a solution of Cu(II). 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 25.679 mg/g. When the non-imprinted silica gel sorbents could only reach 1.2 mg/g around. The adsorption capacity for imprinted particles is higher than for non-imprinted particles at all initial concentrations of copper because in imprinted particles the cavities created after removal of template is complementary to the imprinted ion in size and coordination geometries, wheras in non-imprinted particles there is a random distribution of ligand functionalities in.

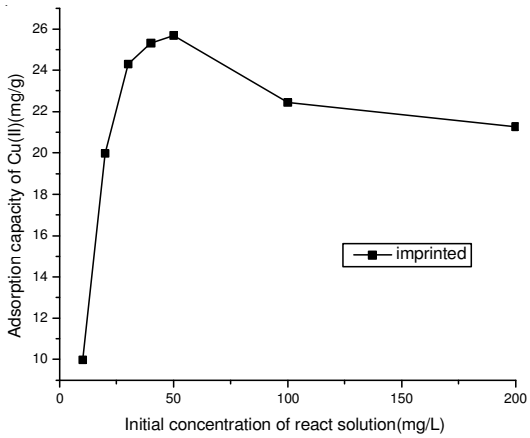

Fig. 3. Effect of concentration on the adsorption of Cu(II) on imprinted silica gel sorbents

TABLE-1
DISTRIBUTION RATIOS, SELECTIVITY FACTOR AND SELECTIVITY COEFFICIENT OF IMPRINTED SILICA GEL SORBENTS

Elements	Distribution ratio (D)		Selectivity factor (S)		E (%)		Sr
	Cu-IISG	NISG	Cu-IISG	NISG	Cu-IISG	NISG	
Cu	1.06	1.2	–	–	51.36	2.40	–
Zn	0.07	3.12	15.8	0.37	6.26	6.24	42.70
Ni	0.22	8.97	4.82	0.11	1.80	17.95	43.82

Effect of coexisting ions: The effects of coexisting ions on the adsorption of Cu(II) in imprinted sorbent were investigated. The results of competitive adsorption of Zn(II)/Cu(II) and Ni(II)/Cu(II) 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 Zn(II) and Ni(II) had no significant interference on determination under the selectivity conditions, which shows that Cu(II)-imprinted silica gel sorbent has a good selectivity for Cu(II).

Conclusion

In this work, a selective and sensitive method for determination of cooper was used by a new type of Cu(II)-imprinted silica gel sorbent. The preparation of was relatively simple and rapid. The ion-imprinted sorbent had high adsorption capacity and selectivity for Cu(II). The maximum adsorption capacity of Cu(II) on ion-imprinted silica gel sorbent was 25.679 mg/g. Competitive adsorption studies showed that Cu(II)-imprinted silica gel sorbent offer the advantage of selectivity towards Cu(II) ion in the presence of Zn(II) and Ni(II) ions.

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