Preparation of a new Cu(II)-imprinted pyridine-functionalized silica gel sorbent and its adsorption characteristic

Dongdong Guo1, Guozheng Wang2, Zhigang Cheng1, Lun Zhao1, Zhihai Xie3,*
1Water injection project area Management Headquarter, Yanchang Oilfield Co., LTD., Yan'an, China,
2Wuqi Oil Production Plant, Yanchang Oilfield Co., LTD., Yan'an, China
3College of Chemistry and Materials Science, Northwest University, Xi'an, China,
*Corresponding author e-mail: xiezhihai8@163.com

Abstract. A new sorbent of Cu(II)-imprinted pyridine-functionalized silica gel (Cu-IIP/SiO₂) was prepared with molecular surface-imprinting technique for selective solid-phase extraction (SPE) of Cu(II). The Cu-IIP/SiO₂ had better adsorption capacity and selectivity for Cu(II) then non-imprinnted polymer. The maximum static adsorption capacity for Cu(II) was 20.67 mg g⁻¹ and 13.36 mg g⁻¹ for the ion-imprinted and non-imprinted sorbents, respectively. The time of adsorption equilibrium was 10 min, and the quantitative desorption only needed 3 min with 0.1 mol L⁻¹ HCl as the eluant. The adsorption kinetic and isotherm of the Cu-IIP/SiO₂ were agreed with pseudo-second-order kinetic model and Langmuir adsorption model, respectively. The Cu-IIP/SiO₂ was recycled ten times and the absorption capacity was no significant decrease.

1. Introduction

Copper is a necessary element for many biological systems, and takes part in connective tissue development and hemoglobin synthesis. But excessive intake of copper has a toxic effect [1]. The main route of the metal elements input to human bodies is through water, medicines, foods and so on. Thus determination of Cu(II) at trace level has become increasingly important.

In order to increase the detection level of the instruments and eliminate the interfering effects of the matrix, different separation and preconcentration procedures were employed. The solid phase extraction (SPE) is useful method to sample pretreatment, and has high enrichment factor, recovery and the ability of connecting with various detection methods. The key factor of SPE was selecting the suitable adsorbent because it could influence sensitivity and selectivity of the method. Various kinds of absorbents, such as chelating resin[2-3], imprinted polymers [4-5], nanoparticles[6], and activated carbon [7] have been utilized in SPE applications.

Silica gel is also used in absorbent because of high surface activity, and the adsorption capacities and selectivity of modified silica gel are higher than untreated silica gel. Thus, silica gel modified with many organic functional groups, such as carboxyl [8], amino [9], curcumin [10], dithizone [11] was used for preconcentration metal ions.

In this study, the sorbent of Cu(II)-imprinted pyridine-functionalized silica gel for the selective Cu(II) recognition was prepared by using 4-vinylpyridine (4-VP) as the functional monomer, Cu(II) as
the template ion and ethylene glycol dimethacrylate (EDMA) as the cross-linker, and was used for enriching trace amount of Cu(II) in environmental samples. The adsorption process accorded closely with Langmuir adsorption isotherm model, and the kinetics of adsorption was followed pseudo second-order model; the reutilization and selectivity of Cu(II)-IIP/SiO2 for Cu(II) were proved to be well; The parameters such as pH of the solution, contact time, type and condition of eluent were optimized. The Cu(II)-IIP/SiO2 absorbent had high selectivity and adsorption capacity for Cu(II).

2. Experiments

2.1 Apparatus

The metal ions were detected by ICP-OES instrument (Perkin Elmer Optima 2100 DV). A pHs-3C digital pH meter (Shanghai Lei Ci Device Works, China) was used for determination of pH of the solution. The solution was stirred by using a magnetic stirrer.

2.2 Activation and modification of silica gel

8 g of silica gel (100–140 mesh) was mixed with 60 mL of 6 mol L⁻¹ HCl and refluxed for 8 h at 110°C, and then cooled down overnight. The mixed solution was filtered. The solid was washed to neutrality by distilled water, and dried vacuum drying at 80°C for 8 h, the activated silica gel was obtained.

6 g of the activated silica gel mixed thoroughly with 60 mL of toluene, and added dropwise 7 mL of KH-570 under stirring. The mixture reacted for 8 h at 110°C, and filtered. The solid was washed sequentially with toluene, ethanol and acetone, and then dried under vacuum.

2.3 Preparation of Cu-IIP/SiO2

To synthesize the sorbent of Cu(II)-imprinted pyridine-functionalized silica gel, 1.0 mmol Cu(NO₃)₂·3H₂O and 6.0 mmol of 4-VP were dissolved in 20 mL of methanol, and stirred for 3 h under room temperature for copper ion and 4-VP to form stable complexe, and then 1.0 g of vinyl-silica gel, 10 mmol EGDMA and 30 mg AIBN were added, respectively. The mixed solution was reacted for 8 h at 60°C under nitrogen protection. The product was washed respectively with acetone and methanol to eliminate the self-polymers formed by monomers and unreacted reagents, and then with 1.0 mol L⁻¹ HCl to remove Cu(II) until the washing solution was free from Cu(II). The fine powder was dried at 80°C under vacuum, the Cu-IIP/SiO2 was synthesized. The non-imprinted silica gel was also synthesized using the same procedure without adding Cu(NO₃)₂·3H₂O.

2.4 Static adsorption experiments

In order to determine adsorption capacity, 100 mg Cu-IIP/SiO2 and NIP sorbents were added to different beakers, respectively. 50 mL of Cu (II) or metal ions solutions with different initial concentration were added into each beaker, and adjusted to the desired pH value. The solutions were stirred for 10 min, and then centrifuged. The metal ions of the solution were tested by ICP-OES.

3. Results and discussion

3.1 Effect of pH

The effect of pH on the adsorption of Cu(II) was evaluated by adding 100 mg of Cu-IIP/SiO2 to 50 mL of 210.0 mg L⁻¹ Cu(II) under different pH conditions. The adsorption capacity increased with the increase pH value of the solution at first, and then remained constant. At pH value >7, precipitation of the metal hydroxide was formed. The suitable value of pH for the absorption of Cu(II) was 6 to 7. So the pH value for subsequent experiments was 6.5.

3.2 Adsorption isotherms

The adsorption capacity can determine how much sorbent is required to quantitatively concentrate the analytes from a given solution. To measure the static adsorption capacity, 100 mg of Cu-IIP/SiO2 or non-imprinted sorbent mixed with 50 mL of different concentration of Cu(II) solutions at pH 6.5.
The adsorption capacity increased with the increase initial concentrations of Cu(II). The max adsorption capacity obtained by experiences was 20.67 and 13.36 mg g\(^{-1}\) for the ion-imprinted and non-imprinted sorbents, respectively. The capacity of Cu-IIP/SiO\(_2\) was superior to non-imprinted sorbent.

The experimental data were substituted into two isotherms equations (Langmuir and Freundlich), and the results were listed in Table 1. Langmuir model was better adapted to the sorption isotherms of Cu(II) at investigated temperatures because the \(R^2\) values of Langmuir isotherm were closer to 1. This demonstrated that the adsorption took place at the surface of the sorbent and formed monolayer coverage of Cu(II) ions.

**Table 1. Adsorption equations of Langmuir and Freundlich**

| T (K) | \(C_e/q_e = 0.0430 C_e + 1.33\) | \(C_e/q_e = 0.0419 C_e + 1.12\) | \(C_e/q_e = 0.0414 C_e + 0.974\) | \(C_e/q_e = 0.0405 C_e + 0.918\) |
|-------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
|       | 288                             | 298                             | 308                             | 313                             |
|       | \(q_e = 23.26, 0.99, 23.87, 0.99\) | \(q_e = 23.87, 0.99, 24.15, 0.99\) | \(q_e = 24.15, 0.99, 24.69, 0.99\) | \(q_e = 24.69, 0.99, 25.92, 0.99\) |
|       | \(K_L = 0.0323, 0.0374, 0.0425, 0.0441\) | \(K_L = 0.0374, 0.0425, 0.0474, 0.0491\) | \(K_L = 0.0425, 0.0474, 0.0524, 0.0541\) | \(K_L = 0.0441, 0.0491, 0.0541, 0.0561\) |

### 3.3. Adsorption kinetics

The influence of contact time on Cu(II) adsorption capacity by Cu-IIP/SiO\(_2\) was shown in Figure 1. It could be seen that the adsorption capacity rapid increased at the first 5 min, and then reached equilibrium. The adsorption rate was fast and the equilibrium time to adsorb Cu(II) ions onto the Cu-IIP/SiO\(_2\) only needed 10 min.

In order to discuss the kinetic mechanism of the solute absorbent process, it was simulated by the kinetics models of the pseudo first order and pseudo second order. The result was listed in Table 2. It could been seen that the \(R^2\) value of pseudo second order kinetic model was closer to 1 and the calculated \(q_e\) value corresponded with the experimental \(q_e\) value for the pseudo second order kinetic model. Thus, the adsorption kinetics conformed to the pseudo second order model, which suggested chemical adsorption with the rate-limiting step of the adsorption mechanism.

**Figure 1. The effect of time on adsorption capacities**

**Table 2. Kinetic parameters**

|                   | Pseudo-first-order model | Pseudo-second-order model |
|-------------------|--------------------------|---------------------------|
| equation          | \(q_e (mg/g)\)           | \(k_1 (1/min)\)          | \(R^2\)            | \(q_e (mg/g)\)           | \(k_2 (g/mg/min)\)       | \(R^2\) |
| \(\text{ln}(q_e-q) = -0.355t + 2.91\) | 18.36                    | 0.355                     | 0.946              | \(t/q = 0.0446t + 0.0901\) | 22.42                   | 0.0221 | 0.997 |
3.4. Effect of desorption condition

The elution was optimized by using 5.0 mL of HCl solution or HNO₃ solution as eluent. The Cu(II) on the sorbent was quantitatively eluted with 5.0 mL of 0.1 mol L⁻¹ HCl at 3 min. Therefore, the solution of 5.0 mL of 0.1 mol L⁻¹ HCl and an elution time of 3 minutes were used for subsequent experiments.

3.5. Regeneration performance of Cu-IIP/SiO₂ sorbent

The sorption–desorption cycle was tested 10 times by using the same sorbent under the optimum conditions in order to evaluate the reusability of the Cu-IIP/SiO₂ sorbent. The adsorption capacity decreased 3.4% in tenth cycle, as compared to the first cycle. Therefore, the Cu-IIP/SiO₂ had excellent stability and practical application.

3.6. Selective adsorption

The selectivity was tested by preparing mixture solution of Cu(II), Zn(II), Co(II), Ni(II), Mn(II), and Fe(II), and the concentration of Cu(II) was equal to other ions in mixed solutions. Table 3 listed the distribution coefficients (K⁺), selectivity coefficients (K) and relative selectivity coefficients (K′), respectively. The K⁺ value of the Cu-IIP/SiO₂ for Cu(II) was largest, and K⁺ values of Zn(II), Co(II), Ni(II), Mn(II), and Fe(II) were very small. The K' values were greater than 1 for Cu-IIP/SiO₂ sorbent of Cu(II)/Zn(II), Cu(II)/Co(II), Cu(II)/Ni(II) Cu(II)/Mn(II), and Cu(II)/Fe(II). The results indicated that the Cu-IIP/SiO₂ sorbent had excellent selectivity for Cu(II) due to the cavities to the imprint ion in size and coordination geometries.

Table 3. Adsorption Selectivity of Cu-IIP/SiO₂ and non-imprinted polymer

| Metal ions | IIPs  | k      | NIPs  | k      | k'    |
|------------|-------|--------|-------|--------|-------|
| Cu²⁺       | 2410  | —      | 357   | —      | —     |
| Zn²⁺       | 15    | 160.7  | 13    | 27.46  | 5.85  |
| Co²⁺       | 13    | 185.4  | 12    | 29.75  | 6.23  |
| Ni²⁺       | 19    | 126.8  | 17    | 21.00  | 6.04  |
| Fe²⁺       | 17    | 141.8  | 14    | 25.50  | 5.56  |
| Mn²⁺       | 21    | 114.8  | 14    | 25.50  | 4.50  |
| Cd²⁺       | 98    | 24.59  | 0.128 | 2.80   | 8.78  |
| Hg²⁺       | 244   | 9.87   | 0.301 | 1.19   | 8.29  |
| Al³⁺       | 279   | 8.64   | 0.236 | 1.51   | 5.72  |
| Pb²⁺       | 254   | 9.49   | 0.149 | 2.40   | 3.95  |

3.7. Maximum sample volume and enrichment factor

The enrichment factor was studied using recommended procedure by increasing volume of sample solution. For this purpose, the different volumes (50, 100, 200, 300, 400, 500 and 600 ml) of sample solution containing 0.2 µg of Cu(II) were tested. The result indicated that the maximum sample volume was 500 mL with the recovery >95%. Therefore, the enrichment factor was 100.

4. Conclusion

A new sorbent of Cu(II)-imprinted pyridine-functionalized silica gel was prepared by using molecular surface-imprinting technique. The Cu-IIP/SiO₂ had good physical and chemical stability, good selectivity, high extraction efficiency for the targeted copper ion. It can be reused at least ten cycles without major change in its properties and be used for preconcentration of Cu(II) from aqueous solutions.
References

[1] Janet Y. Uriu-Adams, Carl L. Keen, Copper, oxidative stress, and human health, Molecular Aspects of Medicine 26 (2005) 268–298
[2] Mojtaba Shamsipur, Javad Fasihi, Alireza Khanchi, Rahim Hassani, A stoichiometric imprinted chelating resin for selective recognition of copper(II) ions in aqueous media, Analytica Chimica Acta 599 (2007) 294–301
[3] Michał Cegłowski, Grzegorz Schroeder, Removal of heavy metal ions with the use of chelating polymers obtained by grafting pyridine–pyrazole ligands onto polymethylhydrosiloxane, Chemical Engineering Journal 259 (2015) 885–893
[4] Mojtaba Shamsipur, Abbas Besharati-Seidani, Javad Fasihi, Hashem Sharghi, Synthesis and characterization of novel ion-imprinted polymeric nanoparticles for very fast and highly selective recognition of copper(II) ions, Talanta 83 (2010) 674–681
[5] Mojtaba Shamsipur, Abbas Besharati-Seidani, Synthesis of a novel nanostructured ion-imprinted polymer for very fast and highly selective recognition of copper(II) ions in aqueous media, Reactive & Functional Polymers 71 (2011) 131–139
[6] Ali Mirabi, AliShokuhiRad, HadisehKhodadad, Modified surface based on magnetic nanocomposite of dithiooxamide/Fe3O4 as adsorbent for preconcentration and determination of trace amounts of copper, Journal of Magnetism and Magnetic Materials 389 (2015) 130–135
[7] Zhenhua Li, Jingwen Li, Yanbin Wang, Yajun Wei, Synthesis and application of surface-imprinted activated carbon sorbent for solid-phase extraction and determination of copper (II), Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 117 (2014) 422–427
[8] Min Li, Ming-yu Li, Chang-gen Feng, Qing-xuan Zeng, Preparation and characterization of multi-carboxyl-functionalizedsilica gel for removal of Cu (II), Cd (II), Ni (II) and Zn (II) fromaqueous solution, Applied Surface Science 314 (2014) 1063–1069
[9] Dang Viet Quang, Jong Kil Kim, Pradip B. Sarawade, Dang Huu Tuan, Hee Taik Kim, Preparation of amino-functionalized silica gel for copper removal from an aqueous solution, Journal of Industrial and Engineering Chemistry 18 (2012) 83–87
[10] Xiangbing Zhu, Xijun Chang, Yuemei Cui, Xiaojun Zou, Dong Yang, Zheng Hu, Solid-phase extraction of trace Cu(II) Fe(III) and Zn(II) with silica gel modified with curcumin from biological and natural water samples by ICP-OES, Microchemical Journal 86 (2007) 189–194
[11] H. Yu, H. Song, M. Chen, Dithizone immobilized silica gel on-line preconcentration of trace copper with detection by flame atomic absorption spectrometry, Talanta 85 (2011) 625.