

# Platinum and Palladium Ions Adsorption at the Trace Amounts by Radiation Crosslinked Carboxymethylchitin and Carboxymethylchitosan Hydrogels

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**ABSTRACT:** Adsorption of palladium and platinum ions at the trace amounts onto radiation crosslinked carboxymethylchitin (CMChit) and carboxymethylchitosan (CMChits) has been investigated. Maximum adsorption capacities for palladium were 2.679 and 1.053 mg/g dry gel, whereas for platinum they were 2.513 and 1.155 mg/dry gel for CMChit and CMChits, respectively. Retention capacity values for palladium were 0.45 and 0.06; for platinum 0.25 and 0.11 mEqiv./g for CMChit and CMChits, correspondingly. It has been shown that adsorption of Pd and Pt ions onto both hydrogels were dependent on the chloric and nitric ions concentration. Desorption experiments in HCl and HNO<sub>3</sub> solu-

tions proved that adsorption is governed by chelating mechanism rather than ion-exchange one. SEM-EDX spectroscopy showed that palladium and platinum ions were homogeneously distributed in all sections of hydrogel matrix. DSC experiments demonstrated decreasing in the decomposition temperature of polymers after inclusion of palladium and platinum ions, suggesting that metals are causing lowering of stability in polymer structural integrity. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 4015–4023, 2007

**Key words:** adsorption; hydrogels; polysaccharides; electron microscopy; crosslinking

## INTRODUCTION

Platinum and palladium are one of the most expensive noble metals though they are commonly used in industry due to excellent catalytic properties.<sup>1,2</sup> Need for cost reduction, the low availability, as well as a limitation of the sources location to selected countries triggers research toward Pt and Pd recovery from industrial wastewaters and seawaters, as alternative sources. Techniques for metal regaining such as ion-exchangers,<sup>3</sup> solvent extraction,<sup>4</sup> and chelating resins<sup>5</sup> are commonly used. The main restriction of aforementioned methods is that they are usually efficient for removing metals only from medium- to high-concentrated solutions. The research of alternative sorbents with high efficiency at low concentrations still remains the priority in the hydrometallurgy field. Recently, biosorption has been proposed as a route to recover metal ions from dilute solutions and some studies have focused on the sorption of strategic metals using fungal biomass,<sup>6</sup> or biopolymers.<sup>7,8,9</sup>

Among natural polymers, chitin and its deacetylated derivative chitosan are well established sorbents

for noble metals adsorption. Sorption properties, both chitin and chitosan are attributed to the presence of nitrogen atom involving two, pH dependant, mechanisms of adsorption: ion-exchange<sup>10</sup> and chelation process.<sup>11</sup>

The outstanding feature of chitin-based polymers is their biodegradability, thus they are harmless to the environment as a waste. Another advantage of chitin is that it is widely distributed<sup>8</sup> in nature what makes it the cheapest form of biomass, just after cellulose.

Chitosan can dissolve readily in several dilute mineral acids, with the remarkable exception of sulfuric acid. Thus, chemical stabilization is necessary for the recovery of metal ions in acidic solutions and several processes have been developed to achieve it. The most popular one is crosslinking, which involves the usage of glutaraldehyde (GA) as a crosslinking agent. Method relies on a Schiff's base reaction between the aldehyde ends of GA and the amine group of chitosan.<sup>12</sup> Alternatively, a new functional groups can be incorporate in the polymer structure by grafting process, to stabilize it and enhance adsorption abilities.<sup>7,13</sup> Finally, the crosslinking methods by ionizing irradiation are frequently used to improve polymer stability in the acidic environment. This surpasses the method with crosslinking agents (glutaraldehyde) in the terms that it does not require purification after irradiation, due to the fact that neither side products

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nor initiators are present. Pure chitin and chitosan do not undergo radiation crosslinking; nevertheless this disadvantage can be easily overcome by chemical modification of these polymers for example in the carboxymethylation process. In addition, such modification also introduces a new important property, which is dissolution of these derivatives at all range of pH.<sup>14</sup> Another advantage of carboxymethylation is that the introduction of carboxymethyl group, which is known of its metal ions binding ability, onto polymer should increase metal adsorption properties of chitin.<sup>15,16</sup>

This work discusses an adsorption investigation of palladium and platinum ions from low concentrated solutions onto radiation crosslinked carboxymethylchitin and carboxymethylchitosan.

## EXPERIMENTAL

### Materials

Carboxymethylchitin (CMChT) and carboxymethylchitosan (CMChTs) used in all experiments were purchased from Koyo Chemicals, Japan. The degree of substitution (DS), which indicates the number of original H atoms of hydroxyl groups being replaced by carboxymethyl substituent in molecule of CMChT and CMChTs, were 0.81 and 0.91, respectively. The average molecular weights estimated by gel permeation chromatography (GPC) measurements were  $2.5 \times 10^5$  for CMChT and  $6.0 \times 10^4$  for CMChTs. The degree of deacetylation value (DDA), the ratio of glucosamine to glucosacetylamine groups per monomer unit, was 24.6 and 84.0% for CMChT and CMChTs, respectively.

Metal ions standard solutions (1000 ppm) were purchased from Kanto Kagaku, Japan. Citric acid, sodium chloride, hydrochloric acid, and sodium hydroxide were supplied by Kanto Chem., Japan.

All chemicals were of analytical grade and were used without further purification. Solutions were prepared using water from Milipore Mili Q gradient A10 deionization system.

### Preparation of hydrogels by EB irradiation

Four grams of selected polymer were added to 6 g of deionized water and mixed using Keyence HM - 500 hybrid mixer, until homogeneity was obtained. The so prepared materials were kept for 2 days to ensure complete dissolution and homogenous distribution of polymer chains in all volume. After that, samples were cold-pressed (200 kPa) for about 45 min to obtain thin film (1 mm) and then sealed in polyethylene bags to ensure air-free conditions after degassing using vacuum apparatus.

Irradiation was performed by electron beam (EB) accelerator at following parameters: current = 1 mA, voltage = 2 MeV, and at the dose per pass = 1 kGy. The total absorbed dose was 75 and 100 kGy for CMChT and CMChTs respectively, according to our earlier findings.<sup>17</sup>

### Adsorption and desorption methods and measurements

Batch sorption experiments were carried out at room temperature in a 200-mL beaker, equilibrated by occasional shaking. The reaction time was 2 h, reaction volume was 100 mL, containing ~100 ppb of metal ions (except for maximum capacities evaluation experiments), with adsorbent weight 50 mg. In all experiments, pH of solution was set to value 4.0 (excluding experiments with NaCl and NaNO<sub>3</sub>) using citric buffer. Such pH was chosen due to comparable swelling properties<sup>17</sup> and adsorption values for both hydrogels. In the desorption experiment, samples after 2 h of adsorption were washed by deionized water, followed by vacuum drying at the temperature of 35°C. Then, dried samples were placed for 2 h into HCl or HNO<sub>3</sub> solutions of different concentrations for desorption.

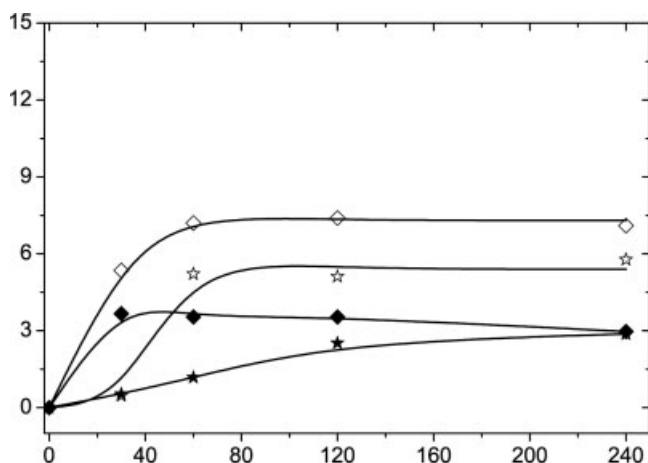
The metal concentrations in solution were measured by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) Hewlett-Packard 4500 Series. Adsorption and desorption rate of metal ions onto hydrogels was measured as a difference in metal ions concentrations in solution before and after the reaction.

### SEM-EDX measurements

Samples with loaded metal ions were frozen in liquid nitrogen and next they were broken to receive cross section of hydrogels; finally, they were freeze dried. After drying, samples were coated with graphite thin layer to enhance conductivity. Next, samples were placed in Hitachi Integrated System Type N SEM-EDX spectrometer running at accelerating voltage of 17 kV at 400 times magnification. Palladium and platinum elements distribution were estimated by an X-ray energy dispersive analysis by attached SiC detector.

### DSC measurements

Differential scanning calorimetry measurements were carried out in DSC Shimadzu C - 60 Spectrometer. All experiments were performed in triplicate. Samples of 2.5 mg were scanned in the range of 50–230°C, at the heating of rate 5°C/min.



**Figure 1** Sorption kinetic of palladium and platinum ions onto crosslinked carboxymethylchitin and carboxymethylchitosan at pH 4.0, at the initial metal ion concentration of 100 ppb. X-axis: Adsorption time (min), Y-axis: Adsorption (%); (○) Pd onto CMChit, (□) Pt onto CMChit, (●) Pd onto CMChTs, (■) Pt onto CMChTs.

## RESULTS AND DISCUSSION

### Adsorption kinetic and sorption of single-metal ions

Figure 1 shows kinetic adsorption experiments of palladium and platinum ions onto carboxymethylchitin and carboxymethylchitosan hydrogels. As we can observe, adsorption of these metal ions occurred in relatively short period of time and equilibrium state was reached after 2 h of contact. Consequently, adsorption time of 2 h was chosen for further experiments.

Several magnitudes have been employed to characterize the adsorption of ions by polymers. Here we will focus on two of them, the distribution coefficient ( $K_d$ )

$$K_d = \frac{\text{amount of metal ion in the hydrogel}}{\text{amount of metal ion in the solution}} \times \frac{\text{volume of solution (mL)}}{\text{weight of dry hydrogel (g)}}$$

and the retention capacity ( $q$ )

$$q = \frac{\text{amount of metal ion in the hydrogel (mEquiv.)}}{\text{weight of dry hydrogel (g)}}$$

**TABLE I**  
Distribution Coefficient and Retention Capacity of Platinum and Palladium Ions Onto CM-Chitin and CM-Chitosan Gels

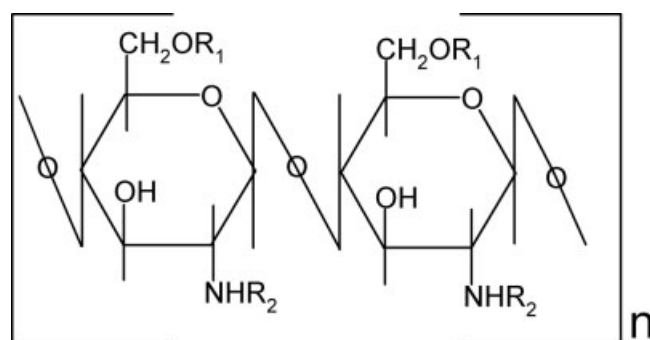
Gel	Ion	$K_d$ ( $10^2$ ) ( $\text{mL g}^{-1}$ )	$q$ (mEquiv. $\text{g}^{-1}$ )
CMChit	Pd	5.16	0.45
CMChTs	Pd	0.73	0.06
CMChit	Pt	1.09	0.25
CMChTs	Pt	0.54	0.11

Summarized data of distribution coefficients and retention capacities for palladium and platinum onto CMChit and CMChTs are shown in Table I. As we can observe, all values are little higher for CMChit than that for CMChTs. It could be explained by difference of ratio of nitrogen atom-containing functional group in both polymer molecules. The difference between chitin and chitosan lies in the content of *N*-acetyl groups (DDA). In case of chitosan, these groups are replaced by *D*-glucoseamine (GlcN) residues (in this case, in Scheme 1,  $R_2$  substituent is just H atom). There is no sharp nomenclature border between chitin and chitosan, but it is assumed that we can use the name chitosan for compound that consists  $\geq 50\%$  of *D*-glucoseamine groups.<sup>12</sup> Therefore, a conclusion can be drawn that amide group of CM-chitin adsorbs much better palladium and platinum ions than amine group of CM-chitosan.

### Adsorption isotherms

Figures 2 and 3 represent experimental adsorption equilibrium isotherms of palladium and platinum onto CMChit and CMChTs hydrogels after 2 h of contact. It was observed that adsorption capacity increases with initial metal concentration for all investigated systems. However, sorbent saturation is not reached at low concentrations (up to ca. 5 ppm), suggesting that not all adsorption capacities of polymers were being used.

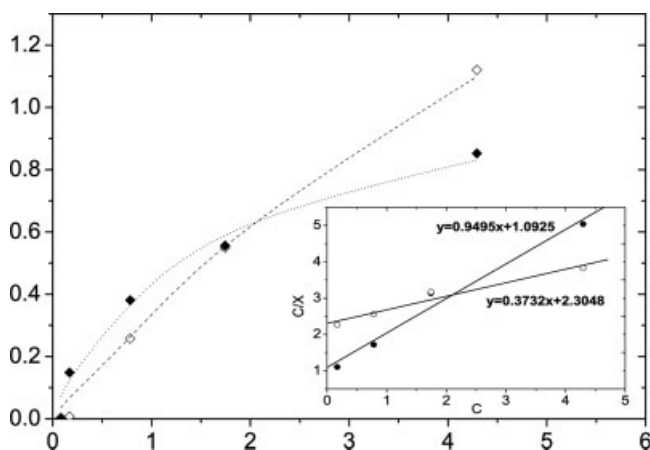
Adsorption equilibrium might be described by few models, which differ in general assumptions. Commonly used models are those proposed by Freundlich, Langmuir, Branauer, Emmet, and Sips.<sup>18</sup> Preliminary screening of the corresponding equations has revealed that the Langmuir models fit best with our experimental data, and the following standard equation was used:



$R_1 = \text{CH}_2\text{COONa}$  or H (DS)

$R_2 = \text{COCH}_3$  (chitin) or H (chitosan) (DDA)

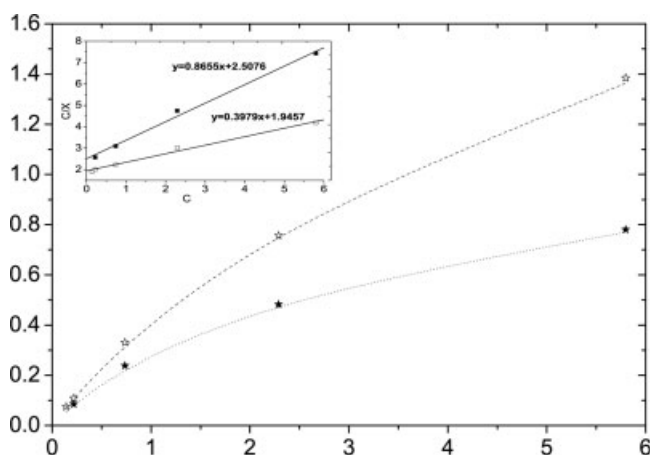
**Scheme 1** Structure of carboxymethyl chitin and carboxymethylchitosan. DS, degree of substitution; DDA, degree of deacetylation.



**Figure 2** Experimental adsorption isotherms and Langmuir theoretical adsorption values of palladium onto crosslinked carboxymethylchitin and carboxymethylchitosan at pH 4.0 in citric buffer. Inset: Linearized form of adsorption isotherms according to the Langmuir equation. X-axis: Concentration of Pd (ppm), Y-axis: Adsorption capacity (mg Pd/g dry gel); (○) Pd onto CMChit, (●) Pd onto CMChTs, (-----) and (.....) Langmuir theoretical values, (—) linear fit (inset).

$$X = \frac{X_m b C}{1 + b C} \quad (1)$$

where  $X_m$  is the maximum adsorption at monolayer coverage (mg/g),  $C$  is the equilibrium (final) concentration of metal ions,  $X$  is the amount of adsorbed metal ions per unit weight of hydrogel at equilibrium concentration (mg/g), and  $b$  is the Langmuir adsorption equilibrium constant (mL/mg) related to the energy or the net enthalpy.



**Figure 3** Experimental adsorption isotherms and Langmuir theoretical adsorption values of platinum onto crosslinked carboxymethylchitin and carboxymethylchitosan at pH 4.0 in citric buffer. Inset: Linearized form of adsorption isotherms according to the Langmuir equation. X-axis: Concentration of Pt (ppm), Y-axis: Adsorption capacity (mg Pt/g dry gel); (□) Pt onto CMChit, (■) Pt onto CMChTs, (-----) and (.....) Langmuir theoretical values, (—) linear fit (inset).

Figures 2 and 3 also present calculated the Langmuir theoretical adsorption values for investigated systems. If we compare our experimental data with theoretical values, we can see that they fit well in all the concentration range, which definitely proves the validity of Langmuir model for these experimental data.

Insets of Figures 2 and 3 show the relation between  $C$  and  $C/X$  for CMChit and CMChTs, respectively. They represent the experimental adsorption isotherm values fitted into the linearized form of Langmuir equation. Correlation coefficients were calculated to be 0.963 and 0.978 for palladium onto carboxymethylchitin and carboxymethylchitosan, respectively; whereas 0.989 and 0.993 for platinum adsorption, accordingly. These values also indicate that both hydrogels fit well into the theoretical Langmuir isotherm model.

From the slope and intercept of Langmuir isotherm, the numerical values of Langmuir equation constants were calculated and summarized in Table II. The maximum adsorption at monolayer coverage  $X_{max}$  of palladium was 1.053 and 2.679 mg/g dry gel for CMChTs and CMChit, respectively. Accordingly, values for platinum were 1.155 and 2.513 mg/g dry gel in the same order. In analogical adsorption of gold ions experiments, maximum capacities were 37.59 and 11.86 mg/g for CM-chitosan and CM-chitin, respectively.<sup>19</sup> Such difference in capacity values might be explained by the fact that polymers reveal much higher selectivity toward gold rather than palladium and platinum ions. Additionally, palladium chlorocomplexes are found to be less reactive in exchange reactions<sup>20,21</sup> than gold chlorocomplexes,<sup>22</sup> which might also be an important factor.

It has been reported that effect of isotherm shape can be used to predict whether an adsorption would be of a "favorable" or "unfavorable" type.<sup>23</sup> The prediction of adsorption type is evaluated from Langmuir isotherms by dimensionless constant separation factor  $R_L$  by the following equation:<sup>24</sup>

$$R_L = \frac{1}{1 + b C_0} \quad (2)$$

where  $b$  is the Langmuir constant [eq. (1)] and  $C_0$  is the initial sorbate concentration.

**TABLE II**  
Langmuir Isotherms Constants for Palladium and Platinum Ions Adsorption Onto CM-Chitin and CM-Chitosan Hydrogels

Gel	Ion	$X_{max}$	$b$
CMChit	Pd	2.679	0.162
CMChTs	Pd	1.053	0.869
CMChit	Pt	2.513	0.205
CMChTs	Pt	1.155	0.345

**TABLE III**  
Effect of Separation Factor on Isotherm Shape

$R_L$ value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Based on the type of isotherm shape (Table III), we can conclude that isotherm type is "favorable" for all investigated adsorption systems (Table IV). Therefore, it justifies the usage of carboxymethylchitin and carboxymethylchitosan as favorable adsorbers for palladium and platinum ions.

### Counter ion/ionic strength effect

Introduction of chloride or nitric ions into solution caused increasing of adsorption capacities in all systems; results are shown in Figures 4 and 5. These results are contradictory to theoretical assumption that any ion would act as a competitor ion to metal complex one, and thus adsorption of metal ions would be lowered.

However, according to Baes and Mesmer,<sup>25</sup> creation and existence of different complexes of palladium and platinum ions are pH dependent, as well as domination of each form is strongly effected by chloride ions presence in the solution. Elding and Oskarsson presented similar pH dependence for metal ions complexes with nitric anions.<sup>26,27</sup>

With changing chloric and nitric ions concentration at constant pH, one can suspect all investigated metal ions to exist in the forms of hydroxyl or chloro/nitro complexes. Indeed, low concentration of chloric/nitric ions allows them to exist in hydroxyl complex forms, whereas high  $\text{Cl}^-$  or  $\text{NO}_3^-$  concentration favors chloro, nitro complex.

At the concentration of about  $0.01 \text{ mol/dm}^3$ , a significant bend-over is observed after which adsorption of most metal ions increases significantly (Figs. 4 and 5). This concentration, at given pH, is concluded to be a transition border between hydroxyl and chloro/nitro complexes. After crossing it, any increment of

chloric, nitric ions causes an increase in the number of created complexes, what indicates that  $\text{PdCl}_4^{2-}$ ,  $\text{PtCl}_4^{2-}$ , and respectively,  $\text{Pd}(\text{NO}_3)_4^{2-}$ ,  $\text{Pt}(\text{NO}_3)_4^{2-}$  anions are the most vulnerable for adsorption onto given hydrogels. Existence of Pt and Pd chlorocomplexes in water solutions and their sorption onto nitrogen-containing groups of aminoguanidine has been confirmed by far range IR spectroscopy.<sup>28</sup> Additionally, by using UV spectroscopy, shift in spectra after adsorption can be detected, which is associated with ligand-to-metal charge transfer for chloride<sup>29</sup> and for nitrate complexes.<sup>30</sup>

The addition of salt into the solution causes change in its ionic strength balance, which significantly influences hydrogel swelling performance. It was mentioned in our previous work<sup>17</sup> that increasing of salt concentration, and as a result the solution ionic strength, leads to the collapse of hydrogels. One may suspect that collapsed hydrogel may reveal worse adsorption performance due to impeded permeability into polymer matrix. However, this effect seems to have the minor influence on metal ions adsorption and it is completely shadowed by the effect of salt anion on the creation of their complexes with metals.

### Desorption of metal ions from hydrogels matrices

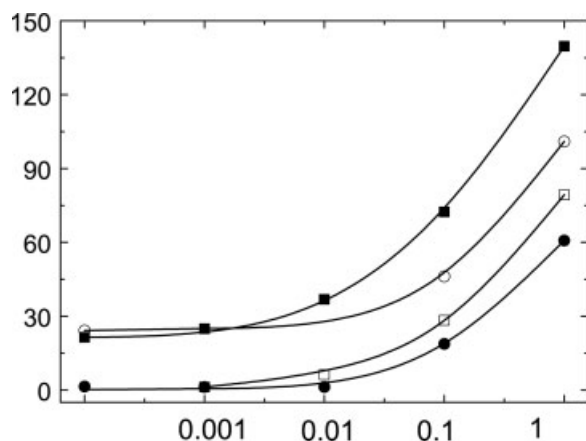
Desorption of metal ions from hydrogels by both HCl and  $\text{HNO}_3$  indicates some variations with increasing of their concentrations in solution. The reason of such dependence might be similar as for adsorption of these metals in NaCl and  $\text{NaNO}_3$  solutions, described in the previous section.

Introduction of any additional ions changes ionic balance in solution, which subsequently may cause shifting of newly released complexes to other forms of occurrence. It can be expected that such newly created forms are more vulnerable for adsorption, and they would be adsorbed much easier onto hydrogel than their parental form. On the other hand, these new forms may interact with solution residue or with themselves resulting in lowering the total adsorption yield.

Desorption experiments (Fig. 6) show that in case of HCl treatment the highest metal ions retrieval was

**TABLE IV**  
Constant Separation Factor Based on the Langmuir Equation for Palladium and Platinum Ions Adsorption Onto Carboxymethylchitin and Carboxymethylchitosan Hydrogels

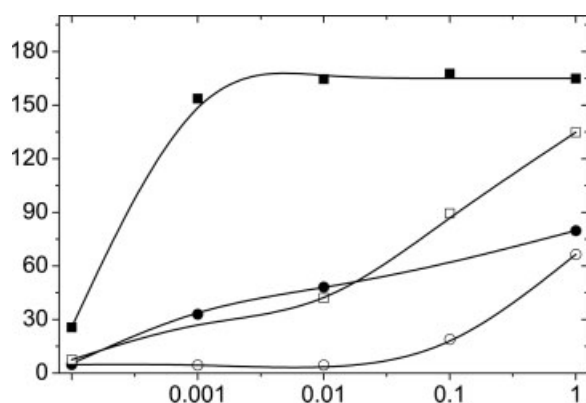
Concentration	Pd		Concentration	Pt	
	CM-Chts	CM-Cht		CM-Chts	CM-Cht
0.08	0.919	0.816	0.14	0.859	0.737
0.17	0.849	0.688	0.22	0.798	0.645
0.78	0.548	0.323	0.74	0.540	0.351
1.74	0.353	0.176	2.29	0.274	0.148
4.29	0.181	0.080	5.80	0.130	0.064



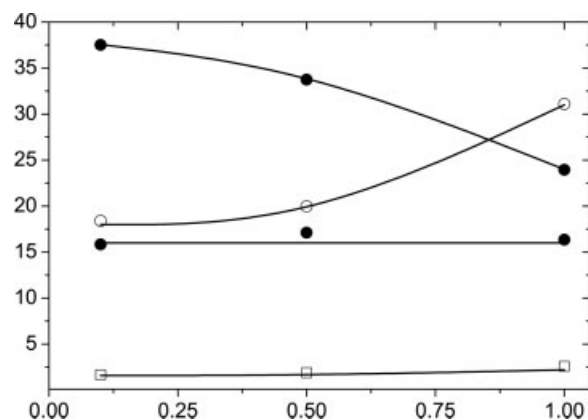
**Figure 4** Influence of ionic strength (NaCl) on adsorption capacities of palladium and platinum ions onto CM-Chitin, CM-Chitosan hydrogels at the initial metal ions concentration of 100 ppb. X-axis: NaCl (mol/dm<sup>3</sup>), Y-axis: Adsorption (µg metal/g dry gel); (○) Pd onto CMChit, (□) Pt onto CMChit, (●) Pd onto CMChts, (■) Pt onto CMChts.

obtained for palladium ions from CMChts exceeding 37% of adsorbed ions at low acid concentration, and 31% from CMChit gel, at 1 mol/dm<sup>3</sup> HCl solution. On the other hand, elution with HNO<sub>3</sub> (Fig. 7) led to achieve the best results for regaining palladium ions from CMChit at acid concentration of 1 mol/dm<sup>3</sup> 45% and for retrieval of platinum ions at low concentrated HNO<sub>3</sub> solution exceeded 42 and 35% from CMChts and CMChit, respectively.

At the pH applied in the experiment, polymer amine and amide groups are protonated, and both metals occur in charged complexes. Thus, adsorption should proceed via chelating mechanism rather than ion-exchange one. Increasing concentration of both acids does not drastically influence desorption pro-



**Figure 5** Influence of ionic strength (NaNO<sub>3</sub>) on adsorption capacities of palladium and platinum ions onto CM-Chitin, CM-Chitosan hydrogels at the initial metal ions concentration of 100 ppb. X-axis: NaNO<sub>3</sub> (mol/dm<sup>3</sup>), Y-axis: Adsorption (µg metal/g dry gel); (○) Pd onto CMChit, (□) Pt onto CMChit, (●) Pd onto CMChts, (■) Pt onto CMChts.

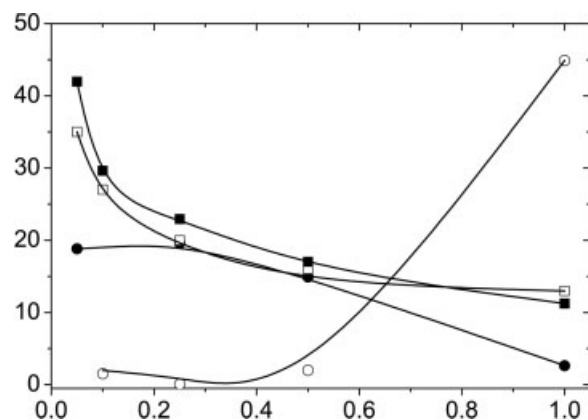


**Figure 6** Desorption rates of palladium and platinum ions adsorbed onto carboxymethylchitin and carboxymethylchitosan hydrogels using HCl at various concentrations. X-axis: HCl (mol/dm<sup>3</sup>); Y-axis: Desorption (%); (○) Pd from CMChit, (□) Pt from CMChit, (●) Pd from CMChts, (■) Pt from CMChts.

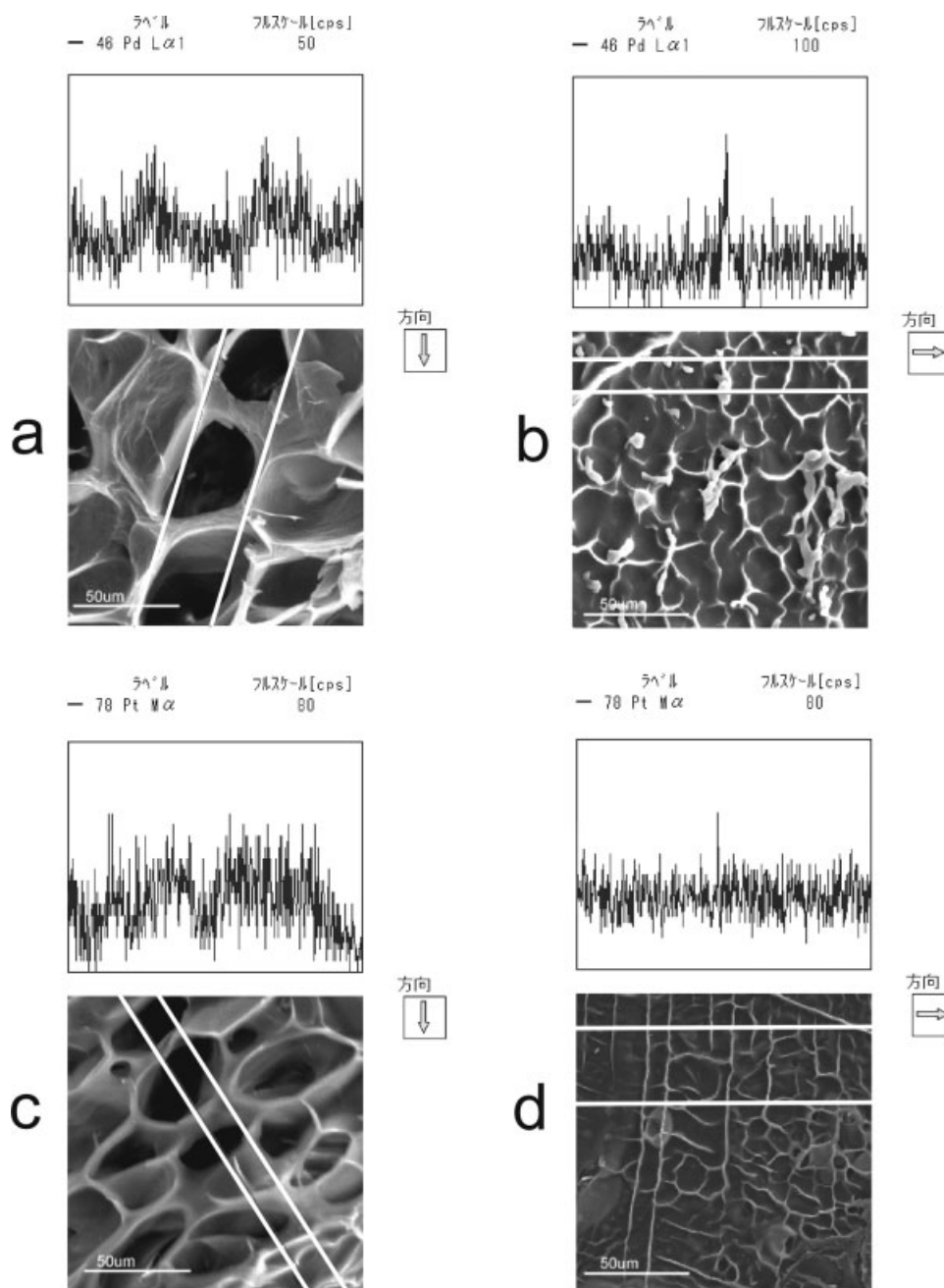
cess and such behavior is typical for desorption of metal ions adsorbed by chelation mechanism. If adsorption would carry on through ion-exchange mechanism, then acidic elution should lead to almost 100% of desorption efficiency, as it was observed for other polymers.<sup>31</sup>

### SEM-EDX investigation

The SEM-EDX technique allows observation of the distribution of adsorbed elements in the sorbent particle, making possible to draw a qualitative cartography of these elements or to detect these species along with cross section of the particle. Figures 8 and 9 show SEM microphotographs together with X-ray



**Figure 7** Desorption rates of palladium and platinum ions adsorbed onto carboxymethylchitin and carboxymethylchitosan hydrogels using HNO<sub>3</sub> at various concentrations. X-axis: HNO<sub>3</sub> (mol/dm<sup>3</sup>), Y-axis: Desorption (%); (○) Pd from CMChit, (□) Pt from CMChit, (●) Pd from CMChts, (■) Pt from CMChts.



**Figure 8** SEM-EDX micrographs of metal ions adsorbed onto crosslinked carboxymethylchitin: (a) cross-section of palladium-loaded gel, (b) surface of palladium-loaded gel, (c) cross-section of platinum-loaded gel, (d) surface of platinum-loaded gel.

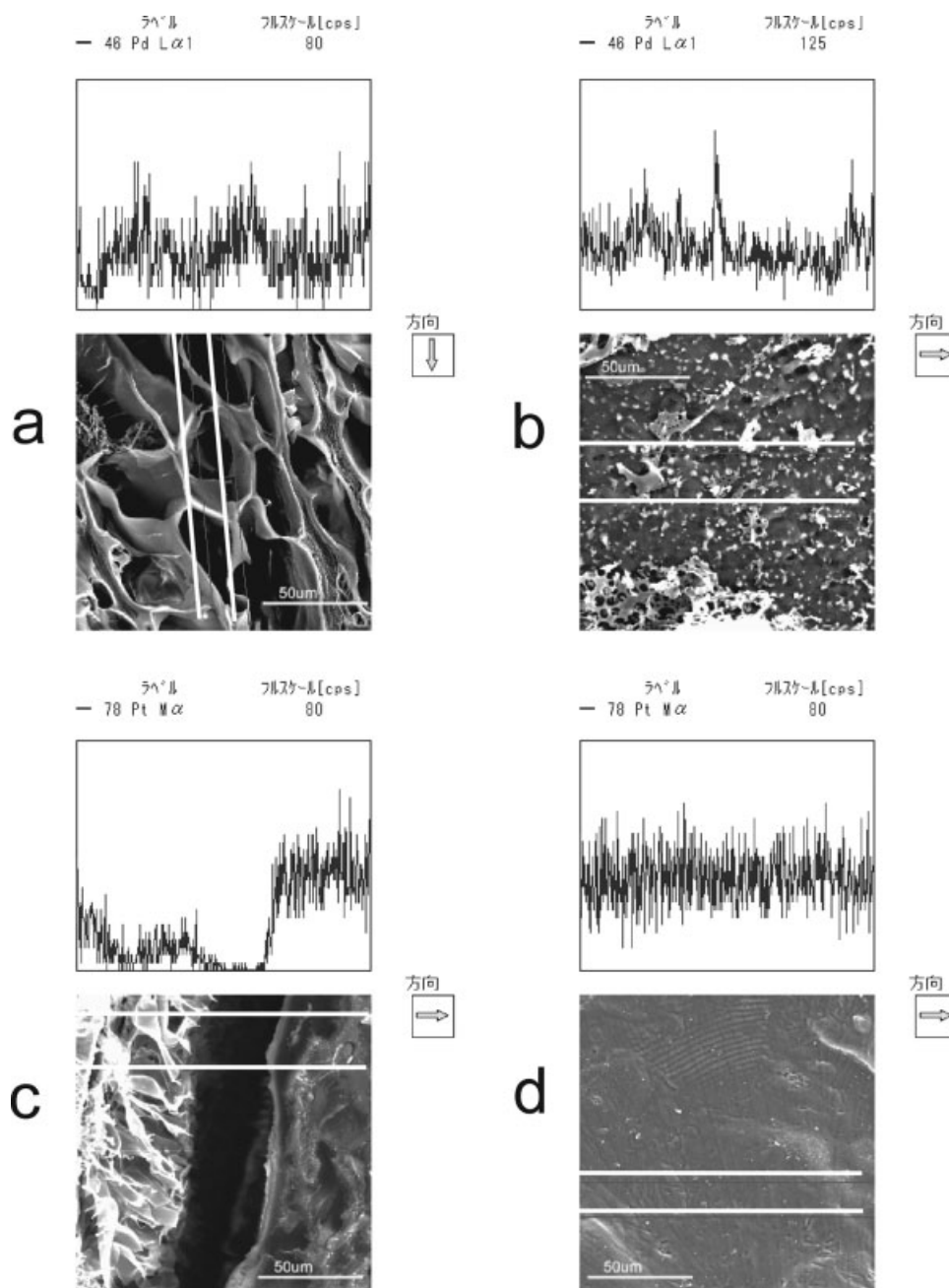
energy diffraction analysis of palladium and platinum metals adsorbed onto CMChT and CMChTs hydrogels.

These results show that palladium and platinum chlorocomplexes are adsorbed homogeneously by both polymers. It seems that there is no specific place where metal ions are adsorbed onto hydrogel, because the same distribution pattern is observed both on polymer surface and inside of polymer matrix. Uniformity of metal ions allocation onto CMChT and CMChTs hydrogel matrices together with their

good mechanical properties<sup>14</sup> makes them potential materials for usage as a column packaging for precious metals adsorption.

#### DSC measurements

Results of DSC measurements of carboxymethylchitin and carboxymethylchitosan loaded with palladium and platinum chlorocomplexes are presented in Figures 10 and 11. It can be seen that metals ions inclusion influences polymer structure integrity, as it



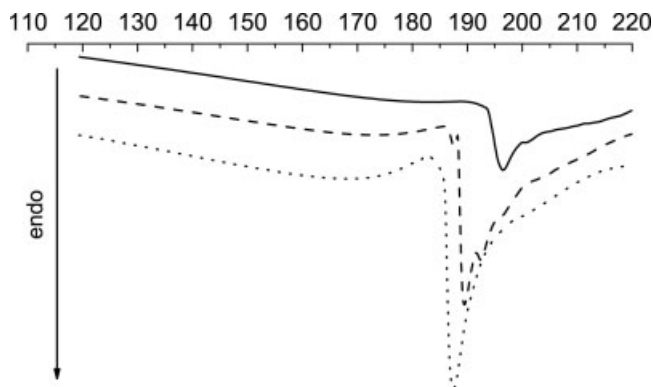
**Figure 9** SEM-EDX micrographs of metal ions adsorbed onto crosslinked carboxymethylchitosan: (a) cross-section of palladium-loaded gel, (b) surface of palladium-loaded gel, (c) cross-section of platinum-loaded gel, (d) surface of platinum-loaded gel.

results in their decomposition temperature decrease. Chelation is known to change the conformation of the polymers structure and we can expect two opposite outcomes of this action. One of them is that metal ions may cause disturbance in natural ordering of the polymer, following-on lowering its thermal stability. On the other hand, additional bridging through metal ion can be expected to lead to enhancement in polymer thermal stability through formation of crystalline phase.<sup>32</sup> However, during cooling and second run heating any peak has not appeared (data not shown).

It strongly suggests that creation of crystalline phase can be debarred. If it would happen, we should obtain two peaks during first run heating. One could be ascribed to decay of polymer–metal ion complex and second one to polymer decomposition itself. Besides, at some point in cooling process, one should observe peak related to the recrystallization of polymer–metal complex. However, none of them was observed.

Based on the above discussion, it is concluded that the first phenomenon, disturbance in natural ordering



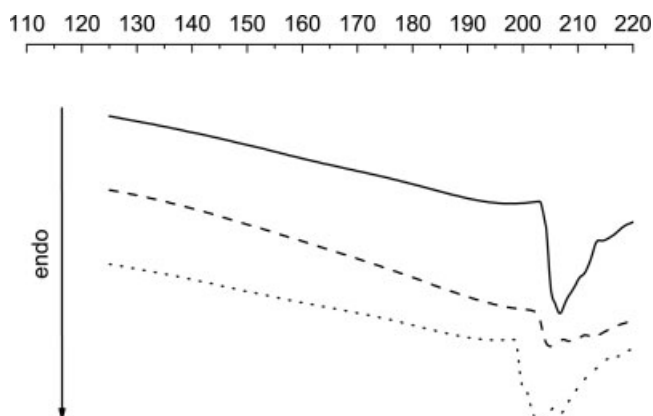


**Figure 10** DSC curves of palladium- and platinum-loaded carboxymethylchitin hydrogels. X-axis: Temperature (°C); (—) control (gel), (·····) with Pd, (-----) with Pt.

of polymer, is prevailing. Introduction of noble metal ions onto CMChT and CMChTs hydrogels results in upsetting their structural integrity and stability of polymeric matrices that influences on decreasing of polymer decomposition temperature.

## CONCLUSIONS

This study demonstrated that crosslinked carboxymethylchitin and carboxymethylchitosan hydrogels are efficient in removing noble metals like palladium and platinum from dilute solutions. Described method might be used as example in recovering these metals from industrial wastewaters. Retrieval of these metals ions in acidic desorption process in 1 mol/dm<sup>3</sup> HCl were 35, 18, 16, 5% for palladium adsorption onto CMChT, CMChTs and platinum adsorption onto CMChTs, CMChT, respectively. Such low desorption values indicate that adsorption of these metal ions onto CMChT and CMChTs occurs via chelating mecha-



**Figure 11** DSC curves of palladium- and platinum-loaded carboxymethylchitosan hydrogels. X-axis: Temperature (°C); (—) control (gel), (·····) with Pd, (-----) with Pt.

nism. It has been revealed that chloric and nitric ions at low concentrations had an influence on adsorption performance. Inclusion of metal ions onto polymer matrices is changing the stability of polymer by disturbing its structural integrity.

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