Selective chelating precipitation of palladium metal from electroplating wastewater using chitosan and its derivative

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Abstract
A study on selective chelating precipitation of palladium metal from real electroplating wastewater using chitosan and its water-soluble derivative was conducted. The pH parameter, the concentrations of chitosan and its water-soluble derivative and the chelating precipitation time were experimentally investigated, and the optimum conditions were determined. The results revealed that both chitosan and its water-soluble derivative acted as chelating precipitation agents. Rapid chelating precipitation occurred when chitosan was added to real electroplating wastewater containing the chitosan derivative, thereby improving removal efficiency of palladium in different

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forms up to 95% under the optimum condition of 0.2 g/L chitosan and 0.16 mg/L derivative at pH 2.5. Then, dissolution experiments showed that chelating precipitation products could be dissolved in aqua regia. Additionally, selective chelating precipitation of palladium by chitosan and its derivative was characterized using X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. Thus, it can be concluded that the combined utilization of chitosan and its water-soluble derivative is a promising approach method for the removal of different forms of palladium from real electroplating wastewater.

Keywords
Chelating precipitation, palladium, removal, electroplating wastewater, chitosan and its derivative

Introduction
Palladium is a rare metal with few repositories; it is proved to be an essential key material in the high-tech fields of aeronautics and astronautics, the automobile industry and the electroplating industry. Usually, electroplating wastewater-containing palladium is mainly a by-product of the activation and passivation processes in various electronic industries. Unfortunately, most wastewaters containing palladium produced by the electroplating industry are discharged as normal wastewaters; such discharge increases the difficulties in the post-treatment of wastewater and wastes of resources. Therefore, enhanced palladium removal from electroplating wastewater can bring great economic and environmental benefits. Many methods including precipitation methods by thiourea or ammonium chloride (Chen and Zhou, 2009; Park and Fray, 2009), reduction method by formic acid (Barakat et al., 2006), ion exchange (Wołowicz and Hubicki, 2011), electro-deposition (Fathirad et al., 2012), membrane separation (Nattaya and Paisan, 2014; Tahmasebi and Yamin, 2014), extraction (Chen et al., 2017; Wei et al., 2016) and adsorption (Awual et al., 2015; Lin et al., 2015; Monier and Abdel-Latif, 2016; Noah et al., 2016; Vojoudi et al., 2017) have been employed for treating palladium (II) solutions. Among them, precipitation method, reduction method and electro-deposition method are generally used for removing palladium from concentrated solutions. However, the palladium concentration of electroplating wastewater is approximately 10 mg/L (Chen et al., 2017; Ebrahimzadeh et al., 2010), which cannot be effectively removed by the above methods. On the other hand, palladium exists in different forms in electroplating wastewater, such as in the form of complex states, colloidal states, ionic states and single metal. Nevertheless, ion exchange and adsorption technology cannot remove palladium in other states, except in ionic states, and let it discharge as normal wastewater.

Chelating precipitation is a method that removes heavy metal ions by using stronger chelating agents to form insoluble chelates by adding a small quantity of precipitant. Chelating precipitation can remove metals at low concentrations existing in both ionic states and complex states, metals which could not be removed effectively by chemical precipitation and other conventional methods (Kanchi et al., 2014). Therefore, it is considered as a suitable method for removing heavy metal ions that exist in different forms from wastewater to meet the discharge criteria. It was reported that dithiocarbamate (DTC),
a heavy metal collector synthesized by diethylenetriamine and carbon disulfide, combined with its derivatives were adopted to remove chelate heavy metal ions from wastewater with the addition of a small quantity of polyacrylamide (PAM) as a flocculant. The concentration of Ni\(^{2+}\) could be decreased from 50.00 mg/L to 0.87 mg/L by using N, N’-bis-(dithiocarboxy) piperazine (BDP) and diethylidithiocarbamate (DDTC) (Fu et al., 2007), and Cd\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\) in chelated states could be removed by another dithiocarbamate groups functionalized multi-walled carbon nanotube (DTC-MWCNT) (Li et al., 2015). However, existing chelating precipitation reagents are mainly designed for removing heavy metals but not for precious metals such as palladium. It is known that soft metal ions, such as Pd\(^{2+}\), Au\(^{3+}\) and Ag\(^{+}\) ions, show affinity to soft bases with donor atoms as O < N < S, whereas hard metal ions, such as Al\(^{3+}\), Cu\(^{2+}\) and Fe\(^{3+}\) ions, show affinity to hard bases with donor atoms as O > N > S (Pearson, 1963). Research reported that chitosan derivatives containing sulphur as an ion exchange resin were found to be able to efficiently remove palladium from dilute acidic solutions (Guibal et al., 1999, 2002). However, this method could only extract palladium existing in ionic states, not in complex states, colloidal states and other states. This is because the use of glutaraldehyde as a linker for the modification of chitosan through grafting sulphur compounds (thiourea, rubeanic acid) on chitosan backbone results in producing chitosan derivatives in an insoluble solid state (Guibal, 2004; Guibal et al., 1999, 2002). To remove palladium from real electroplating wastewater, chitosan, an inartificial high molecular flocculant, and its water-soluble sulphur-containing derivative were used in combination for chelating precipitation.

Since the chelating precipitation of palladium from real electroplating wastewater using chitosan and its derivative has not been reported yet, the aim of this work is to study the removal of palladium existing in different forms when chitosan was used in combination with its water-soluble derivative in real electroplating wastewater. Several parameters such as pH, the concentration of chitosan and its derivative and chelating precipitation time were investigated to find the optimum condition as well as the chelating precipitation mechanism for palladium removal from real electroplating wastewater. Moreover, the dissolution experiment for chelating precipitation products was investigated.

**Experimental**

**Reagents and apparatus**

Electroplating wastewater was obtained from an electroplating factory in Shenzhen, China. Chitosan (deacetylation degree 80%), chloroacetic acid (CICH\(_2\)COOH, 98%), carbon disulphide (CS\(_2\), 99%), acetic acid (CH\(_3\)COOH, 99%), ethanol absolute (CH\(_3\)CH\(_2\)OH, 99.9%), acetone (CH\(_3\)COCH\(_3\), 99%) and other reagents were purchased from Weifang Dongxing Chitosan Factory, China, Shandong Xiya Chemical Co., LTD, China, Aladdin Industrial Corporation and Tianjin Chemical Reagent Factory, China. Additionally, the water-soluble derivative of chitosan was synthesized by chitosan, CS\(_2\), chloroacetic acid, ethanol absolute, acetic acid and acetone, as described by Xie et al. (2018). The dissolution reagents such as nitric acid (98%), sulphuric acid (98%), hydrochloric acid (36–38%) and sodium hydroxide (99%) were obtained from Tianjin Chemical Reagent Factory, China. The apparatuses used in this study include a six-paddle gang magnetic stirrer (HJ-6A, Jintan Medical Instrument Factory, China) for the chelating precipitation experiments and a pH meter (PHS-3CPH) for pH measurement of the wastewater.
Chelating precipitation process

Acetic acid (1%) was used to dissolve chitosan to obtain 1% chitosan solution, while its derivative was dissolved in pure water to obtain 1% derivative solution.

The experiments were performed at a constant temperature by jar tests on a magnetic stirrer with a six-paddle gang. One thousand millilitres of electroplating wastewater were added to the 2000 mL jar. Moderate derivative dosages were added to the jars under rapid stirring. When the derivative was added, the electroplating wastewater was first stirred rapidly at 120 r/min for 2 min, and then the sample was stirred slowly at 40 r/min for 5 min. Chitosan was added under rapid stirring at 120 r/min for 2 min, allowed to settle for 5 min and finally filtered. The concentration of the residual palladium in the filtrate was analysed by flame atomic absorption spectrometry (Varian model 220FS fitted with a hollow cathode lamp and an air-acetylene flame, USA). The chelating precipitation products were characterized using a Bruker Model Vector-22 FT-IR spectrometer (FTIR) and X-ray photoelectron spectroscopy (K-Alpha+, USA).

For the dissolution experiment, after chelating precipitating from the wastewater, the chelating precipitation products were filtered and dissolved in different reagents.

Methodology of characterization

The concentrations of Pd (II) and heavy metals ions were analyzed by FAAS (Varian model 220FS fitted with a hollow cathode lamp and air-acetylene flame, USA) in accordance with the standard method. Each sample was read three times to get the average value.

The pre-treatment of electroplating wastewater for analysis of total palladium was as follows: 100 mL of electroplating wastewater was added to the 250 mL jar and heated to reduce volume by two-thirds. Then, 20 mL of aqua regia (1:1) was added with continued heating for 5 min. After cooling, the wastewater was dissolved with deionized water to 100 mL for analysis of total palladium concentration.

The pre-treatment of electroplating wastewater for analysis of palladium in ionic form was as follows: Enough activated carbon was added to electroplating wastewater to adsorb palladium in ionic form for about 1 h. After adsorption, the activated carbon was filtered and washed with 2% HCl for six times, and then was ashed at 650–700°C for 0.5–1 h in a muffle furnace. The ash was dissolved using aqua regia for analysis of palladium in ionic form.

Data analysis

The removal rate of palladium was calculated using equation (1)

\[
Pd\% = \left(1 - \frac{C}{C_0}\right) \times 100\%
\]

where \(C_0\) and \(C\) are concentrations of palladium in the electroplating wastewater before and after the experiment, respectively.
The concentration of palladium in colloidal form $P_{d_{\text{colloidal}}}$ was calculated using equation (2)

$$P_{d_{\text{colloidal}}} = P_{d_{\text{total}}} - P_{d_{\text{ionic}}}$$  \hspace{1cm} (2)

where $P_{d_{\text{total}}}$ and $P_{d_{\text{ionic}}}$ are concentrations of palladium in total states and in ionic state, respectively.

**Results and discussion**

**Electroplating wastewater characterization**

In general, electroplating wastewater-containing palladium was obtained from the activation and passivation processes of various electronic industries. The wastewater appeared as a canary yellow solution at pH 0.5. The concentration of palladium was 12.84 mg/L, with 9.75 mg/L of palladium existing in ionic states and 3.09 mg/L of palladium existing in colloidal states, which accounted for 24.07% of the total. Consequently, the traditional adsorption method could not effectively remove palladium existing in different states, leaving 3–4 mg/L palladium unable to be treated. In addition, the concentrations of several heavy metal ions were discovered in the electroplating wastewater such as copper (63.15 mg/L), nickel (2.13 mg/L) and tin (0.8 mg/L).

**Effect of pH on palladium removal**

Most of the electroplating wastewater is acidic and most chelating precipitation reagents seem to have no effect under extreme acid and alkali conditions. To determine whether the chelating precipitation reagents could act under extreme acid condition, sodium hydroxide was employed to adjust the pH values, and the effect of pH values on the palladium removal rate was investigated in Figure 1.

The results indicated that the palladium removal rate was 0 at pH 0.5, suggesting that the chelating precipitation reagents did not act under such strong acidic conditions and no chelating precipitation product was found. This probably occurred because decreasing pH enhances the depolymerized of chitosan, resulting in the increase of its water solubility (Cabrera and Cutsem, 2005). The removal rate of Pd was remarkably increased from 43.05% to more than 95%, with the increase of the pH from 1.5 to 5.5, suggesting that pH values higher than 1.5 showed an insignificant effect towards palladium removal. Therefore, the removal performance of chitosan and its derivative was in a wider range of pH values compared with other methods (Awual, 2016; Awual et al., 2015; Lin et al., 2015; Monier and Abdel-Latif, 2016; Noah et al., 2016; Vojoudi et al., 2017).

**Effect of chitosan and its derivative dosages on the removal rate of palladium**

Effect of chitosan and its derivative dosages on the palladium removal rate were examined at pH 2.5, as shown in Figure 2.

Figure 2(a) shows results from experiments conducted with a fixed derivative dosage of 0.16 mg/L. The results indicated that the removal capacity was first increased linearly with
the increase of chitosan dosages, and then the rate was held over 95% at the dosages of more than 0.2 g/L, suggesting that an equilibrium for the removal of palladium was reached with the chitosan dosage of 0.2 g/L and excess chitosan was useless on the removal of palladium. Figure 2(b) was performed with a fixed chitosan dosage of 0.2 g/L. As can be observed, the removal rate was increased with increasing the sulphur-containing derivative dosages, and then reached the equilibrium value of near 95% at the dosage of 0.16 mg/L. Subsequently, no obvious change was found with increasing dosages of sulphur-containing derivative, which also suggested that the removal rate of palladium was not affected by excess sulphur-containing derivative. Figure 2 also indicated that no recovery of palladium was found with the only use of the derivative without chitosan, and about 40% recovery of...
palladium was obtained with the only use of chitosan, suggesting that it was difficult to precipitate palladium with the only use of the derivative because of its low molecular weight, and low recovery rate was obtained with the only use of chitosan. Thus, it can be concluded that the combined utilization of chitosan and its water-soluble derivative could attained high recovery of palladium.

Taking into account the removal capacity for heavy metals such as Cu, Ni and Sn coexisted in the electroplating wastewater as shown in Table 1.

According to Table 1, it showed that at optimum conditions the removal rate of Cu, Ni and Sn were 13.20%, 7.52% and 12.30%, respectively, indicating that chitosan and its derivative showed a weak removal capacity on heavy metals. According to hard and soft acids and bases by Pearson (1963), derivatives of chitosan with S groups are highly efficient for the selective sorption of palladium ions. In addition, the removal rate of Ni changed little with the value less than 10% with increasing concentrations of chitosan and its derivative from their optimum value. Furthermore, the removal rate of Cu, especially Sn increased with increasing the dosages of sulphur-containing derivative, with a maximum removal rate of 26.35% and 77.93% for Cu and Sn, respectively. However, increasing chitosan dosages exhibited an insignificant effect towards their removal rate, which suggested that the sulphur-containing derivative took the main role for chelating precipitating heavy metals. Hence, it could be concluded that chitosan and its derivative had higher selectivity towards palladium than heavy metals.

Effect of chelating precipitation time on the removal of palladium

Effect of chelating precipitation time on the removal of palladium was conducted at pH 2.5 with 0.2 g/L chitosan and 0.16 mg/L derivative (Figure 3).

It was found that the removal rate increased with the time increase of 15 min, and then was kept over 95% with the increasing time, indicating that it took approximately 15 min to reach an equilibrium. This was a little longer than the time required for the synthesized solution (Guibal, 2004) but much faster than that for traditional adsorption methods, which required approximately 3–4 h to attain equilibrium adsorption capacity (Fujiiwara et al., 2007). That is because the interactions between palladium and functional groups in aqueous solutions are much faster than those of the functional groups in solid state, namely, liquid–liquid reaction is much faster than solid–liquid reaction (Atiemo-Obeng et al., 2004).

Chelating precipitation mechanism

Figure 4 illustrates the experimental phenomena of the adding reagents processes.

Table 1. Removal rate of palladium and other heavy metals at different dosages of chitosan and its derivative.

| Number | Derivative (mg/L) | Chitosan (g/L) | Pd (%) | Cu (%) | Ni (%) | Sn (%) |
|--------|------------------|----------------|--------|--------|--------|--------|
| 1      | 0.16             | 0.2            | 97.51  | 13.20  | 7.52   | 12.30  |
| 2      | 0.16             | 0.4            | 95.44  | 13.02  | 7.78   | 12.30  |
| 3      | 0.20             | 0.4            | 96.07  | 26.35  | 8.51   | 38.96  |
| 4      | 0.24             | 0.4            | 96.66  | 18.21  | 8.14   | 38.96  |
| 5      | 0.32             | 0.2            | 97.58  | 11.61  | 9.25   | 77.92  |
According to Figure 4, the visually observed colour of the raw wastewater firstly changed from light yellow to brown with the addition of a chitosan derivative, but no precipitate was observed. After adding the chitosan, a large amount of precipitate with brown colour was observed and the colour of the wastewater changed from dark brown to light brown. After filtering, the filtrate was colourless. It is known that the colour of palladium chloride is brown, thus it can be concluded that the chitosan derivative had reacted with palladium with the change of colour, and the formation the precipitates with the addition of chitosan showed its flocculating property. Finally, the colour of the filtrate changed from light yellow to colourless, suggesting that no remaining chitosan derivative was left. On the other hand, the additive amount of chitosan was more than that of the chitosan derivative, insure that no chitosan derivative was left, only left an environment-friendly chitosan.

Figure 3. Effect of chelating precipitation time on removal rate of palladium at pH 2.5 (0.2 g/L chitosan, 0.16 mg/L derivative).

Figure 4. Experimental phenomena of the adding reagents processes.
The chelating precipitation mechanism of chitosan and its derivative with palladium was studied by FT-IR analyses and XPS analyses of the products, as shown in Figures 5 and 6, respectively.

According to Figure 5, the peak intensity at 1016 cm\(^{-1}\) for sulphur-containing derivative decreased after chelating precipitation with palladium, which indicated that a reaction occurred at this peak. Reportedly, the peak at 1016 cm\(^{-1}\) is attributed to the C=S stretching vibration (Gosavi et al., 1967). Hence, it could be inferred that it was the addition reaction between palladium and the chitosan derivative. In addition, the absorption band of the N–C bond in the N–C=S group at 1450 cm\(^{-1}\) shifted to a lower wavenumber, further indicating a chelation reaction of the chitosan derivative with palladium. On the other hand, a new peak intensity at 1382 cm\(^{-1}\) occurred at the product, suggesting another reaction. It is reported that the peak at 1382 cm\(^{-1}\) is due to the peptide bond (–CO–NH–) stretching vibration. Therefore, it could be concluded that the insoluble product was attributed to the reaction between carboxyl groups in the sulphur-containing derivative and amino groups in chitosan.

To further confirm if the chelating precipitation of palladium could be attributed to sulphur moieties, XPS analyses were conducted (Figure 6).

Figure 6 shows the spectra of Pd, Cu, Ni, Sn, S, O, N and C in the products. The N1s peak at a binding energy of 399.99–401.62 eV corresponded to the nitrogen in the valence bond C–N and N–C=S. Three peaks of the C1s spectra at binding energies of 284.18 eV, 285.93 eV and 288.03 eV corresponded to the carbon in the valence bond C–H and C=O. The peak of the S2p spectra at approximately 162.10–163.60 eV, corresponded to the sulphur in the valence bond sulphur, thioether, mercaptan and R–S–S–R (Moulder et al., 1992). No peak was found for Ni2p, Sn3d and Cu2p, suggesting that chitosan and its derivative had little selectivity on these heavy metals. Although it was found that two peaks for Pd3d were at approximately 334–344 eV, which indicated the presence of Pd\(^{2+}\). Thus, it could be inferred that Pd first coordinated with S atoms and formed a Pd–S bond, and then the –NH\(_2\) group of chitosan reacted with the –COOH group of its derivative to form –CO–NH– group.

![Figure 5. FT-IR spectra of chitosan and its derivative and their chelating precipitation products.](image-url)
Figure 6. Spectra of precipitates.
Figure 7. The reaction mechanism of chitosan and its derivative with palladium.
According to the results of XPS analyses and FT-IR analyses of products, the reaction mechanism of chitosan and its derivative with palladium may be inferred as shown in Figure 7.

It can be inferred that during the chelating precipitation process of palladium, a complex reaction between the palladium ion and the sulphur-containing derivative occurred and formed a Pd–S bond. After the addition of chitosan, the amino group (–NH₂) in the chitosan and the carboxyl group (–COOH) in the sulphur-containing derivative participated in the condensation reaction and formed a peptide bond (–CO–NH–) and meanwhile increased the molecular weight of the chelated products, which made the chelating precipitation products insoluble in water (Pike et al., 1991). Additionally, chitosan is a natural polymer compound and a cationic flocculant that can adsorb negatively charged tiny particles and hence, could also precipitate palladium in other states simultaneously.

Dissolution experiment

The subsequent processing for chelating precipitation products of palladium depended on whether they could dissolve in solutions or not. It has been reported that chitosan is degradable in a strong alkali solution and a strong acidic solution (Cabrera and Cutsem, 2005). Hence, different solution systems with the concentration of 10% were applied to dissolve the chelating precipitation products, as shown in Table 2.

The results indicated that the chelating precipitation products could only dissolve in aqua regia. It is because that strong acid/alkali only can destroy the forces of hydrogen bonding, ionic bonding and hydrophobic effect, but cannot break the peptide bond (Korhonen et al., 1998). On the other hand, the peptide bond can only be broken with the presence of protease. However, aqua regia can dissolve palladium in any state (Popp and Ploegh, 2011).

Conclusions

In conclusion, the combined utilization of chitosan and its soluble sulphur-containing derivative could remove palladium in different states from real electroplating wastewater up to 95% at the optimum condition of 0.16 mg/L and 0.2 g/L. Then, the chelating precipitation products were characterized by FTIR and XPS to analyse the reaction mechanism of chitosan and its derivative with palladium. It was found that the sulphur-containing derivative first reacted with palladium to form chelated palladium and then reacted with chitosan to form insoluble chelating precipitation products. Moreover, aqua regia was employed as a dissolution agent for the dissolution of palladium from the chelating precipitation products for subsequent processing.
Declaration of Conflicting Interests

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