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Adsorption of Ag^+ by a surface molecular-imprinted biosorbent

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ABSTRACT

Using the surface molecular imprinting technology, the Ag^+-imprinted biosorbent for treatment of the wastewater contaminated by Ag^+ was prepared, which showed higher adsorption affinity and selectivity for the imprinting ion (Ag^+) than the other non-imprinting metal ions. Batch adsorption experiments were carried out as a function of imprinted Ag^+ concentration, agitation time, temperature and initial Ag^+ concentration. The optimal imprinted Ag^+ concentration for preparing Ag^+-imprinted biosorbent was 2.0 mg/g (biomass). The maximum adsorption capacity was 199.2 mg/g at the initial Ag^+ concentration of 1200.0 mg/L and the biosorbent dosage of 3.0 g/L, which was much higher than that of previous work. The reaction temperature showed little effect on the adsorption process. The biosorbent could be easily desorbed by using 0.1 M $Na_2S_2O_3$ solution as a desorbent at room temperature (25.0–27.0 °C). The SEM showed that noble metal silver could be well adsorbed by the biosorbent; the silver nanoparticles were of regular geometry shape and relatively uniform.

1. Introduction

With the development of electroplating, coinage, medication and chemical engineering, the pollution caused by silver-bearing wastewater has been increasingly serious. The silver ions could be accumulated in organisms (including human) through the food chain, and then would do harm to their body. Recently, it is found that Ag^+ exposure caused an inhibition of active Na^+ and Cl^- uptake, resulting in ion regulatory failure by inhibition of branchial Na^+-ATPase and K^+-ATPase in *crayfish* and *daphnids* [1,2]. Simultaneously, Ag is widely used in various industries fields due to its excellent malleability, conductivity, thermal conductivity, etc. However, the Ag resources have become relatively short since the extensive applications of Ag are increasing rapidly [3]. Therefore, the effective removal and recovery of Ag^+ has become an urgent assignment [4–6]. Although some conventional methods such as chemical precipitation, ion-exchange and reverse osmosis can remove heavy metals from their effluents, they are not economically feasible for actual wastewater treatment [7]. Considering the viewpoint of sustainable development and comprehensive utilization of resources, biosorption has a promising prospect and a wide application due to its low cost, abundance and good performance over other conventional treatment processes in the removal and recovery of heavy metal ions from wastewater [8–11].

Chitosan is a linear polysaccharide based on a glucosamine unit, obtained through chitin deacetylation, which originates from shells of crustaceans such as crabs and prawns. Chitosan is also considered as one of the most abundant biopolymers in nature. As a new kind of biosorbent, it has been prepared into different forms and widely used in the wastewater treatment because of its higher adsorption capacity and better selectivity for heavy metal ions [1,12–17]. However, its application is limited because of its dissolution in acidic solutions and higher cost. In order to shed light on problems above, a new molecular-imprinted biosorbent which could selectively adsorb heavy metal ions was prepared [18,19]. By using surface molecular imprinting technology, this new biosorbent showed 30.0–50.0% higher uptake for Ni^{2+} in comparison to non-imprinted biosorbents. In addition, it had better mechanical performance and could be reused for up to 15 cycles.

From the mentioned above, reviews of the literature on metal biosorption shows that many studies have been carried out concerning chitosan and the biosorbents based on chitosan. And they mainly focused on the common heavy metal ions such as Cu(II), Ni(II), Pb(II), Cr(IV) and their recovery [12–17]. However, as far as the authors are aware, there is no investigation reported in the literature on the removal of Ag(I) by molecular-imprinted biosorbents.

The aim of this study was to examine the removal efficiency of less-researched metal Ag(I) from dilute solutions by molecular-imprinted biosorbents. Experiments were performed as a function of adsorption time, imprinting concentration of Ag^+, initial Ag^+ concentration in the solution, and the temperature. The effects of different desorbents such as HNO_3, HCl and $Na_2S_2O_3$ on the desorption were also investigated.

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2. Materials and methods

2.1. Chemicals

Mycelium from waste biomass of *Penicillium chysogenum* was obtained from Dongchen Biochemical Engineering Company in Shandong Province; Chitosan with 90.0% degree of deacetylation was extracted from shrimp shells obtained in our laboratory. Silver nitrate, nitric acid, acetic acid, sodium citrate and epichlorohydrin were of analytical grade and all reagents were prepared in Millipore milli-Q deionized water.

2.2. The preparation of the surface Ag^+-imprinted biosorbent

The preparation of the new surface Ag^+-imprinted biosorbent was as follows (Fig. 1) [20]. $AgNO_3$ was dissolved in 2.0 mL dilute acetic acid solution (2.5%v/v) to give an Ag^+ solution of 2.0 mg/L. Then 0.1 g chitosan (dry weight) was dissolved in this solution, and the mixture was stirred for 20.0 min. 2.0 g *mycelium* (dry weight) was then added to the above solution, and the mixture was stirred for 10.0 min. Epichlorohydrin as a cross-linking agent was added into the mixture and allowed to carry out for 8.0–10.0 h at room temperature (25.0–27.0 °C); then, the imprinted Ag^+ on the biosorbent was removed by treating with a 0.2 g/L EDTA solution for 12.0 h. Regeneration was carried out by washing the biosorbent with 0.2 M NaOH for 2.0 h and was shaken on a rotary shaker (170 rpm). The surface Ag^+-imprinted biosorbent was washed twice with running water and five times with deionized water. The washed biosorbent was sun-dried at room temperature (25.0–27.0 °C) for 24 h, crushed with an analytical mill, sieved (size by a 60-mesh sieve) and stored in sealed bottles until use.

2.3. Biosorption and desorption experiment

Batch biosorption studies were conducted in 150 mL Erlenmeyer flasks at about pH 7.0 (at natural pH). Dry biosorbent (0.15 g) was thoroughly mixed individually with 50 mL of Ag^+ solutions (0–1000.0 mg/L) and the suspensions were shaken in a shaker at room temperature. Samples of 1 mL were drawn from the flask at required time intervals and were filtered through Whattman No. 1 filter paper. The filtrates were then analyzed for residual Ag^+ concentrations in the solution. Biosorption procedure was carried out at the concentration of imprinted Ag^+ ions (0, 0.5, 1.0, 2.0, 4.0 and 6.0 mg/g) for equilibrium. The constant volume was maintained by keeping nine numbers of conical flasks at the beginning of the experiments and taking out one by one with a fixed time interval. Similar procedure is repeated for 200.0 mg/L initial concentrations at different temperatures at required time intervals. In addition, equilibrium biosorption experiments were carried out in 150 mL flasks containing Ag^+ solutions (50 mL) of known concentrations.

The biosorption equilibrium uptake capacity for each sample was calculated according to mass balance on the metal ion expressed as

$$Q = \frac{(C_{Ag} - C_e)V}{W} \quad (1)$$

where Q is adsorption capacity (mg/g), C_{Ag} and C_e are the initial and equilibrated concentrations of metal ion (mg/L), respectively. V is volume of added solution (L) and W the weight of the adsorbent (g dry).

The above surface Ag^+-imprinting biosorbent (0.15 g dry adsorbent) which had adsorbed Ag^+ was added into the desorption solution (HNO_3, HAC, $Na_3C_6H_5O_7{\cdot}2H_2O$ and $Na_2S_2O_3$ of 0.1 M, 50 mL), and the mixture was shaken in a shaker (170 rpm) at room temperature (25.0–27.0 °C) within 8.0 h. And HAC was short for CH_3COOH. Then the biosorbent was recovered by filtration through Whattman No. 1 filter paper and then used in desorption tests. Desorption kinetics experiments were conducted in continuously stirred (170 rpm) beakers containing 0.1 M of each type of desorbent (50 mL). Similar procedure is repeated for 0.1 M $Na_2S_2O_3$ at different Ag^+ loadings (49.83 mg/g, 65.40 mg/g, 82.81 mg/g, 125.10 mg/g, 196.50 mg/g, 188.33 mg/g, 189.17 mg/g) at required time intervals.

The Ag^+ concentration desorbed was determined and the desorption efficiency (%) could be calculated by the mass balance.

$$D = 100 \times \frac{C_d}{C_{Ag} - C_e} \quad (2)$$

where D is desorption efficiency (%), C_{Ag} and C_e are the initial and equilibrated concentrations of metal ion (mg/L) during the adsorption process, respectively. C_d is the desorbed equilibrium concentrations of metal ion (mg/L) during the desorption process.

No significant pH changes were observed during the experiments, so that they were considered to be performed at constant pH level. All tests were carried out at least three times. And the experimental results were presented as mean values.

2.4. Analytical methods

2.4.1. Analysis of metal ion

The metal ion Ag^+ content was analyzed by an Atomic Spectroscopy (SpectrAA 55-B, Varian Company, US) under 328.1 nm; and the optimum work range of Ag^+ was 0.02–10 μg/mL.

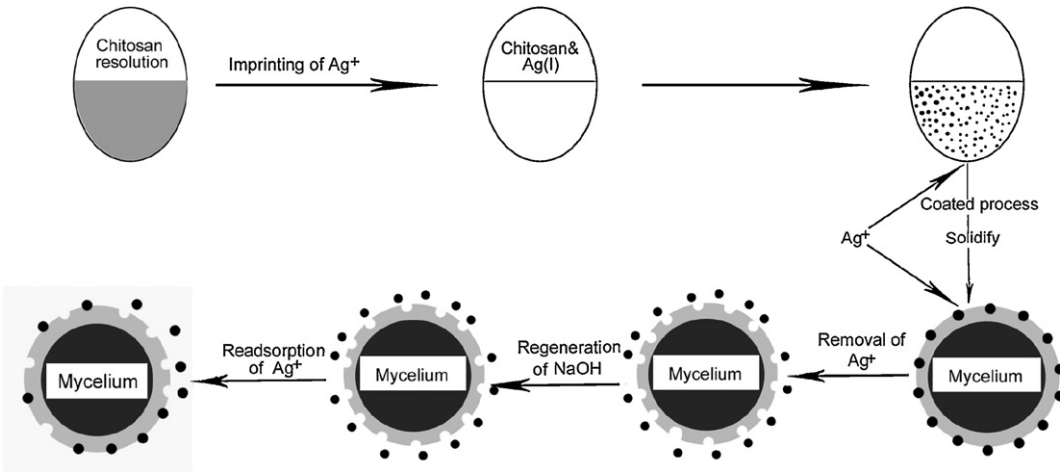

Fig. 1. Flow chart of the preparation of the surface Ag^+-imprinted biosorbent.

2.4.2. Surface structure of adsorbent

Scanning electron micrographs (SEM) were taken on a scanning electron microscope (SEM, S-250MK, Cambridge Company, Cambridge, UK). The morphology of the surface Ag^+-imprinting biosorbent (before adsorption, after adsorption, after desorption) was coated with carbon and gold to be observed and photographed.

The conditions of adsorption and desorption of this sample obtained were as follows:

- Adsorption condition: 50 mL single Ag^+ solution (200.0 mg/L) was contacted with 3.0 g/L of Ag^+-imprinted biosorbent (Ag^+ imprinted concentration: 2.0 mg Ag^+/g) at about pH 7.0 and room temperature (25.0–27.0 °C) for 1.5 h. Because the plateau values were reached after about 1.5 h.
- Desorption condition: 0.1 M HCl (50 mL) was contacted with 3.0 g/L of Ag^+-imprinted biosorbent at about pH 7.0 and room temperature (25.0–27.0 °C) for 4.0 h. Because it reached equilibrium after approximately 4.0 h.

3. Results and discussion

3.1. Biosorption studies

3.1.1. Effect of the imprinting ions concentration on biosorption

As shown in Fig. 2, the concentration of the imprinted Ag^+ ions was an important parameter to adsorption ability in the range of 0–6.0 mg/g (biomass). The imprinted Ag^+ concentration used in preparation of the biosorbent had an optimal value of 2.0 mg/g (biomass) and the maximum adsorption capacity of about 50.0 mg/g at the initial concentration of 200.0 mg/L, which was about 40.0% higher than non-imprinted biosorbent. One reason is probably that more functional groups ($-NH_2$) are retained at higher imprinted Ag^+ concentrations. On the contrary, at Ag^+ imprinted concentrations greater than 2.0 mg/g (biomass), the adsorption capacity of the surface-imprinted biosorbent decreased. It is speculated that the binding sites for the complex of chitosan with Ag or the adsorptive Ag(I) by chitosan is insufficient at higher Ag^+ concentration. Ag^+ including the adsorptive Ag(I) by chitosan is instable, and can be easily reduced as Ag^0, especially in the illumination condition [21,22]. Another reason may be the incomplete desorption during the preparation of the surface Ag^+-imprinted biosorbent. Therefore, 2.0 mg Ag^+/g (biomass) was selected as the optimal Ag^+ imprinted concentration in this experiment.

Table 1
The adsorption for Ag^+ of different imprinting biosorbents; 50 mL single Ag^+ solution (200.0 mg/L) was contacted with 3.0 g/L of imprinting biosorbent for 1.5 h at about pH 7.0 and room temperature (25.0–27.0 °C).

The types of imprinting biosorbents	Adsorption capacity (mg/g)
Ag^+	49.833
Cu^{2+}	37.458
Ni^{2+}	35.402
Pb^{2+}	35.249
Cr^{3+}	39.387

3.1.2. Comparison of different imprinted ions on adsorption selectivity of the biosorbent

The adsorption selectivity of the Ag^+-imprinted and other ion-imprinted biosorbents were investigated (Table 1). The Ag^+-imprinted biosorbent exhibited higher adsorption affinity and selectivity for Ag^+ than the other ion-imprinted biosorbents. The reasons are as follows: by the surface template polymerization technique, Ag^+ selective binding sites could be effectively created on the surfaces of the Ag^+-imprinted biosorbent. But the surfaces of the other ion-imprinted biosorbents would provide less suitable binding sites for Ag^+. This result was similar to that reported on zinc ion adsorption using metal ion-selective membrane [23].

3.1.3. Effect of time on biosorption

Effect of time on adsorption capacity for Ag^+ by the surface Ag^+-imprinted biosorbent was shown in Fig. 3. The amounts of Ag^+ adsorbed were calculated using Eq. (1). The adsorption conditions were given in the figure legends. The slope of the lines joining the data points in the figure reflected the adsorption rates. As can be seen, the adsorption capacity for Ag^+ increased abruptly with the adsorption time increasing, and then plateau values were reached within 1.5 h. In a previous study, several adsorbents were used for silver (I) removal and 5.0 h was reported as an equilibrium adsorption time [24]. The adsorption rate of the surface Ag^+-imprinted biosorbent seemed to be very satisfactory. Due to the preference of short adsorption time for the minimum energy consumption, the surface Ag^+-imprinted biosorbent could be accepted as a good candidate for Ag^+ removal in effluent treatment. So 1.5 h was chosen as adsorption time in the following adsorption experiments.

3.1.4. Effect of temperature on biosorption

The adsorption capacity for Ag^+ hardly changed over the temperature range from 27.0 to 55.0 °C (Fig. 4). That is to say, the effect

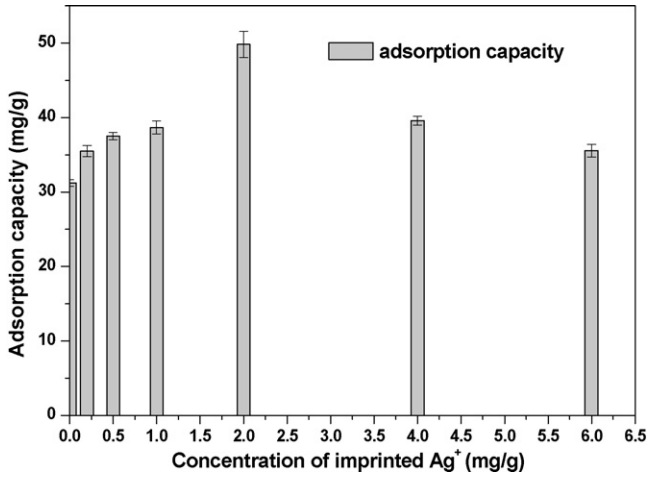

Fig. 2. Effect of concentration of imprinted ions on adsorption capacity; 50 mL single Ag^+ solution (200.0 mg/L) was contacted with 3.0 g/L of Ag^+-imprinted biosorbent at about pH 7.0 and room temperature (25.0–27.0 °C).

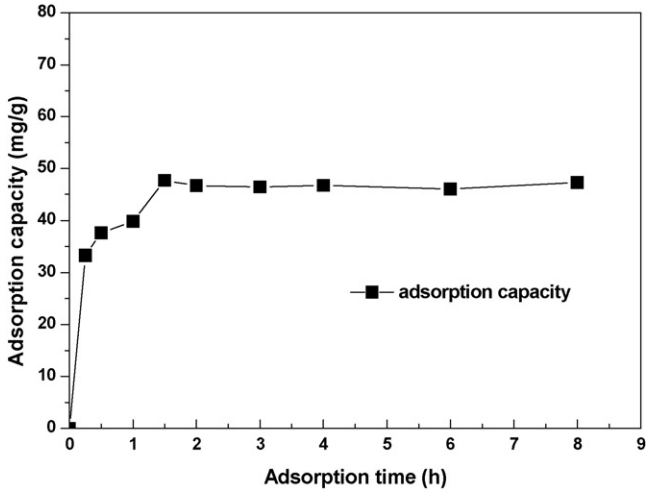

Fig. 3. Effect of time on adsorption capacity; 50 mL single Ag^+ solution (200.0 mg/L) was contacted with 3.0 g/L of Ag^+-imprinted biosorbent at about pH 7.0 and room temperature (25.0–27.0 °C).

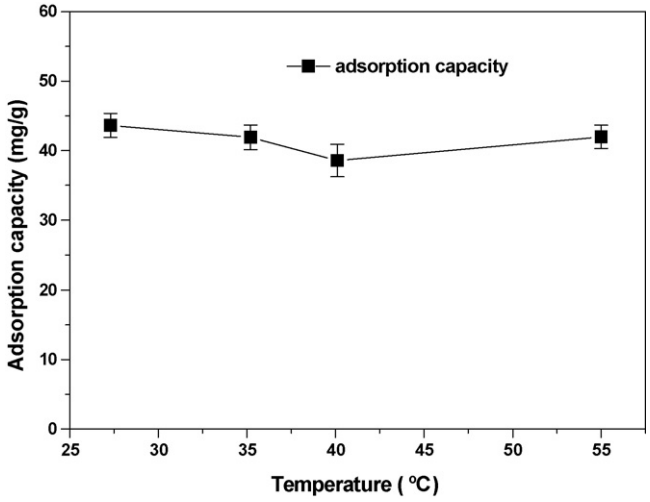

Fig. 4. Effect of temperature on adsorption capacity; 50 mL single Ag^+ solution (200.0 mg/L) was contacted with 3.0 g/L of Ag^+-imprinted biosorbent for 1.5 h at about pH 7.0.

of temperature could be neglected during the research process. As we know, the temperature of actual wastewater was mostly in the range of 25.0–40.0 °C. It was indicated that the practical adsorption of the surface Ag^+-imprinted biosorbent for heavy metal ions was not dominated by physical adsorption, which was large affected by temperature. This was quite same as that of cellulose/chitin beads for heavy metal ions [25]. Therefore, the room temperature (25.0–27.0 °C) was chosen in the following experiments for commercial application.

3.1.5. Effect of initial Ag^+ concentration on biosorption

Experiments conducted with different initial Ag^+ concentrations, showed that the adsorption capacity of the surface Ag^+-imprinted biosorbent increased with the initial concentration of Ag^+ ions (Fig. 5). This increase continued up to 1000.0 mg/L Ag^+, and there was not a significant change at the amount of adsorbed Ag^+ ions beyond this value. The metal uptake could be attributed to chelation as chitosan and Ag could form complex through chelation between Ag^+ and $-NH_2$ [21]. Different adsorbents have been reported for the adsorption of Ag^+ [26–29]. Table 2 represented a comparison among adsorptions of different adsorbents

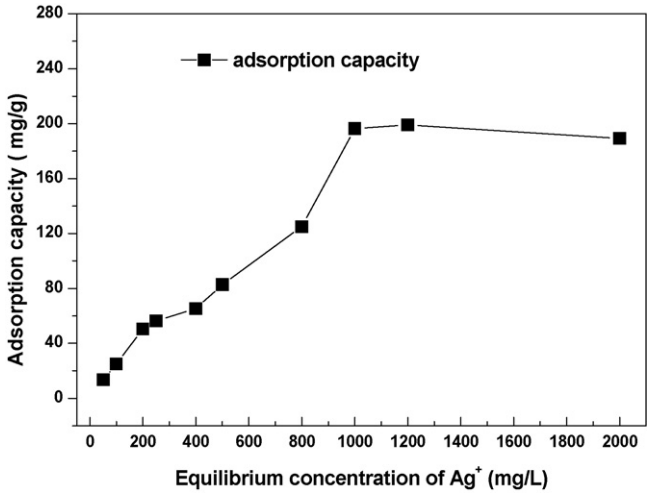

Fig. 5. Effect of initial concentration (50.0–2000.0 mg/L) on adsorption capacity; 50 mL single Ag^+ solution was contacted with 3.0 g/L of Ag^+-imprinted biosorbent for 1.5 h at about pH 7.0 and room temperature (25.0–27.0 °C).

Table 2
Comparison among adsorptions of different adsorbents for Ag^+.

Adsorbent	Q_m (mg/g)	Ref.
Clinoptilolite	43.0	[26]
Coal	1.9	[27]
Chitosan	33.2	[28]
Mordenite	61.0	[29]
Surface Ag^+-imprinted biosorbent	199.2	This work

Q_m, highest experimentally observed value of specific adsorption capacity.

for Ag^+. The results showed that the maximum adsorption capacity of Ag^+-imprinted biosorbent for Ag^+ was 199.2 mg/g, which was far higher than those obtained from other adsorbents given above. The reasons may be that, using the surface molecular imprinting technology, the surface Ag^+-imprinted biosorbent could gain higher adsorption affinity and selectivity for the imprinting ion (Ag^+).

3.2. Desorption characteristics

The final recovery of adsorbed silver from the biosorbent could be carried out using any one or a combination of the commonly used physical and chemical processes. Generally, common diluted acids such as nitric acid, hydrochloric acid was considered as desorbents for heavy metal ions [14]. Sodium citrate used by Meng et al. [30] could well desorb Ag^+ adsorbed on Zeolite and the desorption efficiency reached above 99.0%. Since thiosulfate is a known silver complexing agent used for silver extraction. Solution of thiosulfate could also be employed for the desorption of silver so as to get a highly concentrated solution of silver. Metallic silver could then be obtained by electrolytic recovery or electrowinning.

3.2.1. Effect of different desorbents on desorption

In metal ion removal process, it is important to easily desorb the adsorbed metal ions under suitable conditions. The desorption efficiency for Ag^+ from the biosorbent were calculated using Eq. (2). As shown in Fig. 6, the desorption efficiencies of HNO_3, HAC, $Na_3C_6H_5O_7.2H_2O$ and $Na_2S_2O_3$ increasing abruptly within 0.25 h, reached equilibrium after approximately 4.0 h; but the desorption efficiency of HCl was obviously low; the maximal desorption efficiency could be over 99.0% when using $Na_2S_2O_3$ as a desorbent;

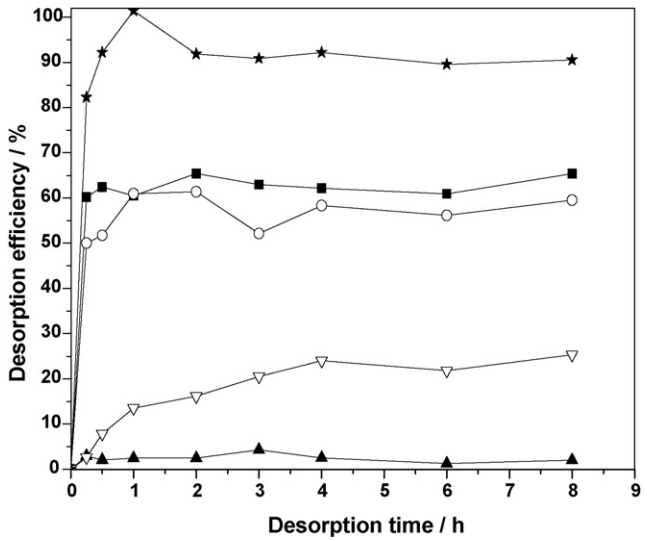

Fig. 6. –■–, 0.1 M HNO_3; –○–, 0.1 M HAC; –▲–, 0.1 M HCl; –▽–, 0.1 M $Na_3C_6H_5O_7{\cdot}2H_2O$; –★–, 0.1 M $Na_2S_2O_3$. Effect of time on desorption of different desorbents; 50 mL desorbent solution was contacted with 3.0 g/L of Ag^+-imprinted biosorbent which adsorbed Ag^+ solution (200.0 mg/L) for 1.5 h at about pH 7.0 and room temperature (25.0–27.0 °C).

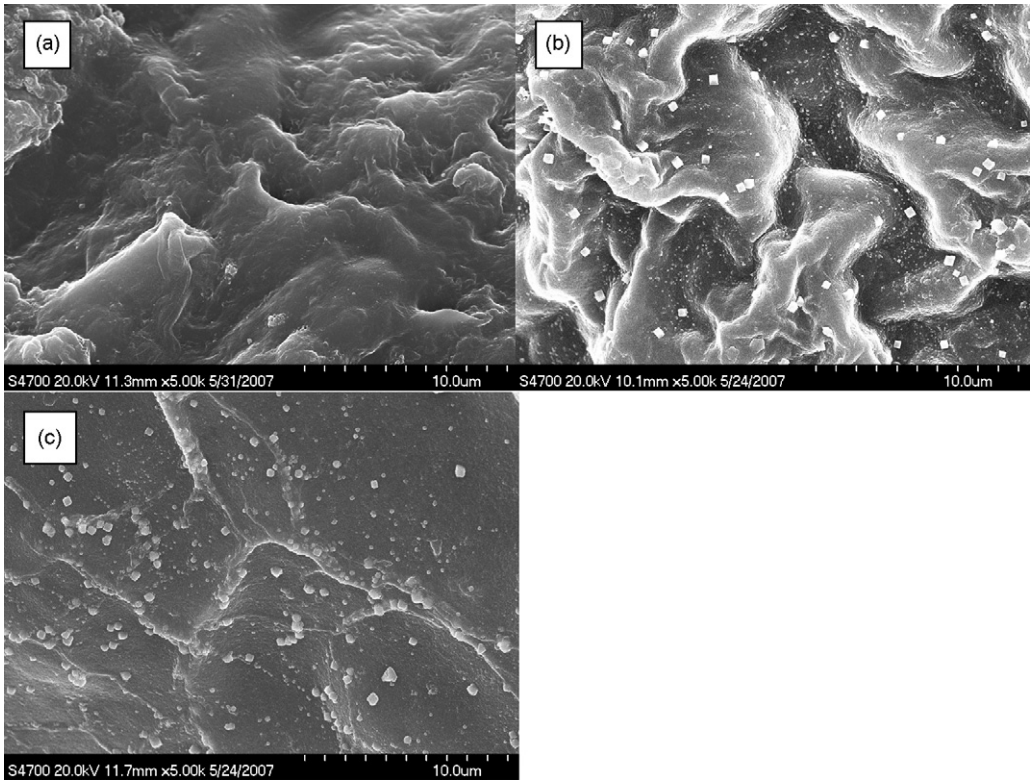

Fig. 7. (a) SEM image of the surface Ag^+-imprinted biosorbent, before adsorption of Ag(I) (×5000times); (b) SEM image of the surface Ag^+-imprinted biosorbent, after adsorption of Ag(I) (×5000); (c) SEM image of the surface Ag^+-imprinted biosorbent, after desorption of Ag(I) (×5000).

that is to say, $Na_2S_2O_3$ could easily desorb Ag^+ adsorbed from the biosorbent; besides, 65.5% and 61.3% Ag^+ could also be desorbed by HNO_3 and HAC respectively; however, HCl basically did not desorb Ag^+ from the biosorbent surfaces. And sodium citrate also did not display the better desorption ability for Ag^+(Fig. 6); Therefore, $Na_2S_2O_3$ was chosen as a better desorbent in this experiment.

The surface morphology and distribution of Ag on the biosorbent could be explored by SEM. An interesting phenomenon could be observed (Fig. 7). Fig. 7 showed the typical SEM images of the biosorbent before adsorption, the biosorbent after adsorption (before desorption) and the biosorbent after desorption. From Fig. 7a, it could be seen that the biosorbent surfaces were more smooth and without any granules. As shown in Fig. 7b, a large number of smaller particles (bright spots) on the biosorbent surfaces, the size range of them was from 10 to 100 nm. That is to say, noble metal ion (Ag^+) could be well adsorbed by the biosorbent. Compared with SEM image of biosorbent before desorption, using HCl as a desorbent, there were still as much as small particles on the biosorbent surfaces (Fig. 7c). But we do not know whether this led to the lower desorption ability of HCl or not. However, which kind of nanoparticle, Ag or AgCl, still need to be further researched.

3.2.2. *Effects of Ag^+ loading on desorption*

As shown in Fig. 8, the desorption of the surface Ag^+-imprinted biosorbent adsorbed different adsorption capacity of Ag^+ showed a rather significant difference. Obviously, less than 82.81 mg/g Ag^+ adsorbed on the biosorbent could be rapidly desorbed by 0.1 M $Na_2S_2O_3$; the desorption efficiency basically reached over 90.0%; and the maximum value could be about 99.0%; that is to say, noble metal Ag could be easily recovered within this range. However, once more than 82.81 mg/g, the desorption efficiency decreased with an increase of Ag^+ loading on the biosorbent; just about 50.0% Ag^+ were reclaimed at adsorption capacity of 189.2 mg/g, which

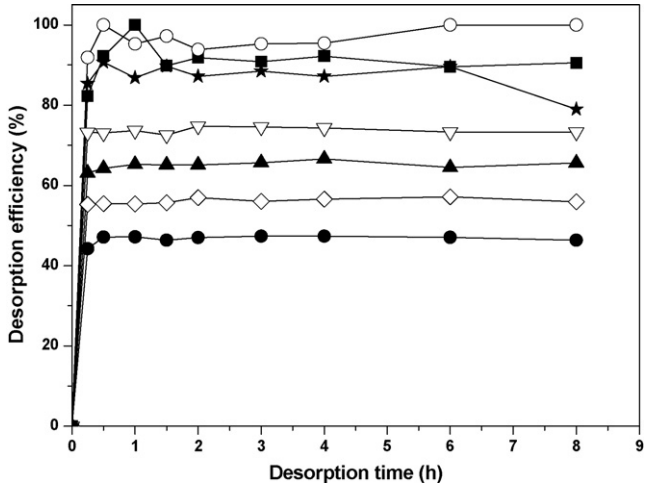

Fig. 8. –■–, 49.83 mg/g Ag^++; –○–, 65.40 mg/g Ag^++; –★–, 82.81 mg/g Ag^+; –▽–, 125.10 mg/g Ag^+; –▲–, 196.50 mg/g Ag^+; –▲–, 188.33 mg/g Ag^+; –●–, 189.17 mg/g Ag^+. Effect of time on desorption efficiency of the biosorbent after adsorbing different adsorption capacities of Ag^+; 50 mL desorbent solution (0.1 M $Na_2S_2O_3$) was contacted with 3.0 g/L of Ag^+-imprinted biosorbent which adsorbed Ag^+ solution (200.0–2000.0 mg/L) for 1.5 h at about pH 7.0 and room temperature (25.0–27.0 °C).

was corresponding to the initial Ag^+ concentration of 2000.0 mg/L. Under this experimental condition, the equilibrium of all desorption processes could be almost reached after 2.0 h. Generally, it was reported that most of the desorption processes were finished within 3.0 h [31]. This means that desorption process was performed very quickly. Since Ag^+ concentration of wastewater was much lower than 2000.0 mg/L [1–3,6], 0.1 M $Na_2S_2O_3$ was chosen as a rather available desorbent in the reclaiming of Ag^+.

4. Conclusions

Ag^+-imprinted biosorbent prepared by using molecular imprinting technology, showed higher adsorption affinity and selectivity for the imprinted silver ion than the other imprinted metal ions. The results indicated that the adsorption process was influenced by the factors such as imprinting Ag^+ concentration and adsorption time. 0.1 M $Na_2S_2O_3$ was chosen as a better desorbent. The desorption efficiency of $Na_2S_2O_3$ (0.1 M, 50 mL) achieved as high as 99.0%. Therefore, the precious metal could be effectively reclaimed. That is to say, it was potential for using the biosorbent in the recovery of precious metal silver. An unusually high loading of Ag could be demonstrated by the SEM analysis. Compared with other adsorbents produced from pure chitosan, the surface Ag^+-imprinted biosorbent offers the advantages of little dosage of chitosan and reduction of the cost, which will be hopefully applied in the treatment and recovery of silver-bearing wastewater from electroplating, coinage, photo fixation and so on. However, further studies are still needed for understanding the interaction mechanisms between the biosorbent and silver before or after desorption by HCl.

Acknowledgements

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