Review Article

Advance in Environmental Waste Management & Recycling

Recovery of Precious Metals Using Microalgae Waste

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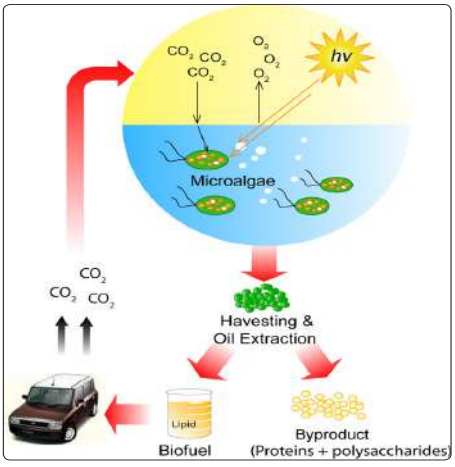
Abstract

From waste residue of microalgae after extracting biofuel, some novel adsorption gels were prepared for the recovery of precious metals such as gold, palladium and platinum. The adsorption gel for gold was prepared in a simple manner by treating in boiling concentrated sulfuric acid. Although the feed material, the microalgae waste itself, was found to selectively adsorb gold(III), palladium(II) and platinum(IV) from hydrochloric acid solution over base metals such as copper(II), nickel(II) and so on, the adsorption of gold(III) was dramatically enhanced by the treatment using boiling concentrated sulfuric acid; it was recovered as metallic gold particles. In order to improve the adsorption behavior for palladium (II) and platinum (IV), some chemically modified microalgae gels were also prepared by immobilizing some functional groups such as dithiooxamide, polyethyleneimine and trimethylamine. On the basis of the basic investigation about the adsorption behaviors of these biosorbents, recovery of precious metals was investigated also from actual leach liquor of waste printed circuit boards of electronic devices using these adsorbents in order to verify their effectiveness for practical application.

Introduction

In summer of 2018, nearly all people on northern hemisphere including Japan, North America, European countries such as Greece have suffered from abnormally hot weather which have not been experienced in the past. Needless to mention, the main reason of such abnormal weather is global warming by the increase in carbon dioxide gas caused by large consumption of fossil fuels. For the purpose of decreasing the emission of warming gasses, big efforts have been devoted all over the world to effectively use various natural energies such as solar energy, wind energy and biomass energy. Among biomass energies, big attention is attracted to lipid produced by special kinds of microalgae. Scheme 1schematically shows the concept of use of the lipid produced by such microalgae.



Scheme 1: Concept of the use of biofuel produced by microalgae

Carbon dioxide gas emitted from various industries and our daily life into air are absorbed into bodies of microalgae and converted into lipid, from which biofuels are produced. At Saga city in Japan, more advanced project is proceeded at present, where,by using carbon dioxide gas generated from municipal incineration plant, microalgae are multiplied to produce lipids for biofuels [1].

However, the problem is its high production cost, which impedes the actual commercialization of such biofuels. One of the strategies to overcome such problems is to effectively use the residues after extracting biofuels. For this purpose, although some candidates for their effective uses may be the use as feed materials for cattle feeds and fertilizers, their values are too low to improve the economical balance. More effective uses of microalgae residue yielding more significant benefit are strongly required.

In recent years, recycling and recovery of various metals from spent electric and electronic appliances (e-wastes) has become an emerging research subject. This is due to the acute limitation of metal resources along with the fast growing rate of the development of advanced materials and devices such as cell phones, televisions, and computers [2, 3]. The recovery of valuable metals from such spent appliances is greatly beneficial from both of environmental and economic viewpoints. This is due to the facts that recycling of these metals reduces the cost of metallurgical treatments associated with their mining activity, and sharply decreases the destructive impacts on the environment. Of various recovery technologies, hydrometallurgical treatments are most suitable for feed materials containing various metals in complicated forms such as e-wastes. In the hydrometallurgical processes of precious metal recovery,

solvent extraction and precipitation processes have been employed in case their concentrations are high enough [4]. On the other hand, in the case of solutions containing trace concentration of targeted metals, ion exchange and adsorption techniques are more suitable for their recovery [5, 6]. The commercially available ion exchange resins employed in the separation process of metals are polymeric petrochemical products. From the viewpoint of establishing a green sustainable technology, materials produced from petroleum should be replaced by environmentally benign alternatives produced from naturally available biomaterials or biomasses.

In recent years, biomass wastes have found their uses as potential alternatives for the separation and recovery of toxic and precious metal ions from industrial solutions (for example, see [7]). As unique adsorbents, high selectivity to a targeted metal ion is strongly required, and, consequently, the selection of a suitable ligand is essential for designing specific adsorbents exhibiting high selectivity. To meet such requirements, one approach is to take the advantage of the creation and/or immobilization of active functional groups onto the biomass matrices, so as to enhance the affinity as well as the selectivity of the original materials.

Based on such background, we investigated to prepare novel adsorbents for precious metals from the microalgae residue after extracting biofuel. Of various microalgae, DENSO CORPORATION attracted attention in *Coccomyxa* sp. Strain N1 as those for biofuel production. This microalga comprises 36 % lipid, 33 % proteins and 19 % carbohydrates. By using the residue of this microalgae after extracting biofuel, two types of adsorption gels were prepared; one was prepared in a simple manner by treating in boiling concentrated sulfuric acid for cross linking for the selective recovery of gold, while others were the microalgal residue chemically modified by immobilizing some functional groups for the recovery of palladium and platinum [8-11].

Preparation of Adsorption Gels

Sample of dried microalgae residue of *Coccomyxa* sp. Strain N1, obtained after extraction of lipid was used as the raw material for the preparation of all kinds of adsorbents. Roughly mentioning, this sample is mixture of proteins and carbohydrates, or polysaccharides such as cellulose and hemicellulose. Figure 1 shows the photographs of this sample and its SEM (scanning electron microscope) image.

Figure1: Photograph of residual waste of microalgae, *Coccomyxa* sp. (left) and its SEM image at magnification of ×1000 (right).

From the elemental analysis, it was found that this sample contains 49.63 wt.% C, 6.92 wt.% H, 7.56 wt.% N, 1.89 wt.% S and 34 wt.% O.

Preparation of Adsorption Gel Cross linked Using Concentrated Sulfuric Acid

To avoid dissolution of the adsorption gel in aqueous solutions, it was cross linked using concentrated sulfuric acid in a very simple manner as follows [8]. Some amount of small particles of raw material, dried microalgae residue, was mixed and stirred together with concentrated sulfuric acid at boiling temperature in a round-bottom flask. By this treatment, polysaccharides and proteins present in the raw material were allowed to undergo a cross linking-condensation reaction. Then, the mixture was cooled to room temperature, and the product was slowly transferred to a 10% (w/v) $NaHCO_3$ solution for neutralization. The black solid product was collected by filtration followed by washing with distilled water and hot water to remove water-soluble substances until the pH of filtrate reached neutral pH. The product was dried overnight in a convection oven at 70°C and was ground before sieving into a uniform particle size of 75-150 μm. The yield was around 50 %.

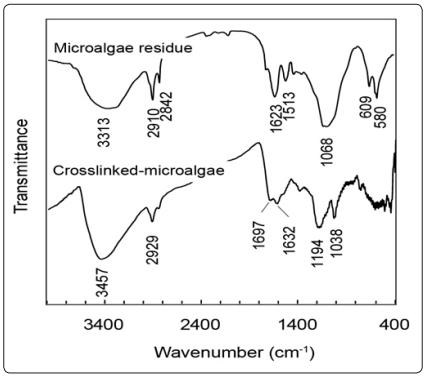


Figure 2: FT-IR spectra of the original microalgae residue and cross linked microalgae [8]

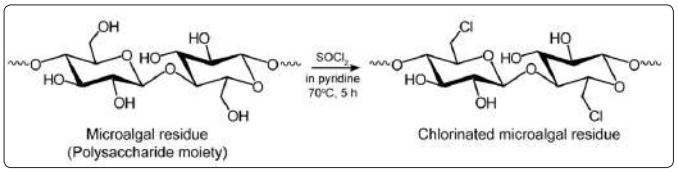
Figure 2 shows the Fourier-transformation infrared (FT-IR) spectra of the original microalgae residue and cross linked product. The spectrum of the original microalgae shows the presence of O–H stretching at 3313 cm^{-1} and C–H stretching at 2910 and 2842 cm^{-1}. The sharp absorption band at 1623 cm^{-1} indicates the presence of C=O groups. The spectrum of cross linked microalgae shows shifts of the O–H and C–H stretching bands to higher frequencies. The broad band at 1697 and 1632 cm^{-1} represents carboxylate or carbonyl groups. A new peak at 1194 cm^{-1} represents the C–O–C stretching vibration; C–O–C was formed by the condensation reactions between hydroxyl groups. The spectral changes indicate the rearrangement of surface functional groups of the microalgae including the random formation of ether linkages between polymer chains of polysaccharides contained in microalgae residue during the cross linking reaction with concentrated sulfuric acid.

From the elemental analysis, it was found that this cross linked product contained 54.74 wt.% C, 3.02 wt.% H, 1.74 wt.% N, 2.82 wt.% S. This final product is abbreviated as CMA (cross linked microalgae), hereafter.

Preparation of Adsorption Gels Chemically Modified with Various Functional Groups

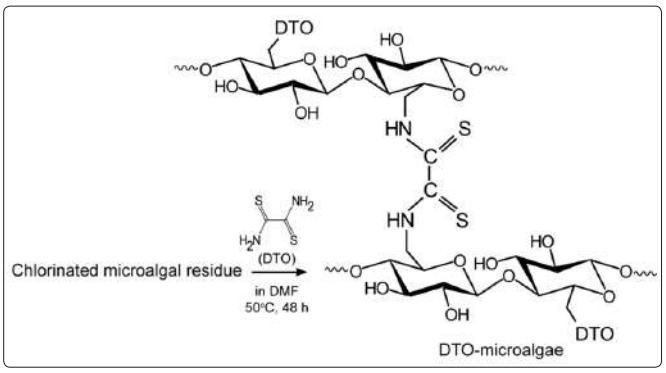
In the present work, three kinds of modified gels were prepared by immobilizing three types of functional groups onto polymer matrices of microalgae residue: dithiooxamide (DTO), polyethyleneimine (PEI), and two kinds of quaternary ammonium (QA) compounds (triethyl- and trimethyl-ammonium), which are abbreviated as DTO,

PEI and QA gels (or TMA and TEA gels), respectively, hereafter [9-11]. Although, as mentioned earlier, roughly mentioning, microalgae residue is mixture of proteins and carbohydrates, or polysaccharides such as cellulose and hemicellulose, these functional groups are considered to be immobilized onto polymer matrices of polysaccharides. Prior to the immobilization of the functional groups, the feed materials were interacted with thionylchloride ($SOCl_2$) to prepare chlorinated microalgae, the intermediate product, according to the following reaction.

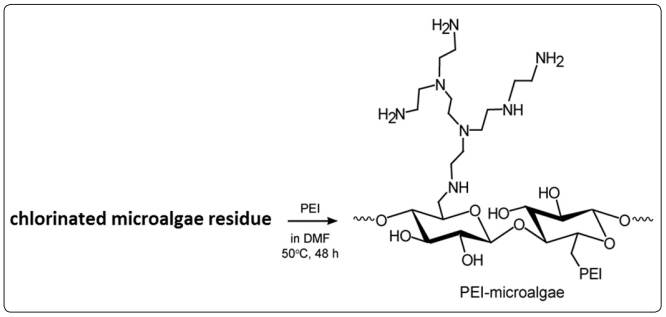


Scheme 2: Chlorination reaction of microalgae residue to prepare the intermediate product

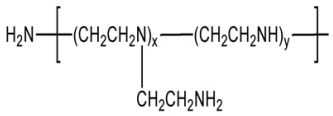
Various functional groups mentioned above were immobilized via this chlorinated intermediate product as shown below.



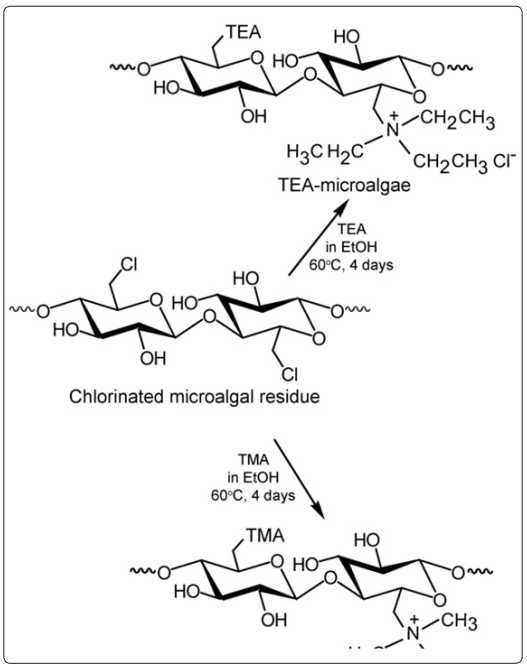
Scheme 3: Preparation of DTO gel [9].



where PEI (polyethyleneimine) is shown below.



Scheme 4: Preparation of PEIgel [10].



Scheme 5: Preparation of QAgels [11].

For example, in the preparation of QA gels, sample of microalgae residue was first interacted with $SOCl_2$, for chlorination and, subsequently, modified with trimethylamine or triethylamine. In a typical preparation process, 5 g of dry microalgae residue was taken together with 200 ml pyridine in a 500-mL three-necked flask, which was kept in an ice bath. Thirty milliliters of $SOCl_2$ was added drop wise to the mixture under a N_2 atmosphere and it was further stirred at 70ºC for 5 h to obtain the intermediate product for further treatment. After filtration, the intermediate product was washed with distilled water and dried overnight in a convection oven at 70ºC. To immobilize the functional groups of trimethylamine, 5 g of this intermediate product was dispersed in 200 ml of ethanol, to which 100 ml of 30% trimethylamine solution was added while stirring. The mixture was further stirred at 65ºC for 4 days to obtain the QA gel. After the mixture was allowed to cool down at room temperature, the final product was collected by filtration and washed with distilled water until neutral pH was obtained. Finally, the product was dried in a convection oven at 70ºC for 24 h. It was further ground and sieved to uniform particle size.

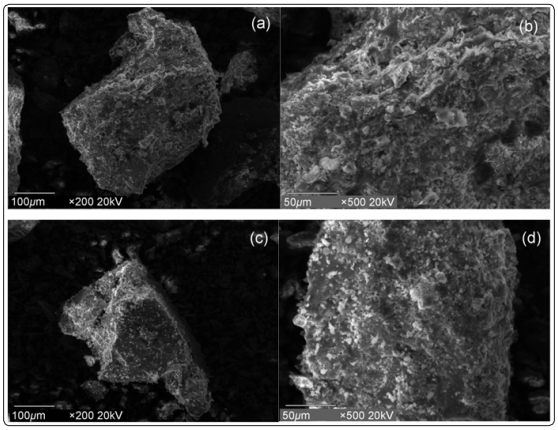


Figure 3: SEM images of (a), (b) the TMA-microalgae and (c), (d) the TEA-microalgae.

Figure 3 shows the SEM images of QA gels as examples of these modified microalgae gels. As seen in these figures, all modified gels prepared in the present works are not porous materials similar to CMA gel.

Adsorption Tests

The adsorption tests were carried out batch-wise from aqueous solutions of individual metal ion dissolved in varying concentrations of hydrochloric acid solution from 0.1 to 5.0 M (M = mol/L), taking into consideration that commercial recovery of precious metals are operated from acidic chloride solutions. Adsorption isotherms were measured to evaluate the maximum adsorption capacities for precious metal ions. The adsorbent (10 mg) was mixed with 10 ml of solutions containing varying concentrations of Au(III), Pd(II), and Pt(IV) in 0.1 M HCl and shaken in a thermo stated shaking incubator at 30ºC to attain adsorption equilibrium. The metal concentration in aqueous solution was measured before and after adsorption by using a Shimadzu model ICPS-8100 inductively coupled plasma atomic-emission (ICP/AES) spectrometer.

From the concentrations of metal ions in aqueous solutions before and after adsorption, % adsorption and amount of adsorption was calculated according to the following equations.

% Adsorption [-] = (concentration before adsorption – concentration after adsorption) / concentration before adsorption × 100
Amount of adsorption (q [mol/kg] or [mmol/g])
= {(concentration before adsorption – concentration after adsorption)×volume of test solution}/dry weight of adsorbent used in adsorption test

Adsorptive Recovery of Gold using CMA Gel

Adsorption behavior of CMA gel for some metal ions from hydrochloric acid solution

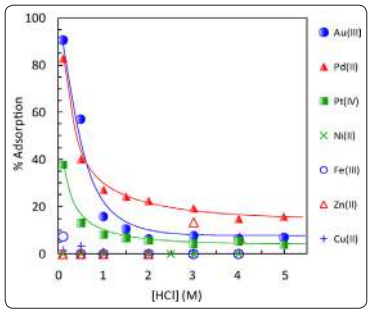


Figure 4: % adsorption of some metal ions on original microalgae residue, the feed material, from varying concentration of hydrochloric acid [8].

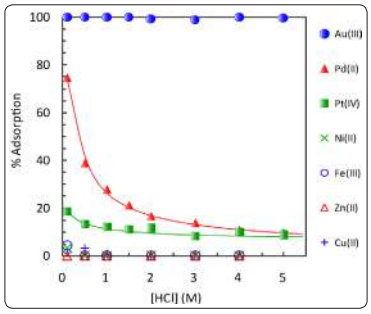


Figure 5: % adsorption of some metal ions on CMA gel from varying concentration of hydrochloric acid [8].

Figures 4 and 5 show % adsorption of some metal ions on original microalgae residue, the feed material, and CMA gel, respectively, from varying concentration of hydrochloric acid. From the comparison of these figures, it is apparent that although the adsorption of gold (III) on original microalgae residue is much decreased with increasing hydrochloric acid concentration and is lower than that of palladium(II) in the high concentration range of hydrochloric acid, it is much improved by cross-linking using boiling concentrated sulfuric acid and quantitatively adsorbed over the whole concentration range tested. Although adsorption of base metals such as nickel(II), iron(III), copper(II) and zinc(II) is negligibly low on microalgae residue regardless of cross-linking, considerable amount of palladium(II) and platinum(IV) are adsorbed on both original microalgae residue and CMA gel in the low concentration range of hydrochloric acid. Although the treatment using boiling concentrated sulfuric acid for cross-linking greatly affects the adsorption of gold(III), its effect is negligible for other metal ions. The selective adsorption of palladium(II) and platinum(IV) belonging to typical soft Lewis acids over base metals may be ascribed to the coordination of these metal ions with nitrogen and sulfur atoms, typical soft Lewis bases, of proteins contained in microalgae residue. Because these precious metal ions give rise to stable chloro-complexes with chloride ion such as $PdCl_4^{2-}$ and $PtCl_6^{2-}$, the increase in chloride ion in aqueous solution impedes the coordination of these metal ions with nitrogen and sulfur atoms contained in microalgae residue and lower the adsorption as observed in these figures. The adsorption of gold(III) on microalgae residue itself as well as on CMA gel may be also ascribed to the similar coordination with sulfur and nitrogen atoms because gold(III) is also belong to the soft Lewis acids. However, it can be reasonably inferred that the big structural change in polysaccharide polymers contained in microalgae residue caused by the treatment using boiling concentrated sulfuric acid greatly changed the adsorption behavior for gold(III).

Formation of elemental gold on CMA gel

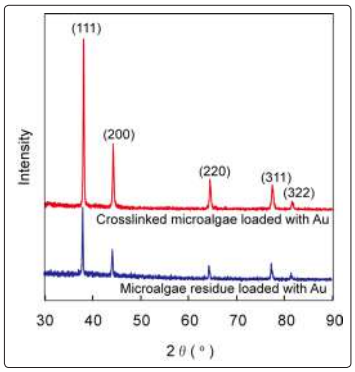


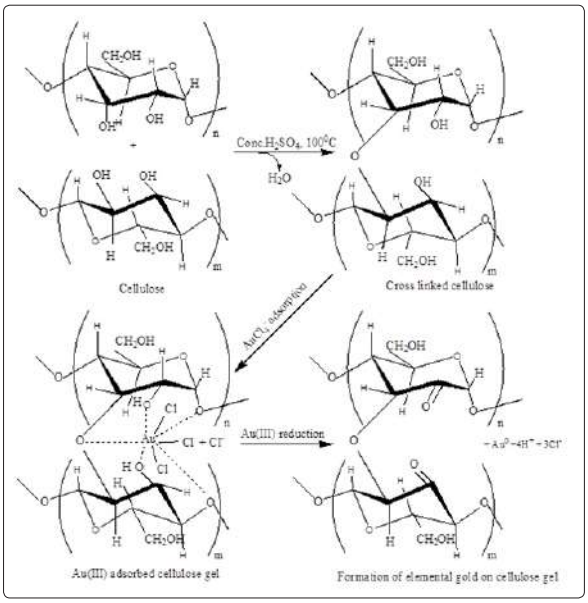
Figure 6: XRD patterns of CMA gel and microalgae residue after the adsorption of gold(III) [8].

Figure 6 shows XRD patterns of the original microalgae residue and CMA gel after adsorption of gold(III). This figure reveals that the intense peaks corresponding to the crystalline structure of gold (0) are clearly observed for both adsorbents; i.e., sharp peaks are observed at 2θ values of 38°, 44°, 64°, 77°, and 82° corresponding to the (111), (200), (220), (311), and (222) crystal planes of the metallic face-centered cubic (fcc) structure [12]. These results surely evidence the formation of metallic or elemental gold in the adsorptions both on original microalgae residue and CMA.

Figure 7: Image of aggregates elemental gold formed in the adsorption on CMA gel observed by optical microscope.

Figure 7 shows the image of gold aggregates formed in the adsorption on CMA gel observed by optical microscope. In this photograph, brilliant golden colored lumps are the aggregates of elemental gold particles while black is particles of CMA gel.

From these results, it can be reasonably concluded that the high selectivity for gold(III) over other metal ions exhibited in Figures 4 and 5 is attributable to the high oxidation reduction potential (ORP) for gold(III) over other metal ions; e.g., ORP for some metal ions are as follows: Pd^{2+} (+0.915 V), Pt^{4+} (+0.62 V), Cu^{2+}(+0.34 V). That is, gold(III) is selectively reduced into elemental gold (gold(0)) during the contact with CMA gel, the structure of which was transformed by the aid of boiling concentrated sulfuric acid so as to enhance the reduction reaction of gold(III). On this respect, we had reported the similar phenomena of the reductive adsorption of gold(III) by various biomass adsorbents such as orange juice residue, in which we reached the conclusion that the reduction of gold(III) is enhanced by the cross linked structure of polysaccharides such as cellulose formed by condensation reaction using boiling concentrated sulfuric acid and inferred the mechanism of the reductive adsorption of gold(III) as shown below [13-16].



Scheme 6: Mechanisms of cross linking reaction of cellulose by boiling concentrated sulfuric acid and reductive adsorption of Au (III) on the cross linked cellulose [16].

Adsorption Isotherms of Gold(III) on CMA Gel

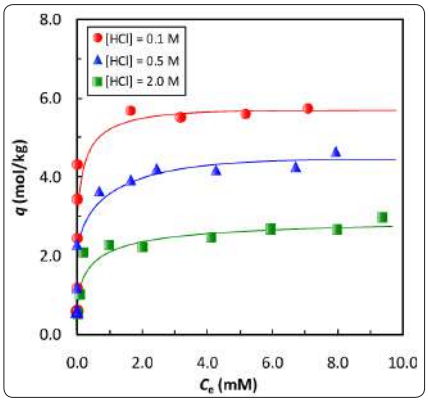


Figure 8: Adsorption isotherms of gold(III) on CMA gel at 303 K from various concentrations of hydrochloric acid.

Figure 8 shows the adsorption isotherms of gold(III) on CMA gel at 303 K from various concentrations of hydrochloric acid. It is seen from this figure that the adsorption of gold(III) is decreased with increasing concentration of hydrochloric acid suggesting that chloride ion suppresses the adsorption of gold(III); i.e., gold(III) which presents as tetrachloro-complex, $AuCl_4^-$, in chloride media undergoes adsorption reaction coordinated by some oxygen atoms of CMA gel, releasing chloride ion as follows.

$$Ⓟ + AuCl_4^- = ⓅAuCl_3 + Cl^-$$

Where Ⓟ denotes glucose unit of polysaccharides in CMA gel. Consequently, as chloride ion increases, the amount of gold (III) adsorbed on CMA gel decreased.

The maximum adsorption capacities of gold (III) (q_{max}) were evaluated from the constant values at plateau region for each concentration of hydrochloric acid. Thus evaluated maximum adsorption capacities of gold(III) on CMA gel and original microalgae residue are listed in Table 1.

Table 1: Maximum adsorption capacity of gold (III) on CMA gel and original microalgae residue

concentration of hydrochloric acid (M)	qmax (mol/kg)	
	CMA gel	original microalgae residue
0.1	5.67	0.31
0.5	4.47	0.21
2	2.87	0.07

It is evident from this table that the adsorption of gold(III) is drastically improved by the treatment using boiling sulfuric acid for cross-linking. According to this table, the maximum adsorption capacity on CMA gel is 5.67 mol/kg or 1.12 kg-Au/kg at 0.1 M HCl, suggesting that gold(III), the weight of which is greater than that of the adsorbent, is adsorbed. This is attributable to the formation of elemental gold mentioned above.

Chromatographic Separation of Gold(III) using a Column Packed with CMA Gel

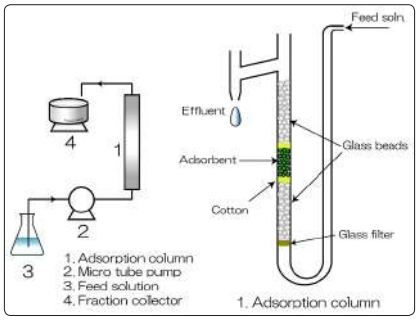


Figure 9: Diagram of the adsorption column used in the present work.

In order to verify the high selectivity to gold(III) over other metals exhibited by CMA gel, chromatographic separation of gold(III) from other metals was carried out using a column packed with 100 mg CMA gel shown in Fig. 9. Here, breakthrough tests were carried out using two kinds of test solutions; one was the synthetic solution containing 90 mg/L gold(III), 10 mg/L platinum(IV) and palladium(II), 100 mg/L copper(II) and iron(III) in 0.1 mol/L hydrochloric acid solution while another was the sample of actual waste solution kindly provided by TANAKA KIKINZOKU KOGYO K.K., Hiratsuka Factory, Hiratsuka, Japan. This solution was generated in the treatment of scraps of electronics by conventional aqua regia leaching and contained128 mg/L gold(III), 45 mg/L platinum(IV), 9 mg/L palladium(II), 7985 mg/L copper(II), 4883 mg/L nickel(II), 2120 mg/L zinc(II) and total acid concentration was about 2 M. The former and latter test solutions were fed to the column at the feed rate 5.3 and 4.5 mL/h, respectively.

Figure 10 depicts the breakthrough profiles of the metal ions in the case of the synthetic test solution, where the breakthrough profiles represent the plots of the ratio of the metal concentration at the outlet to their feed concentration vs. bed volume (B.V. = volume of the feed solution supplied until time = t / volume of the packed gel) representing the contact time in the column. This figure shows that although all metals except for gold(III) were immediately broken through just after the initiation of the feed, the breakthrough of gold(III) was initiated after 300 B.V., verifying the excellent selectivity of CMA gel to gold(III) over other metals as expected from the result of batch experiment shown in Fig. 5. From this breakthrough profile of gold(III), the adsorption capacity for gold was evaluated as 1.02 mol/kg (= 201 g/kg), which is lower than the value evaluated in the batch adsorption test, 5.67 mol/kg, shown in Table 1. This difference is attributable to the short contact time in this column operation.

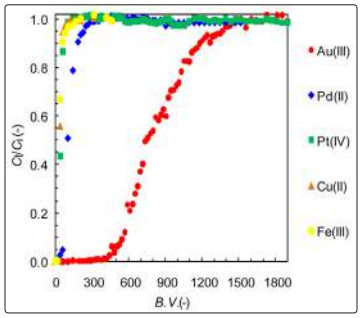


Figure 10: Breakthrough profiles of gold(III), palladium(II), platinum(IV), copper(II) and iron(III) from the column packed with CMA gel in the case of synthetic test solution [8].

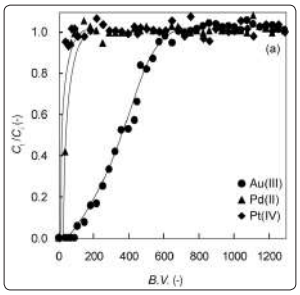


Figure 11: Breakthrough profiles of gold (III), palladium (II) and platinum (IV) from the column packed with CMA gel in the case of the actual waste solution [8].

Figure 11 depicts the breakthrough profiles of the metal ions in the case of the actual waste solution. Similar behaviors are observed also in this case (in this figure, the plots for base metals were omitted to avoid the congestion of the plots); i.e., all metals except for gold(III) were immediately broken through just after the initiation of the feed while the breakthrough of gold(III) was initiated after around 100 B.V., verifying the excellent selectivity of CMA gel to gold(III) over other metals also in the case of actual waste solution. However, the effectiveness for treating the actual waste solution appears to be less efficient compared with the synthetic solution mentioned earlier. The amount of adsorbed gold(III) was evaluated to be 192 mg/g of Au (0.96 mmol/g), which is a little less than that using the synthetic solution (1.02 mol/kg) mentioned earlier. This differences is considered to be attributable to the nature of the actual waste solution; i.e., it is inferred that small amounts of nitric acid, strong oxidizing agent, remained in the feed solution impeded the reduction of the adsorbed gold(III).

However, for both test solutions, the formation of elemental gold was observed in the packed adsorbent during the column test.

Post-Treatment of Gold Loaded CMA Gel for the Final Recovery of Gold

Although it was found that the elution or desorption of gold loaded on CMA gel is easily achieved by using the mixture of thiourea in hydrochloric acid, it would bring about another problem of the post-treatment which is difficult to be dissolved. Consequently, the simple incineration leaving incineration residue rich in gold is only one economical resolution in this case. Figure 12 shows the result of the thermo gravimetric analysis, the relationship between the weight loss of CMA gel before and after the loading of gold and the incineration temperature. From this figure, it is evident that it is completely incinerated also at around 500 °C leaving elemental gold; i.e. particles of elemental gold can be easily and directly obtained by incinerating gold-loaded CMA gel at relatively low temperature.

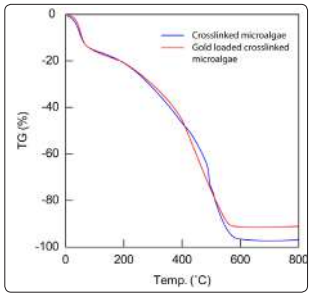


Figure 12: Thermo-gravimetric curves of CMAgel before and after the adsorption of gold (III) [8].

Adsorption behaviors of modified microalgae gel for metal ions.

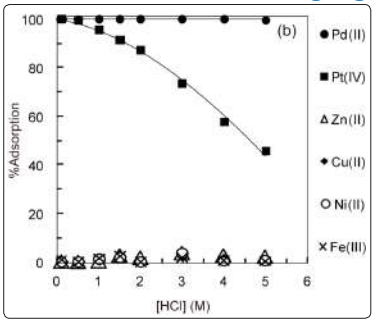


Figure 13: Effect of hydrochloric acid concentration on the adsorption of some metal ions on DTO gel [9].

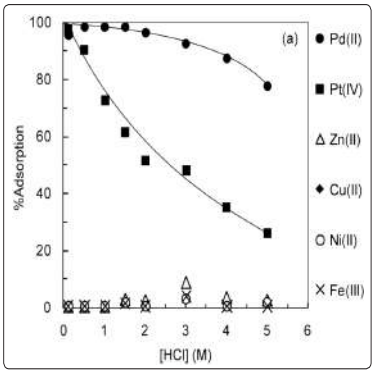


Figure 14: Effect of hydrochloric acid concentration on the adsorption of some metal ions on PEI gel [10].

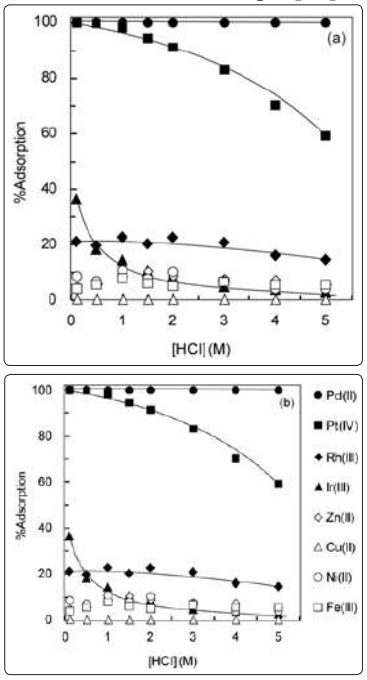


Figure 15: Effect of hydrochloric acid concentration on adsorption of various metal ions on (a) TMA and (b) TEA gels [11].

Figures 13 and 14 show the adsorption behaviors of DTO and PEI gels for precious metals such as palladium(II) and platinum(IV) and base metals such as zinc(II) and copper(II) from various concentrations of hydrochloric acid solutions. As shown in Fig. 13, palladium (II) was quantitatively adsorbed by DTO gel over the whole concentration range of hydrochloric acid while more than 80 % of palladium (II) was absorbed by PEI gel as shown in Fig. 14.

Although nearly quantitative adsorption of platinum (IV) was achieved at low concentration range, it decreased with increasing concentration of hydrochloric acid by both adsorbents. However, base metals were not adsorbed at all over the whole concentration range, exhibiting high selectivity for precious metals, especially for palladium (II),of these adsorbents.

Figures 15 (a) and (b) show the adsorption behaviors of TMA and TEA gels for precious metals such as palladium(II), platinum(IV), rhodium(III) and iridium(III) and base metals, respectively. Similar adsorption behaviors were observed with that of DTO gel also in these cases; palladium(II) was quantitatively adsorbed over the whole concentration range while adsorption of platinum(IV) decreased with increasing concentration of hydrochloric acid though it was also quantitatively adsorbed at low concentration range. Small amount of rhodium (III) was adsorbed over the whole concentration range of hydrochloric acid while also small amount of iridium (III) was adsorbed at low concentration range of hydrochloric acid. Base metals such as iron (III) and copper (II) were not practically adsorbed also on these gels.

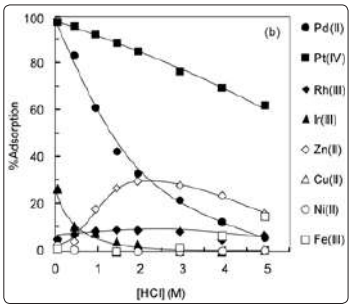


Figure 16: Effect of hydrochloric acid concentration on adsorption of various metal ions on DIAION PA312resin [11].

Figure 16 shows the adsorption behavior of DIAION PA312 resin, a commercially available strongly basic anion exchange resin also containing quaternary ammonium functional groups, for comparison. Contrary to those exhibited by TMA and TEA gels, quantitative adsorption was not observed for both palladium(II) and platinum(IV); the adsorption of these metal ions on this resin is apparently inferior to those on TMA and TEA gels. Furthermore, some amounts of base metals such as zinc (II) in particular were adsorbed on this resin; suggesting inferior selectivity compared with TMA and TEA resins.

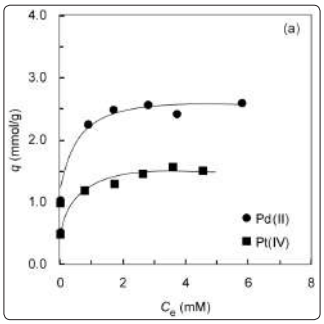


Figure 17: Adsorption isotherms of palladium(II) and platinum(IV) from 0.1 mol/L hydrochloric acid solution on TMA gel [11].

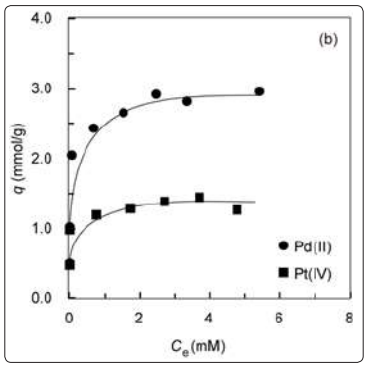


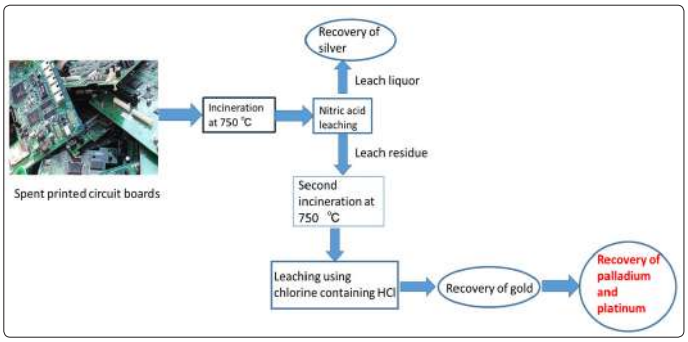
Figure 18: Adsorption isotherms of palladium(II) and platinum(IV) from 0.1 mol/L hydrochloric acid solution on TEA gel [11].

Figures 17 and 18 show adsorption isotherms of palladium(II) and platinum(IV) from 0.1 mol/L hydrochloric acid solution at 30°C on TMA and TEA gels, respectively. All of these adsorption isotherms exhibit the typical Langmuir type adsorption. The maximum adsorption capacities of TMA gel for Pd(II) and Pt(IV) were evaluated as 2.95 and 1.33 mmol/g, respectively, while those of TEA gel for Pd(II) and Pt(IV) were 2.57 and 1.54 mmol/g, respectively. Table 2 shows the maximum adsorption capacities of palladium(II) and platinum(IV) from acidic chloride media on various adsorbents reported in literatures including TMA and TEA gels for comparison. It is obvious that the gels modified on microalge residue prepared in our works exhibit higher adsorption capacities both for palladium(II) and platinum(IV) than other adsorbents.

Table 2: Maximum adsorption capacities of palladium(II) and platinum(IV) on various adsorbents

Adsorbent	maximum adsorption capacity (mmol/mg)		reference
	palladium(II)	platinum(IV)	
Cross linked microalgae gel (CMA gel)	0.25	0.15	8
Dithiooxamide modified microalgae gel (DTO gel)	3.63	1.48	9
Polyethyleneimine modified microalgae gel (PEI gel)	2.10	0.78	10
Trimethylammonium modified microalgae gel (TMA gel)	2.95	1.33	11
Triethylammonium modified microalgae gel (TEA gel)	2.57	1.54	11
Dimethylamine modified persimmon waste gel	0.42	0.28	17
Trimethylammonium modified persimmon tanningel	0.84	0.52	18
Tetraethylenepentamine modified persimmon tanningel	1.76	1.48	19
Glycidyltrimethyl ammonium chloride modified persimmon tannin gel	1.67	1.00	20
Aminoguanidine modified persimmon tannin gel	2.00	1.00	21
Bisthiourea modified persimmon tannin gel	1.72	0.70	22
Crosslinked chitosan	2.1	1.6	23
Collagen fiber immobilized bayberry tannin	0.80	0.495	24
Lysine modified crosslinked chitosan	1.03	0.66	25
Glycine modified crosslinked chitosan	1.13	0.62	26
Ethylenediamine modified chitosan nanoparticle	1.30	0.87	27
Thiourea modified chitosan microsphere	1.06	0.16	28
Dimethylamine modified waste paper	2.10	0.90	29
2-Mercaptobenzothiazole-bonded silica gel	0.17	0.03	30
Polyallylamine modified Escherichia coli	2.50	-	31
Duolite GT 73 resin	0.26	-	32
Amberlite IRC 718 resin	0.55	0.34	33

Selective Recovery of Palladium(II) and Platinum(IV) from Actual Leach Liquor of Cell Phone Scraps.



Scheme 7: An example of flow sheet for the recovery of precious metals from spent printed circuit boards

To confirm the effectiveness of the modified microalgae gels for practical cases, recovery of palladium(II) and platinum(IV) was carried out from actual leach liquor of spent printed circuit boards (PCBs) using DTO gel as a typical example of the modified gels.

Spent electric and electronic devices are dismantled into various parts, of which PCBs containing comparatively high amount of valuable metals are the targets for metal recovery. Scheme 7 shows a typical flow sheet for the recovery of precious metals from spent PCBs. They are incinerated at first to extinguish boards of epoxy resin on which various parts are placed at 750 °C. Then, the residues are leached using nitric acid solution to remove silver, which impedes the recovery of gold and other precious metals in the latter steps, together with some base metals. It was found in our previous work that PEI and DTO gels can effectively adsorb silver (I) from nitric acid solution; consequently, these gels may be promising tools also for the selective recovery of silver from such nitric acid leach liquors.

The leach residues are totally dissolved into aqua-regia or hydrochloric acid solution into which chlorine gas was blown, where the chlorine gas is converted into hypochlorite acid in the aqueous solution according to the following reaction.

$$Cl_2 + H_2O \leftrightarrows HClO + HCl$$

Nitric acid in aqua-regia and hypochlorite acid function as strong oxidation agents for metals, dissolving all metals in hydrochloric

acid solutions. The dissolved metals present in the leach liquors as stable chloro-complexes such as $AuCl_4^-$, $PdCl_4^{2-}$ and $PtCl_6^{2-}$. The metal-loaded aqua-regia is boiled to dissociate nitric acid into NOx gas and expel from the solution. However, in the case of hydrochloric acid solution into which chlorine gas was blown, hypochlorite acid formed by the above-mentioned reaction is unstable and easily converted into hydrochloric acid. So, the metal recovery from such solutions is actually the same with that from hydrochloric acid solutions.

In the conventional recovery processes, gold(III) is recovered at first by means of cementation using zinc powder, electro-winning or solvent extraction using dibutyl-carbitol (BUTEX) or methylisobutyl-ketone (MIBK). In the present work, recovery of palladium(II) and platinum(IV) was carried out from the sample acidic chloride solution after the recovery of gold(III), kindly donated by Shonan Factory of TANAKA KIKINZOKU KOGYO Co. Ltd., Hiratsuka, Japan. The metal concentrations of this solution measured by ICP-AES were as follows (mg/L): Pd(10), Pt(350), Fe(2900), Cu(250), Ni(370), and Zn(40).The concentration of total acids measured by acid-base titration was around 3.0 M.

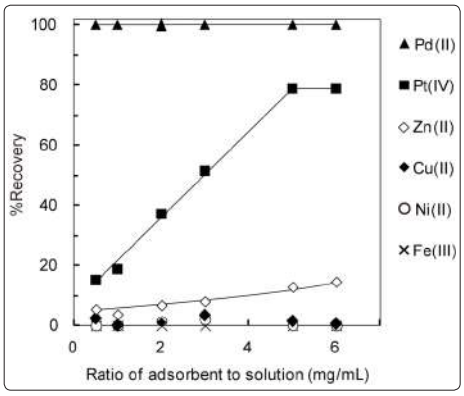


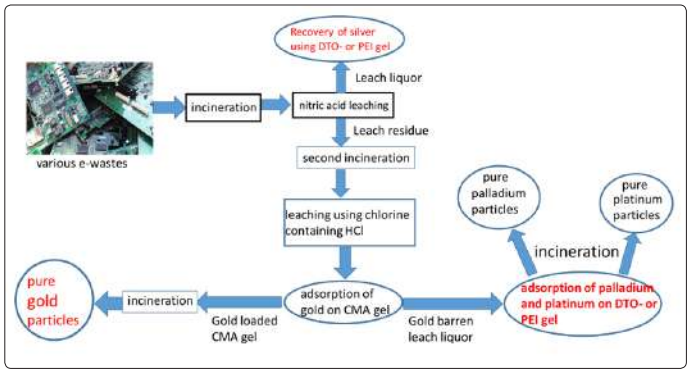
Figure 19: Effect of adsorbent dose on % adsorption of some metal ions on DTO gel from the actual solution. Conditions: volume of test solution = 10 mL, temperature = 30°C, shaking time = 48 h

Figure 19 shows the effect of adsorbent dose on percentage recovery of the metals contained in this sample solution by the adsorption using DTO gel. As seen in this figure, trace concentration (10 mg/L) of palladium(II) was quantitatively recovered using only small mass of DTO gel (even at 0.5 mg gel per unit mL of the solution). Although the recovery of platinum(IV) was only small at low solid/liquid ratio (for example, it is around 15 % at 0.5 mg gel per unit mL of the solution), it increased with increasing solid/liquid ratio and reached 80 % at 5 mg gel per unit mL of the solution. The adsorption of base metals is negligibly small. From this result, the selective recovery process for trace concentrations of palladium(II) and platinum(IV) can be proposed as follows. At first, palladium(II) can be selectively recovered at low solid/liquid ratio (for example, at 0.5 mg solid per unit mL of liquid), after which platinum(IV) can be selectively recovered at high solid/liquid ratio (for example, at 5 mg solid per unit mL of liquid).

The elution and recovery of the adsorbed Pd(II) and Pt(IV) on DTO gel was found to be achieved by using acidic thiourea ($CS(NH_2)_2$) solution as the regenerating agent. By mixing the metal loaded DTO gel with the mixture of 0.5 M $CS(NH_2)_2$ and 0.5 HCl, more than 90% of adsorbed Pd(II) and Pt(IV) was successfully recovered. However, the simple incineration of the modified gels loaded with these metals, similar to the recovery of gold using CMA gel, may be another approach for the final recovery of these metals though it depends on the production costs of the modified gels.

From these experimental results, it can be concluded that the modified microalgae gels such as DTO gel is promising for the recovery of palladium(II) and platinum(IV) from acidic chloride leach liquors of various wastes including e-wastes.

Conclusion



Scheme 8: An example of the flow sheets for the recovery of all precious metals from e-wastes using microalgae gels

In the present work, it was exhibited that gold(III) can be effectively recovered from acidic chloride media using CMA gel prepared in a simple manner from microalgae waste after extracting biofuel while palladium(II) and platinum(IV) can be recovered using the gels modified with functional groups of dithiooxamide (DTO) and polyethyleneimine (PEI). By effectively using these interesting characteristics of microalgae wastes, we can propose an effective recovery process of precious metals such as gold, silver, palladium and platinum from various wastes including e-wastes as shown in Scheme 8 [17-33].

Acknowledgement

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