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Sorption of Cu^{2+} and Zn^{2+} by Natural Biomaterial: Duck Feather

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Abstract Feather fibers were modified by treatment with 5% tannic acid (TA) solution. Kinetics of the modification was investigated as a function of the reaction time. The maximum loading of TA on feather reached 8.3% after being treated by TA for 9 h. The adsorption of metal cations (Cu^{2+}, Zn^{2+}) by unmodified and TA-modified feather fibers was investigated as a function of fiber weight gain, temperature, and pH of the metal solution. The adsorption was enhanced at alkaline pH and ambient temperature and increased with the weight gain of TA. The maximum uptake of metal cations (Cu^{2+}, 0.77 mmol/g; Zn^{2+}, 0.95 mmol/g) was obtained by TA-modified feather at weight gain: 8.3%, pH 11, while at the acidic pH, the adsorption of metal cations by either unmodified or TA-modified feather was negligible. The influence of anions on the adsorption of metal cations was also studied. The uptake of Cu^{2+} from chloride was higher and faster than that from nitrate. Desorption of the metals was performed at acidic pH 2.5 for 48 h. The feather–TA–metal complexes exhibited higher stability for metal cations than the feather–metal complexes. All these experiments reveal that TA-modified feather fibers have good adsorption to metal cations and can be used as metal adsorbent in wastewater treatment.

Keywords Feather fiber · Tannic acid · Metal adsorption · Desorption · Column

Introduction

As a natural protein material, feather fiber has polar and ionizable groups on the side chain of constant amino acid residues, which are able to bind charged species. Studies on binding of metal cations to chicken feather were previously reviewed by Friedman [1] and Goto [2].

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The rate and extent of uptake was reported to depend on various factors, such as metal type and its valence state, solution concentration, pH, time, temperature, and so forth.

The adsorption of metal cations by feather fibers can be contributed by many characteristics, such as low solubility, complex physical form, relatively high content of reactive groups that can serve as binding sites or that can be chemically modified, variety and juxtaposition of reactive sites that can allow cooperative reaction etc. The most likely binding sites are the free carboxyl groups of aspartic and glutamic acid occurring in the amorphous polypeptide sequences. These acidic groups have a pK_a of about 4–4.8 and are almost completely dissociated at pH 7, therefore, providing negatively charged binding sites over a wide range of pH conditions. Coordination bonds can be formed with nitrogen atoms of amine and amide groups, especially at alkaline pH. It was previously shown that cystine reacts as well, leading to formation of stable metal mercaptides [1]. The absorbed metal can be quantitatively desorbed at acidic pH, apart from that bound to cystine. The reversibility of the protein–metal interaction is attributed to the competition between metal and hydrogen ions for the same binding sites.

The treatment of protein fibers with metals may induce many useful changes to fiber properties, such as shrinkage resistance [3], flame proofing [4], bacterial inhibiting [5] etc. Changes in capacities and rates of metal cations uptake were influenced by various modifications. Keratin fibers can be reduced by S-alkylation with 2-vinylpyridine, sodium dithionite [4], and thioglycollic acid [6], or oxidized by $KMnO_4$ solution. The uptake also can be enhanced by chemically modifying the keratin fibers with chelating agents, such as: ethylenediaminetetraacetic acid (EDTA) dianhydride and tannic acid (TA), which are able to coordinate metal cations. In the previous works, some of the authors investigated the adsorption and binding of metal cations onto B. mori silk [7] and wool [5] either by treatment with TA or acylation with EDTA dianhydride, as a function of fiber weight gain and pH of the metal solution. The results revealed that the adsorption of metal cations could be enhanced by the treatment with TA effectively.

Heavy metal pollution is currently receiving much attention. Many methods were used to remove the metal cations from aqueous solutions, such as: ion exchange, active carbon adsorption, precipitation, and reverse osmosis. Recently, biosorption by animal fibers, has been drawing many attentions of researchers, mostly because they are cheaper than chemical adsorbents and never exhausted. Wool has been used as sorbent to remove heavy metal pollutants from industrial effluents and to purify contaminated water supplies [2].

Fowl feather is a low-cost natural polymeric material with abundant resource. As wool could be used as sorbent [2], we decide to use the same technique for developing the duck feather as a new absorbent to remove heavy metal pollutants. The binding of metal cations (Cu^{2+}, Zn^{2+}) by duck feather, unmodified or TA-modified, was investigated as a function of fiber weight gain, pH of metal solution, and anions type, etc. in the present work. Desorption of metal cations from feather–metal complexes in acid solution was studied as well. Furthermore, the adsorption of metal cations by TA-modified feather in column was investigated for exploiting the industrial-scale application.

Experimental

Materials and Reagents

The feather fibers used in our experiment were in the form of barbs, which were detached from the shaft of duck feather, provided by Guangzhou Zhongyu Jiye Down Textile Co., Ltd. Tannic acid (TA) was obtained from Wenzhou Ouhai Fine Chemicals Corporation (Zhejiang, China), with an average molecular mass of 1,701.18 g mol^{-1}. Metal solutions were prepared from analytical grade reagents: $CuCl_2 \cdot 2H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, which were purchased from Qianhui Reagents Company (Guangzhou, China).

Chemical Modification

Loading with TA was performed by immersing feather fibers into a 5% (w/v) aqueous solution of the TA reagent (material-to-liquor ratio 1:100) at 70°C for 1–13 h. Feather fibers were removed after the contact time, washed thoroughly in a porcelain funnel with distilled water, and then dried at room temperature before metal adsorption experiments.

Sorption and Desorption

To study the sorption behavior of the metal cations, either unmodified or TA-modified feather fibers was immersed in aqueous solutions of 20 mM metal cations, at ambient temperature, for 30 h. The solution pH was adjusted with HNO_3 and ammonia. In alkaline condition (pH>7), the metals were in the form of amine complexes. These conditions were considered more favorable for metal uptake [8]. The influence of anions on adsorption was investigated with TA-modified feather fibers in 20 mM $CuCl_2$ and 20 mM $Cu(NO_3)_2$ in the nearly neutral aqueous solution of pH 6.0, the immersing time was changed with the proceeding of the reaction from 0–45 h. Desorption of metal cations was conducted by immersing different feather–metal complexes in the acidic solution of pH 2.5 for 48 h.

Industrial Exploration

Column experiment, similarly to the ion exchange column, is essential for industrial designing of technical systems. A quartz glass column (20-cm length, 3-cm diameter) was designed for this experiment (Fig. 1); porous plugs at each end of the column were applied to hinder the moving of the feather fibers, the valve was used to control the flow velocity. The column was filled with 3.5 g TA-modified feather fibers evenly. Investigations were carried out by feeding the column which was laid flatly with solutions of 20 mM $Cu(NO_3)_2$ and 20 mM $Zn(NO_3)_2$, respectively, at the desired flow velocity (20 ml/min). The pH of the metal solutions was adjusted to 11.0 with ammonia.

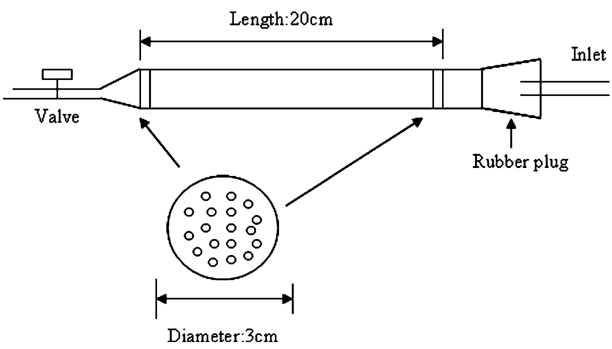


Fig. 1 Adsorption column

Instrumental Analysis and Measurements

The weight of the feather fibers and the uptake of TA were weighed on the Precision Weighing Balance with a sensitivity of 0.1 mg (CARLO GAVAZZI, Switzerland). The pH values of the solutions were measured with PHS-3C pH meter (Shanghai Science Equipment Co. Ltd., China), the calibration of which was conducted by using standard buffer solutions.

The changes of the concentration of the metal cations were measured with Hitachi Z-5000 Series Polarezed Zeeman Atomic Absorption Spectrophotometer (Hitachi High-Technologies Corporation, Japan). The adsorption capacities of the metal cations by unmodified and TA-modified feather fibers were calculated according to the following equation:

$$Q = (C_b - C_a)V/Mm$$

Q the adsorption capacity for metal cations (mmol metal/g feather fiber)
C_b the concentrations of metal cations (mg metal/l) in solutions before sorption
C_a the concentrations of metal cations (mg metal/l) in solutions after sorption
V the reaction volume (l) of the metal solution
M the molecular weight (g/mol) of the metal cation
m the weight of feather fibers (g)

Results and Discussion

Chemical Modification of Feather Fibers with TA

Tannin acid (TA) is a kind of plant polyphenol, the structure formula of which is shown in Fig. 2. It is reported that TA can form insoluble products with keratin by tanning reaction, which can increase the chemical and physical stability of protein. Moreover, TA can form chelates with many metal cations via the ortho dihydroxy (catehol) or trihydroxy-benzene (galloyl) group [9].

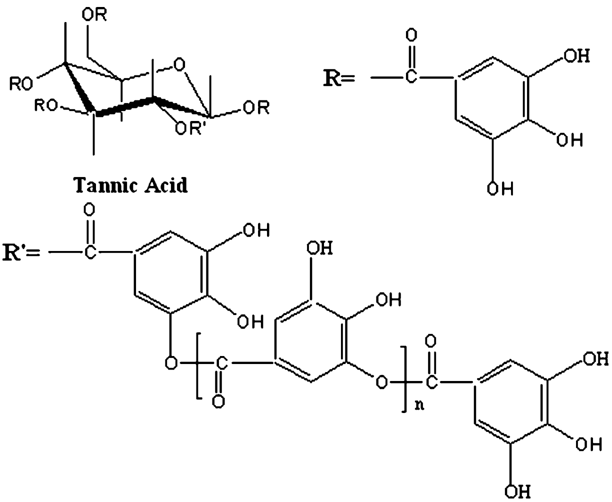


Fig. 2 Structure formula of tanning acid (TA)

The uptake of TA by feather fibers was investigated as a function of the reaction time. Since the weight gain of TA on the feather fibers was easily influenced by the ambient humidity, the humidity was controlled at 70% in this experiment.

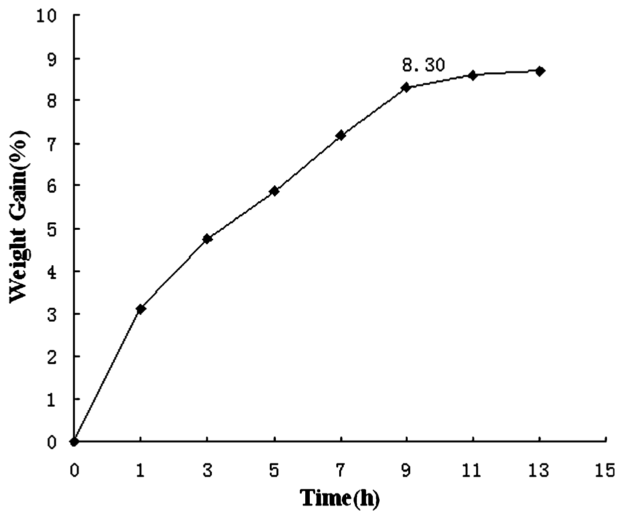
TA is physically absorbed and held in the feather matrix through chemical interactions other than covalent. In our experiment, the uptake of TA showed an initial rise with turning point at 60 min, corresponding to a weight gain of 3% (Fig. 3). Afterwards, it proceeded at a markedly lower rate, reaching a balanced weigh gain of 8.3% after a 9-h treatment. This behavior was in striking contrast with that recently reported for silk, which exhibited a noticeably higher affinity for TA (about 18% weight gain in 90 min) [7].

The different uptake of TA may be influenced by the secondary structure of the keratin fibers. The secondary structure of silk keratin is mainly in the form of β-sheet [10], while that of the feather keratin, about 30% are in the form of α-helix [11]. As we know, in the structure of β-sheet, the peptide chains exhibit extending twist, which can decrease the steric hindrance of the adjacent side chains effectively. However, in the structure of α-helix, the whole structure seems more tight, many side chains are being buried, and having low activity. Therefore, there are more available binding sites on the side chains of amino acid residues in β-sheet keratin, such as amide groups and carboxyl groups, which are available for forming hydrogen bonds or other coordination bonds with TA. In addition, the lower uptake of TA by feather fibers than that by the silk can also be partly attributed to the complex cellular structure, hydrophobic external layer, complicated morphology of the feather fibers. It was noteworthy that the uptake of TA by feather fibers still increased with the extending of the treating time for many hours, but not significantly as the uptake in initial 9 h. It revealed that the weight gain was 11.9% when the treating time was extended to 15 h. This result was similar to the principle of the leather tanning [8].

Effect of TA-modification of Feather Fibers on the Adsorption of Metal Cations

The adsorption of Cu^{2+} and Zn^{2+} by TA-modified feather with increasing weight gains was studied in alkaline solutions (pH 11). The results obtained are shown in Fig. 4.

Fig. 3 Weight gain of feather fibers modified with tannic acid as a function of reaction time



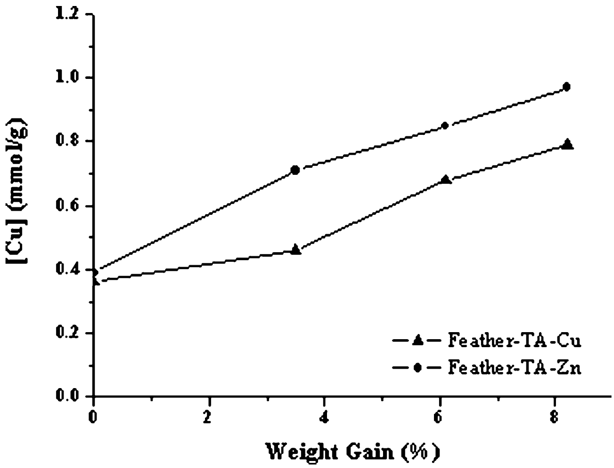


Fig. 4 Adsorption of metal cations in the alkaline solution of pH (11) by TA-modified feather as a function of weight gain

Figure 4 shows that loading with tannic acid resulted in a steady increase in the adsorption of both Zn^{2+} and Cu^{2+}. The adsorption of metal cations by TA-modified feather fibers was linearly correlated with the weight gain of TA. These results were consistent with those recently reported for silk fibers and wool fibers [5, 7]. Modification with TA was effective in enhancing the adsorption and binding of metal cations by protein fibers at alkaline pH. This behavior can be explained by the increased number of the available binding sites, which were introduced into the fiber matrix by the modification agent of TA.

It is also indicated that the uptake of Zn^{2+} was higher than that of Cu^{2+} in the figure. This may depend on the properties of the metals and the metal–protein ligands and on the kinetic and thermodynamic parameters of the metal complex formed within the fiber matrix.

Effect of Temperature on the Adsorption of Metal Cations

As the alkaline condition strengthens the metal uptake, the effect of temperature on the adsorption of metal cations was carried out at pH 11. The temperature was adjusted from 25 to 65°C, increasing by 10°C.

In Fig. 5, with the increasing temperature from 25 to 35°C, the metal uptake by feather increased. The biggest metal uptake obtained in this study was: 0.81 mmol/g by TA-modified feather, 0.46 mmol/g by unmodified feather. At high temperature, the behavior of the Cu^{2+} diffusing into the feather matrix and the activity of the binding sites in feather were strengthened. Above 35°C, with the increasing temperature, the adsorption of Cu^{2+} by both TA-modified and unmodified feather decreased markedly. From 45 to 65°C, the adsorption of Cu^{2+} by unmodified feather decreased by 0.22 mmol/g, about two-fifths of that by TA-modified feather, which was 0.56 mmol/g. Above 50°C, the adsorption of Cu^{2+} by both TA-modified and unmodified feather were lower than those at ambient temperature. It was known that the adsorption behavior was reversible. With the temperature increasing, the balance of the adsorption was broken up, and some metals began to desorb from feather. Therefore, the adsorption of Cu^{2+} by feather decreased with the increasing of the temperature. The decrease of the metal uptake by TA-modified was higher than that by unmodified feather. This was attributed to the desorption of TA. As we know, the normal tanning reaction of leather was carried out at the temperature of 35~45°C. Because this temperature can help TA to diffuse into the interior of leather fiber, it can prevent the TA

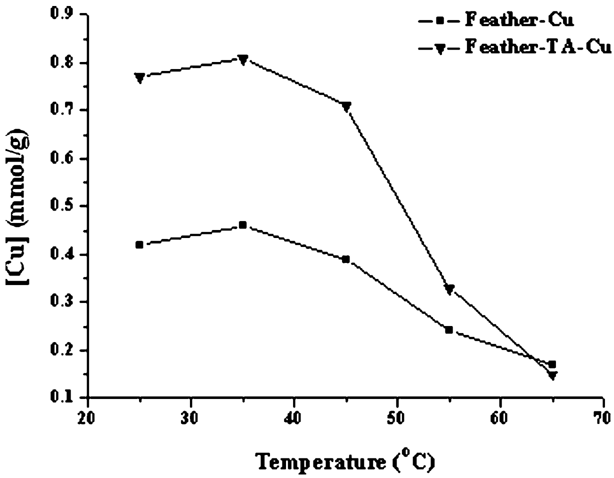


Fig. 5 Adsorption of Cu^{2+} by feather unmodified, modified with tannic acid (8.3% weight gain) as a function of temperature

from desorbing. It was observed in the experiment, from 55 to 65°C, after the completion of the adsorption of Cu^{2+} by TA-modified feather, the color of the solution became brown. This was due to the desorption of TA at higher temperature.

Effect of Solution pH on the Adsorption of Metal Cations

The pH of the metal solution was known to affect the uptake of metal cations [8, 9, 12]. To study the influence of pH on the binding of Cu^{2+} and Zn^{2+} by feather fibers, the pH value of the metal solution was changed from acidic pH 2.5 to alkaline pH 11.0.

The adsorption of Cu^{2+} by unmodified and TA-modified feather was almost negligible below pH 6.0 (Fig. 6). After pH 6.0, the uptake of Cu^{2+} by TA-modified feather increased more significantly than that by unmodified feather, attaining a maximum uptake of 0.77 mmol/g at pH 11.0.

The same feature was observed in the adsorption of Zn^{2+}. Figure 7 shows, The adsorption of Zn^{2+} by unmodified feather kept constant increasing over a wide range of pH,

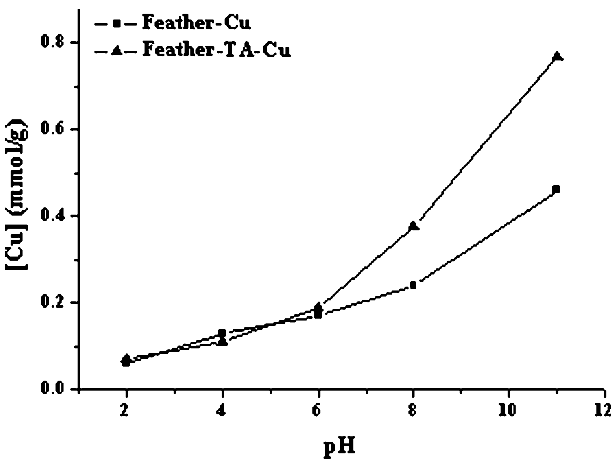


Fig. 6 Adsorption of Cu^{2+} by feather unmodified, modified with tannic acid (8.3% weight gain) as a function of pH

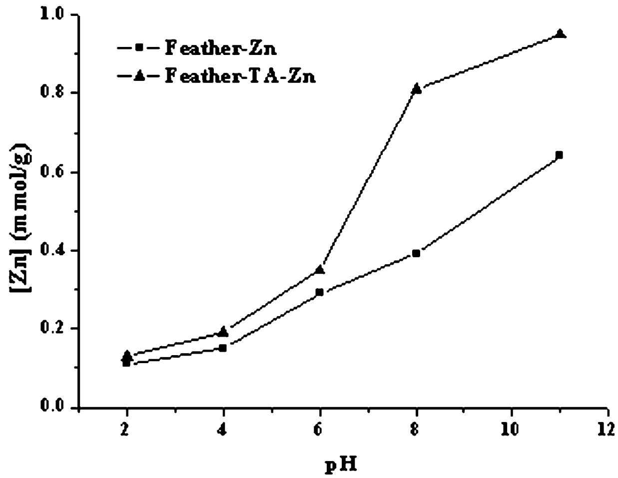


Fig. 7 Adsorption of Zn^{2+} by feather unmodified, modified with tannic acid (8.3% weight gain) as a function of pH

while that by the TA-modified feather showed a sharp increase at above pH 6.0, attaining a maximum of 0.95 mmol/g at pH 11.0.

The ascending of the adsorption of Zn^{2+} and Cu^{2+} with the increase of the solution pH was attributed to the dipolar properties of feather keratin. As expected, alkaline conditions were more favorable for binding metal cations than either neutral or acidic conditions for both unmodified and TA-modified feather. The aspartic and glutamic residues in the feather keratin dissociated completely in the strong alkaline solution; therefore, the strong negatively charged groups such as carboxyl anions were available for binding metal cations. In addition, the nitrogen of amine and peptide groups should participate as well in metal coordination. These can be used to explain the high uptake of the metal cations by unmodified feather fibers in the alkaline solution. Further more, the reason for the higher uptake of metal cations by TA-modified feather fibers was attributed to the polyphenol structures that were introduced by the TA modification, which dissociated in the alkaline solution and reacted with metal cations as additional negatively charged groups.

Actually, some other factors also influenced the metal uptake, such as the formation of complexes with higher coordination number, the low concentration of metal in the solution, and the treatment conditions (soaking time, temperature), etc. At alkaline pH, the –S–S– cystine bridges are susceptible to attack by metal cations, causing cystine degradation and formation of stable mercaptides, which are always accompanied by a color change of fibers from white to deep brown [8]. In the present work, the treatment of feather fibers with alkaline metal solution at ambient temperature prevented extensive cystine degradation, as evidenced by the only slightly yellowish color displayed by feather after a 30-h treatment at pH 11.0.

Effect of Anions on the Adsorption of Metal Cations

The anions also influenced the rate of binding in the neutral or weak acidic conditions [6, 13]. Figure 8 shows the uptake of the copper ions increased with the extending of the immersion time of the feather fibers. The highest uptake in this experiment occurred at the time of 45 h. The highest uptake of Cu^{2+} from chloride was 0.31 mmol/g and that from nitrate was 0.27 mmol/g. The uptake of Cu^{2+} from $CuCl_2$ was almost complete in the first 5 h, while that from $Cu(NO_3)$ lasted tens of hours. It was reported that the completion of the metal uptake from the nitrate required almost several days for wool [13].

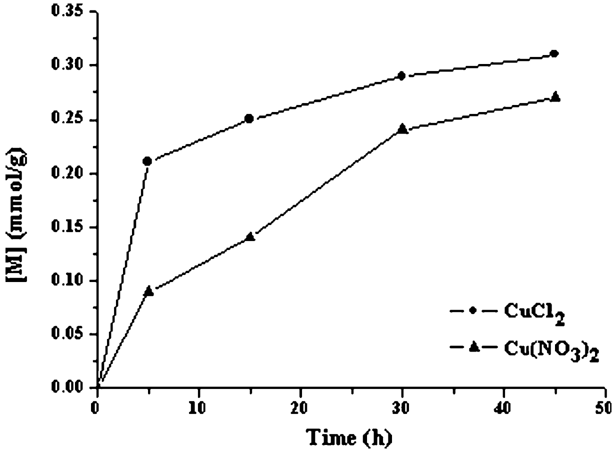


Fig. 8 The effect of anions on the adsorption of Cu^{2+} by TA-modified feather

This difference in the sorption behavior might be attributed to the interference of the anions in the solution. It was reported that Cu^{2+} dissociated completely from the nitrate, while few of Cu^{2+} dissociated from the chloride. The dissociated Cl^- tended to coordinate with $CuCl_2$, and the coordination compounds were undissociated and preferential to be bound by the feather fibers. Since $Cu(NO_3)_2$ dissociated easily in the solution, the adsorption of Cu^{2+} from nitrate was higher than that from chloride, although the uptake of Cu^{2+} by feather fibers from both salts were comparable eventually. However, this interference of the anions was inhibited at the alkaline condition for the effect of OH^-.

Desorption of Feather–Metal Complexes

The adsorption of metal cation by keratin fibers is a reversible process, which can be enhanced by acidic pH as a result of the competition of the H^+ for the same binding sites [10]. Once immersed in an acidic solution, the feather–metal complex may release variable amounts of metal cations. The desorption behavior is influenced by the solution pH and the stability of the metal complex.

Table 1 lists the results of the desorption tests carried out on the different feather–metal complexes prepared in this study. The extent of release varied among the samples as a function of the kind of metal and of the properties of the fibrous substrate (unmodified, TA-modified). Unmodified feather showed lower binding strength for either Zn^{2+} or Cu^{2+}, which was almost completely released. By comparing two sets of samples, the extent of metal release of unmodified and chemically modified feather followed the same order,

Table 1 Release of metal cations by immersion of feather–metal complexes in aqueous solution at pH 2.5 for 48 h.

Sample	[M] (mmol/g)		Metal
	Before	After	Released (%)
Feather–Cu	0.42	0.27	35.7
Feather–TA–Cu	0.77	0.67	13.0
Feather–Zn	0.64	0.23	64.0
Feather–TA–Zn	0.97	0.79	16.8

unmodified feather> TA-modified feather, in which the difference among the samples of the same series was much larger for the feather–zinc system.

On the other hand, the released amount of Zn^{2+} was higher than that of Cu^{2+} in either feather–metal complex or feather–TA–metal complex. The reason is that TA can increase the chemical and physical stability of the keratin fibers by tanning reaction. The variable tendencies of the feather–metal complexes to release metal cations can be regarded as a useful functional property for recycling some costly metals.

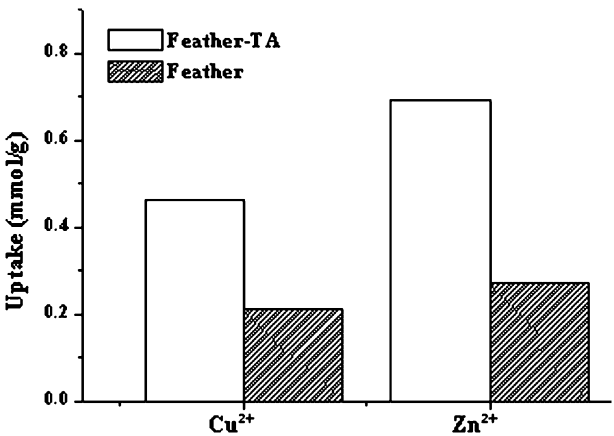
Column Experiment

Column flow operation is important for practical use of feather fibers for scavenging metal cations from polluted water. The results of the column adsorption of metal cations by unmodified and TA-modified feather fibers were compared in Fig. 9. The adsorption by TA-modified feather fibers was 0.46 mmol/g for Cu^{2+} and 0.69 mmol/g for Zn^{2+}, while that by unmodified feather fibers was 0.21 mmol/g for Cu^{2+} and 0.27 mmol/g for Zn^{2+}. Obviously, the uptake of metal by TA-modified feather was higher than that by unmodified feather fibers. On the other hand, the uptake of Zn^{2+} also kept higher than that of Cu^{2+} by either TA-modified or unmodified feather fibers. As previously described, the adsorption behavior can be enhanced in the alkaline solutions. Also, it was influenced by the properties of the metal–protein ligands and the metal itself.

It is noteworthy that the uptakes of the metals in the column were lower than that of the metals immersing in the ammonia bathe by either unmodified or TA-modified feather fibers. In the case of the TA-modified feather fibers in the ammonia bath, the uptake was 0.77 mmol/g for Cu^{2+} and 0.95 mmol/g for Zn^{2+}. This may be attributed to the shorter contact time of the feather fiber and the metal solution in the column than that in the ammonia bath (less than 8 min, which was calculated by the volume of the column and the feeding velocity of the solution). In addition, compactness and hydrophobic surface of the feather fibers also influenced the uptake of the metal in column.

The results revealed that the TA-modified feather fibers in column were effective in collecting heavy metal cations form their aqueous solutions. Although many factors needed to be improved, such as the design of the column, the flow velocity of the metal solution, and the evenly filling of the feather fibers etc., the adsorption by TA-modified feather fibers in column is a valuable and important exploitation for the industrial-scale designing and application.

Fig. 9 The adsorption of Cu^{2+} and Zn^{2+} by TA-modified and unmodified feather in column



Conclusions

This study reveals that the duck feather, as a low-cost natural polymeric material with abundant resource, after being modified by TA, is effective for the removal and collection of heavy metal cations from industrial effluents and waste aqueous solutions. Also, they can be the basis for exploiting an effective processing technique for producing versatile metal-container feather fibers. Further studies of exploiting the fowl feather resources for new industrial-scale adsorption designing and application are needed.

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