



Effective Recovery of Palladium(II) Ions using Chitosan-Based Adsorbent Material

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Abstract

Chitosan is one of the naturally abundant, biodegradable, and low-cost adsorbent materials for metal adsorption purposes. In this work, we evaluated the application of chitosan materials derived from seafood wastes in Depok beach, Yogyakarta, for an effective recovery of the palladium(II) ions. First of all, the seafood wastes were treated to obtain chitin and then followed by the deacetylation process to produce chitosan material with a deacetylation degree of 78.42%. The chitosan material was characterized using Fourier transform infrared (FTIR) spectrophotometer. It was found that chitosan gave high adsorption percentage (90%) for palladium(II) ions due to the complexation with hydroxyl, amino and carbonyl functional groups. The palladium(II) adsorption onto chitosan material followed the pseudo-second-order ($R^2 = 0.9978$) and Langmuir ($R^2 = 0.9979$) models for kinetic and isotherm experiments, respectively, with a maximum adsorption capacity value of 0.70 mmol g^{-1} . The palladium(II) ions could be easily desorbed in 90% percentage using 1.0 M HCl solution from metal-laden chitosan to regenerate the adsorbent material. The chitosan-based adsorbent material did not lose its adsorption capability after three consecutive cycles with no significant structural change as revealed from the FTIR data. These results showed the potential application of natural chitosan materials derived from seafood wastes for the effective recovery of palladium(II) ions.

Keywords: adsorption, chitosan, palladium, recovery, selective

1. INTRODUCTION

Palladium is a precious metal that is widely applied in batteries, catalysts, and other advanced materials in our daily life [1][2]. However, the supply of palladium metals is unstable due to global maldistribution and limited resources. Because of that, the palladiums' recovery from electronic wastes and wastewaters shall be seriously considered as an alternative resource of palladium metals in the future. Efforts on the palladiums' recovery have been given over the past several years [3]-[5]. Effective recovery of precious metal ions from electronic wastes has been reported by Sathuluri et al. [6] in 2018 using calixarene derivatives. They reported the presence of nitrogen functional groups was crucial for palladium(II) complexation [6]-[9]. However, calixarenes are expensive materials thus limiting their usage for palladium(II) recovery in a commercial application.

Therefore, the search for a cheap and convenient recovery process of palladium ions needs to be established.

Chitosan is a nitrogenated biomaterial that is naturally abundant, biocompatible, and biodegradable. Chitosan is composed of a mixture of *N*-acetylglucosamine and *D*-glucosamine monomers as minor and major building blocks, respectively [10]. Chitosan materials can be obtained through a deacetylation reaction of chitins derived from Crustacean shells [11]. Nowadays, chitosan materials have been extensively investigated as adsorbent materials for metal ions adsorption through chemical interactions. From the molecular point of view, chitosan contains hydroxyl, ether, carbonyl, amide and amino groups that could act as Lewis bases to form a stable complex with positive charge metal ions as Lewis acids. This phenomenon could be exploited for both heavy metal removal and precious metal recovery [12]-[14].

To the best of our knowledge, an investigation on the chitosan production from seafood wastes in Depok beach, Yogyakarta, for palladium(II) ions recovery has not been reported yet. Because of that, the utilization of Crustacean shell wastes to produce chitosan materials for precious metal ions recovery through the adsorption process is an excellent solution to increase the economic value of seafood wastes. Herein, we reported the preparation of chitosan material through the deacetylation of

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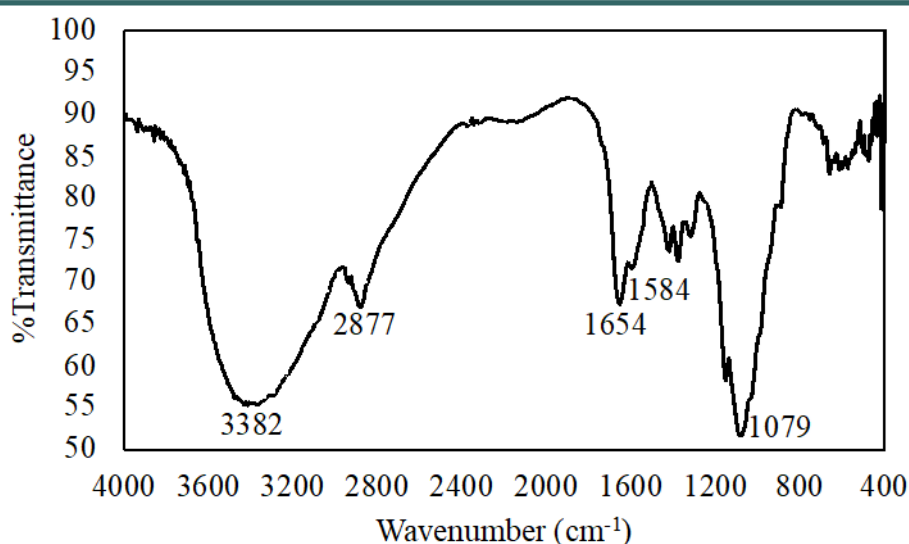


Figure 1. FTIR spectrum of chitosan material.

chitins derived from seafood wastes obtained at Depok beach. The produced chitosan material was applied for palladium(II) adsorption from an individual metal system and then the adsorption kinetics and isotherm models were studied. The palladium(II) ions were recovered under the acidic condition to regenerate the chitosan-based adsorbent materials for the other three consecutive cycles of the adsorption process.

2. MATERIALS AND METHODS

2.1. Materials

Seafood wastes were kindly donated by a fisherman from Depok beach, Yogyakarta, while sodium hydroxide (NaOH), hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄), and palladium(II) nitrate were purchased from Merck in pro analytical grade.

2.2. Instruments

The Fourier transform infrared (FTIR) spectra of chitosan materials were recorded from a Shimadzu IR Prestige-21 spectrophotometer. Meanwhile, the adsorption percentage (% Adsorption) was calculated by measuring palladium (II) ions concentration using an atomic absorption spectrophotometer (AAS) apparatus. The mathematical equation to calculate the % Adsorption is mentioned as follows.

$$\% \text{ Adsorption} = \frac{[\text{Pd(II)}]_{\text{Initial}} - [\text{Pd(II)}]_{\text{After adsorption}}}{[\text{Pd(II)}]_{\text{Initial}}} \times 100\% \quad (1)$$

2.3. Methods

2.3.1. Preparation of Chitosan Material from Seafood Wastes

The chitin isolation was conducted in a similar manner to the previous report [11] with some modifications. At first, the seafood wastes were mashed with the aid of a mortar and subjected to deproteination, demineralization, and depigmentation processes. The deproteination method was conducted to remove the proteins from the chitin by refluxing the seafood waste powders in 0.1 M NaOH in 1:10 mass to volume ratio for 2 hours. The residue was rinsed with distilled water until the pH of the filtrate was neutral. Afterward, the demineralization process was performed by mixing the residue in 1 M HCl in 1:20 mass to volume ratio at room temperature for 3 hours. The solid was then washed with distilled water until the pH of the filtrate reached 7. Furthermore, the depigmentation process was carried out by mixing the residue in 0.05 M NaOCl in 1:10 mass to volume ratio at room temperature for 1 hour. The produced chitin material was washed with distilled water and dried. The chitosan material was prepared by refluxing chitin in 1.5 M NaOH in 1:20 mass to volume ratio for 3 hours. The produced chitosan was rinsed with distilled water until the pH of the filtrate was neutral. Then, the chitosan material was dried and characterized by FTIR analysis, while the deacetylation degree was estimated using Moore and Robert method [15]. The mathematical equation to estimate the deacetylation degree is

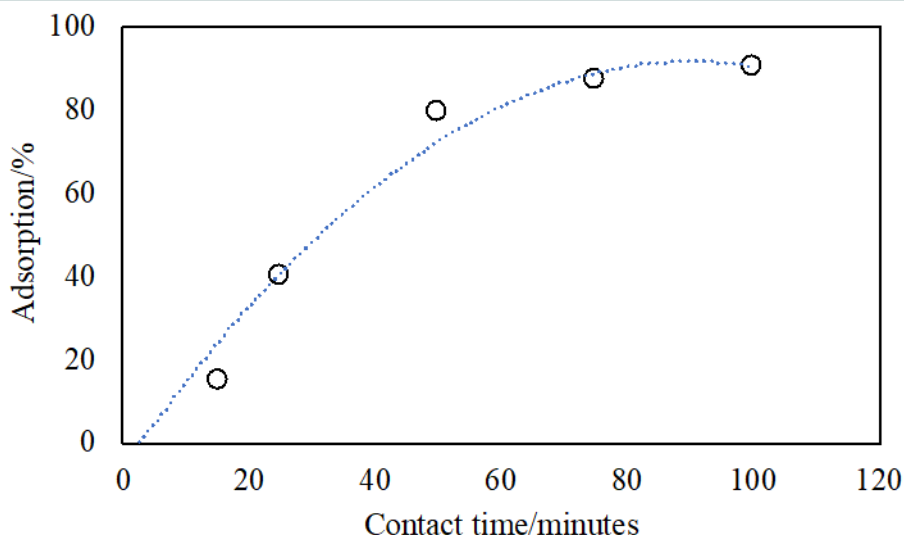


Figure 2. Effect of contact time on the palladium(II) ions adsorption using chitosan-based material. Mass of the adsorbent = 200 mg. Volume of the aqueous solution = 50 mL. [Palladium(II)] = 0.1 mM. Shaking speed = 150 rpm.

mentioned as follows.

$$\text{Deacetylation Degree} = \frac{\text{Absorbance at } 1655 \text{ cm}^{-1}}{\text{Absorbance at } 3450 \text{ cm}^{-1}} \times \frac{100}{1.33}$$

(2)

2.3.2. Palladium(II) Adsorption from Aqueous Solution

A stock solution of palladium(II) ions was prepared by dissolving 230 mg (1 mmol) palladium (II) nitrate in 100 mL distilled water to give a final concentration of 10 mM. Chitosan material (200 mg) was added into 50 mL of palladium(II) solution and stirred at room temperature. The kinetics of palladium(II) adsorption was studied by changing the contact time by 15, 25, 50, 75, and 100 minutes, while the palladium(II) adsorption isotherm was investigated by varying the initial concentration of palladium(II) ions of 0.1, 1, 2.5, 5, 7.5, and 10 mM. The palladium(II) ions concentration after the adsorption process was then determined by AAS

analysis.

3. RESULTS AND DISCUSSIONS

3.1. Preparation of Chitosan Material from Seafood Wastes

Isolation of chitin from seafood wastes was performed through three consecutive steps, *i.e.*, deproteination, demineralization and depigmentation. These consecutive processes were required to remove protein, mineral and pigment impurities from chitin material, respectively. Protein is easily denaturated under alkaline conditions while inorganic minerals (mostly calcium carbonate) are highly soluble under acidic conditions. The pigments from Crustacean shells are commonly bleached with the help of NaOCl through reduction-oxidation reactions [11]. The deproteination, demineralization, and depigmentation processes produced each targeted material in 54, 48, and 91% yield, respectively.

Table 1. Mathematical models of palladium(II) adsorption kinetics using chitosan-based material.

Kinetic model	Mathematical equation	R ²
Pseudo-first-order	$\log (q_e - q_t) = -0.0238 t - 1.3472$	0.7750
Pseudo-second-order	$t/q_t = 47.414 t + 1404.2$	0.9978
Elovich	$q_t/t = -2.52 \times 10^{-6} (\ln t)/t + 0.0005$	0.9135
Intraparticle diffusion	$q_t = 0.0031 t^{0.5} + 0.0060$	0.9015
Liquid film diffusion	$\ln(1 - q_t/q_e) = -0.0548 t - 0.6921$	0.9780

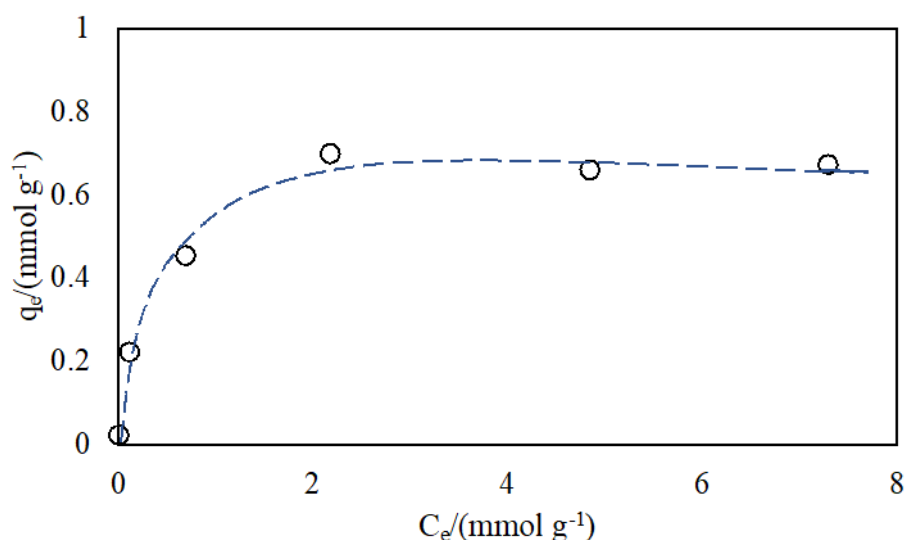


Figure 3. Isotherm adsorption for palladium(II) ions using chitosan-based material. Mass of the adsorbent = 200 mg. Volume of the aqueous solution = 50 mL. Shaking speed = 150 rpm. Adsorption time = 100 min.

Then, chitosan material was prepared from the deacetylation reaction of chitin. The amide functional groups are hydrolyzed under alkaline conditions to give free amino functional groups which are useful for metal ion complexation. The deacetylation reaction yielded chitosan in 20% yield. These data showed that the preparation of chitosan material from seafood wastes was achieved in 4% overall yield in this work. The FTIR spectrum of chitosan (Figure 1) showed characteristic signals of O–H and –NH₂, C–H sp³, C=O, N–H, and C–O functional groups at 3382, 2877, 1654, 1584, and 1079 cm⁻¹, respectively. It was found that the deacetylation degree of the obtained chitosan material was 78.42% according to Moore and Roberts' calculation.

3.2. Palladium(II) Adsorption from Aqueous Solution

The adsorption of palladium(II) ions onto the

chitosan material was evaluated. The time dependence adsorption profile is depicted in Figure 2 by varying contact times. The equilibrium of palladium(II) ions adsorption was achieved after 75 minutes to give around 90% adsorption percentage with an experimental amount of palladium(II) ions adsorbed per gram of chitosan (q_e) value of 0.0225 mmol g⁻¹. The kinetic analysis of palladium(II) ions adsorption was studied by implementing pseudo-first-order, pseudo-second-order, Elovich, intraparticle diffusion, and liquid film diffusion models. The kinetics data are listed in Table 1 in which the palladium(II) ions adsorption fits well with the pseudo-second-order mathematic model as indicated by the highest R² value (0.9978) with a reaction rate constant of 1.60 g mmol⁻¹ min⁻¹. Furthermore, the theoretical q_e value (0.02109 mmol g⁻¹) was close to the experimental q_e value (0.02250 mmol g⁻¹) demonstrating the validity of the pseudo-second-order kinetic model in this work.

Table 2. Isotherm adsorption model of palladium(II) ions using chitosan-based material.

Isotherm adsorption model	Mathematical equation	R ²
Langmuir	$C_e/q_e = 1.4267 C_e + 0.3730$	0.9979
Freundlich	$\ln q_e = 0.5410 \ln C_e - 1.0877$	0.9375
Temkin	$q_e = 0.1048 \ln C_e + 0.5134$	0.9561
Dubinin-Radushkevich	$\ln q_e = 8.3 \times 10^{-7} [RT \ln (1 + 1/C_e)]^2 - 2.6011$	0.6867

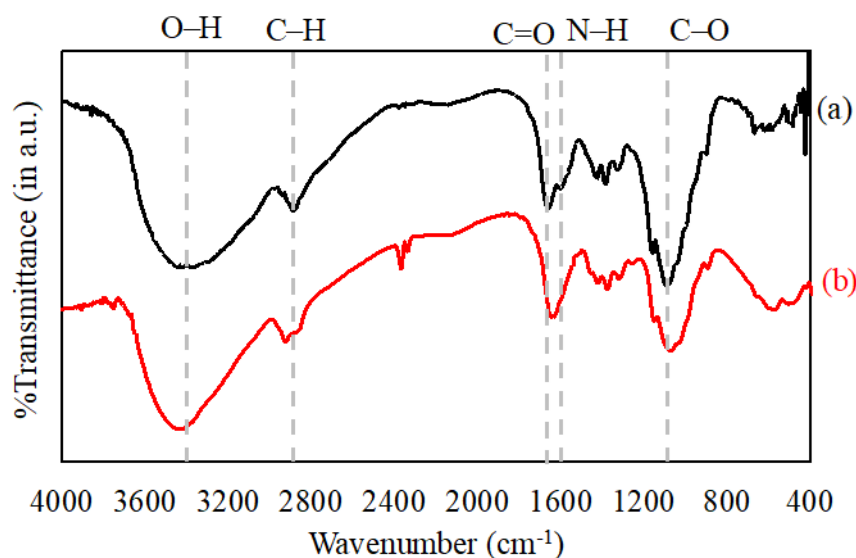


Figure 4. FTIR spectra of chitosan-based material (a) before and (b) after palladium(II) loading. [palladium (II)] = 10 mM.

The isotherm adsorption of palladium(II) ions was studied by varying the initial concentration of palladium(II) ions in the aqueous phase. The isotherm adsorption profile of palladium(II) ions is depicted in Figure 3. The equilibrium state of palladium(II) ions adsorption was achieved at a q_e value of 0.70 mmol g^{-1} . The isotherm adsorption analysis of palladium(II) ions was further studied by implementing Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models. The isotherm adsorption data are listed in Table 2 in which the palladium(II) ions adsorption perfectly matches with the Langmuir model indicated by the highest R^2 value (0.9979). Based on the Langmuir model, the maximum adsorption capacity (q_{max}) and Langmuir constant (K_L) of palladium(II) ions adsorption using chitosan-based material were 0.70 mmol g^{-1} and 3.82 L mmol^{-1} , respectively. The separation constant (R_L) is a critical parameter to determine whether the adsorption is favorable or not. The R_L value of palladium(II) adsorption using chitosan-based

material was 0.025 demonstrating that the adsorption process was highly favorable ($0 < R_L < 1$). Furthermore, it was estimated from the Temkin model that the heat of adsorption was around $23.80 \text{ kJ mol}^{-1}$ indicating chemisorption of palladium(II) ions on the surface of chitosan material.

Since the chitosan is composed of *N*-acetylglucosamine and *D*-glucosamine monomers in 22.58 and 78.42%, respectively, thus the chitosan could interact with palladium(II) ions through hydroxyl, amino and carbonyl functional groups. To elucidate the adsorption sites of chitosan, FTIR analysis was performed. The FTIR spectra of chitosan before and after palladium(II) loading are shown in Figure 4. The signal of O-H and $-\text{NH}_2$ functional groups was shifted from 3382 to 3433 cm^{-1} indicating that the interaction of chitosan with palladium(II) ions broke the intermolecular and intramolecular hydrogen bonds of chitosan. The signal of C-H sp^3 was shifted from 2877 to 2908 cm^{-1} due to conformational change of

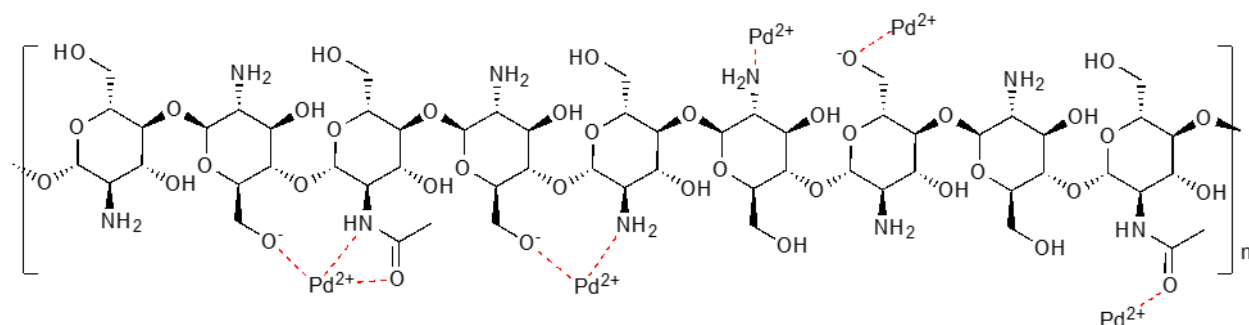


Figure 5. Plausible chemical interactions for palladium(II) adsorption on the chitosan-based material.

Table 3. Maximum adsorption capacities of reported adsorbent materials for palladium(II) ions.

No	Adsorbent material	q_{\max} (mmol g ⁻¹)	Reference
1	Dimercapto-thiodiazole-chitosan	0.13	[16]
2	Activated carbon-coated-chitosan	0.41	[17]
3	Chitosan	0.59	[17]
4	Chitosan from seafood wastes	0.70	Present work
5	Carboxymethylcellulose-crosslinked-chitosan	0.83	[18]
6	L-lysine-crosslinked-chitosan	1.03	[19]
7	Thiourea-chitosan	1.06	[20]
8	Glycine-crosslinked-chitosan	1.13	[21]
9	Thiocarbamoyl-chitosan	1.24	[22]
10	Bipyridinedicarbaldehyde-crosslinked-chitosan	1.45	[13]
11	Glutaraldehyde-crosslinked-chitosan	1.69	[23]
12	Ethylenedisulfide-chitosan	2.41	[24]
13	Phenantrolinedicarbaldehyde-crosslinked-chitosan	2.47	[13]
14	Glutaraldehyde-8hydroxyquinoline-crosslinked-chitosan	3.20	[13]
15	Rubeanic acid-chitosan	3.31	[25]
16	Chitosan-beads gel	3.38	[26]
17	Polyethyleneimine-chitosan	3.75	[27]

tetrahydropyran heterocyclic of glucose after palladium(II) adsorption which was in agreement with the previous report [16]. The signal of C=O shifted from 1654 to 1620 cm⁻¹ indicating that dipole-cation interaction was observed between the oxygen atom of carbonyl (acted as Lewis base) and palladium(II) ions (acted as Lewis acid). The signal of N-H bending shifted from 1584 to 1620 cm⁻¹ and overlapped with the signal of C=O due to dipole-cation interactions which agreed to the shift of O-H and -NH₂ signals. Meanwhile, the signal of C-O slightly changed from 1079 to 1078 cm⁻¹ due to conformational change in glucose. It meant that the main mechanism of palladium(II) adsorption happened through electrostatic and dipole-cation interactions as supported by the Langmuir and Temkin isotherm data. The plausible adsorption site of palladium(II) ions is depicted in Figure 5.

On the other hand, Table 3 shows the q_{\max} parameters for palladium(II) adsorption using other

reported adsorbent materials. Compared to the commercial chitosan material ($q_{\max} = 0.59$ mmol g⁻¹), the prepared chitosan in this work gave a slightly higher q_{\max} value ($q_{\max} = 0.70$ mmol g⁻¹) due to the variety in the bio-composition of Crustacean shell sources in the seafood wastes at Depok beach. The q_{\max} value of chitosan in this work still can be improved by several materials modifications such as crosslinking, impregnation and copolymerization methods (see Table 3 no. 5-17). This result demonstrates that chitosan material derived from seafood wastes is a promising adsorbent material for palladium(II) ions adsorption.

Effective recovery of precious metal ions not only depends on the high adsorption capability but also on the ease of the desorption stage. In this work, acid reagents were used to recover palladium (II) ions from the metal-laden chitosan material. Since the adsorption mechanism depends on the electrostatic and dipole-cation interactions thus the

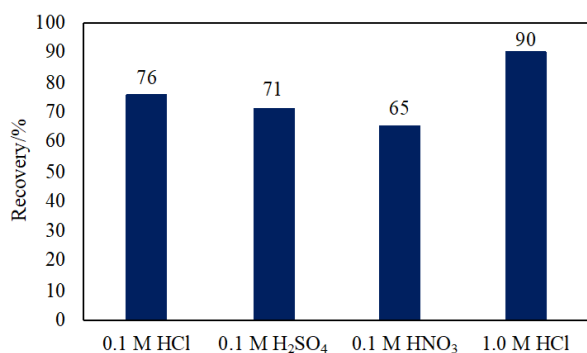


Figure 6. Recovery of palladium(II) ions from metal-laden chitosan-based materials. [Loaded palladium(II)] = 0.09 mM.

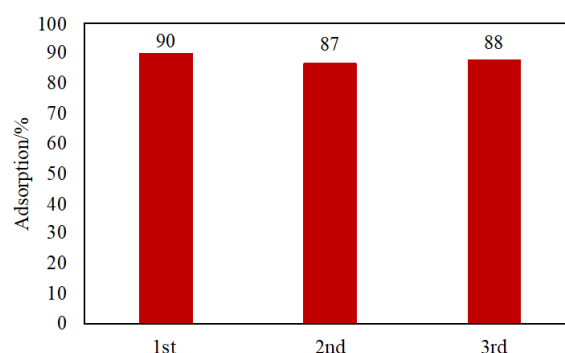


Figure 7. Reusability of chitosan-based materials for palladium(II) recovery.

palladium(II) ions shall be easily desorbed by protonation of hydroxyl, amino and carbonyl functional groups [28]. As expected, acidic reagents were able to recover palladium(II) ions in 65–90% as shown in Figure 6. The recovery percentage of palladium(II) ions using 0.1 M H₂SO₄ (71%) was higher than 0.1 M HNO₃ (65%) due to a stronger acidic property of H₂SO₄. Meanwhile, the recovery percentage of palladium(II) ions using 0.1 M HCl (76%) was higher than 0.1 M H₂SO₄ (71%) due to the complexation of palladium(II) ions with chloride anions to form [PdCl₄]²⁻. A higher concentration of HCl reagent (i.e., 1.0 M) yielded a higher recovery percentage (90%), which was remarkable. Furthermore, the chitosan was reprecipitated by adjusting the pH value to neutral and then filtered for a reusability study.

The reusability of chitosan-based material was performed by subjecting the regenerated chitosan-

based material after the desorption process to another adsorption process. The reusability data of palladium(II) ions adsorption using chitosan-based material are shown in Figure 7. It was found that the chitosan-based material did not lose its adsorption capability (87–90%) even after three consecutive cycles. Furthermore, the FTIR spectra of reused chitosan-based material (see Figure 8) showed no significant change in the chitosan structure demonstrating the high stability of chitosan-based material for palladium(II) ion recovery purposes. This work successfully demonstrated the excellent solution for the utilization of seafood wastes in Depok beach as the chitosan materials resource for palladium(II) ions recovery through an adsorption process.

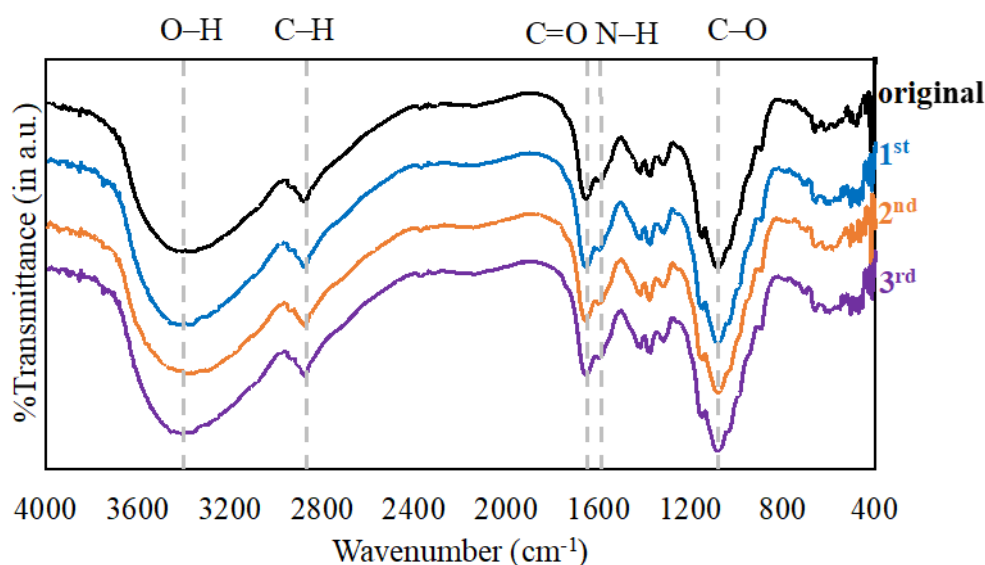


Figure 8. FTIR spectra of recycled chitosan-based material for each cycle.

4. CONCLUSIONS

Chitosan material has been successfully prepared through chemical processes from seafood wastes in Depok beach, Yogyakarta in a 4% overall yield. The chitosan-based material showed effective palladium(II) ions adsorption from the aqueous solution. The adsorption required 75 minutes to reach a plateau in which the adsorption kinetics followed the pseudo-second-order model with a reaction rate constant of $1.60 \text{ g mmol}^{-1} \text{ min}^{-1}$. On the other hand, the isotherm adsorption of palladium(II) ions fit well with the Langmuir model giving q_{max} , K_L , and R_L values of 0.70 mmol g^{-1} , 3.82 L mmol^{-1} , and 0.025 , respectively, demonstrating a favorable chemical adsorption process. The estimated heat of palladium(II) ions adsorption was $23.80 \text{ kJ mol}^{-1}$ indicating a chemisorption process as supported by the FTIR data. Employing 1.0 M HCl gave a high desorption percentage (90%) thus the chitosan-based material can be reused for three consecutive cycles without losing its adsorption capability and structural stability, which was remarkable. These results demonstrate the potential application of seafood wastes as an alternative resource of bio-adsorbent material for effective palladium(II) ions recovery in the future.

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Conflicts of Interest

The author(s) declared no conflict of interest

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REFERENCES

- [1] T. T. V. Phan, T. C. Huynh, P. Manivasagan, S. Mondal, and J. Oh. (2020). "An Up-To-Date Review on Biomedical Applications of Palladium Nanoparticles". *Nanomaterials*. **10** (1): 66. [10.3390/nano10010066](https://doi.org/10.3390/nano10010066).
- [2] A. Chen and C. Ostrom. (2015). "Palladium-based Nanomaterials: Synthesis and Electrochemical Applications". *Chemical Reviews*. **115** (21): 11999-12044. [10.1021/acs.chemrev.5b00324](https://doi.org/10.1021/acs.chemrev.5b00324).
- [3] C. S. Brooks. (2018). "Metal Recovery from Industrial Waste". CRC Press.
- [4] O. Grad, M. Ciopec, A. Negrea, N. Duteanu, G. Vlase, P. Negrea, C. Dumitrescu, T. Vlase, and R. Voda. (2021). "Precious Metals Recovery from Aqueous Solutions using A New Adsorbent Material". *Scientific Reports*. **11**: 2016. [10.1038/s41598-021-](https://doi.org/10.1038/s41598-021-)

- 81680-z.
- [5] S. Sharma, A. S. K. Kumar, and N. Rajesh. (2017). "A Perspective on Diverse Adsorbent Materials to Recover Precious Palladium and The Way Forward". *RSC Advances*. **7** (82): 52133-52142. [10.1039/C7RA10153H](https://doi.org/10.1039/C7RA10153H).
- [6] R. R. Sathuluri, Y. S. Kurniawan, J. Y. Kim, M. Maeki, W. Iwasaki, S. Morisada, H. Kawakita, M. Miyazaki, and K. Ohto. (2018). "Droplet-based Microreactor System for Stepwise Recovery of Precious Metal Ions from Real Metal Waste with Calix[4]arene Derivatives". *Separation Science and Technology*. **53** (8): 1261-1272. [10.1080/01496395.2017.1366518](https://doi.org/10.1080/01496395.2017.1366518).
- [7] K. T. A. Priyanga, Y. S. Kurniawan, L. Yuliati, B. Purwono, T. D. Wahyuningsih, and H. O. Lintang. (2021). "Novel Schiff Base Azo-Imine for Ultra-Sensitive and Highly Selective Fluorescent Chemosensor of Fe³⁺ Ions". *Luminescence: The Journal of Biological and Chemical Luminescence*, **36** (5): 1239-1248. [10.1002/bio.4049](https://doi.org/10.1002/bio.4049).
- [8] Y. S. Kurniawan, R. R. Sathuluri, W. Iwasaki, S. Morisada, H. Kawakita, K. Ohto, M. Miyazaki, and J. Jumina. (2018). "Microfluidic Reactor for Pb(II) Ion Extraction and Removal with Amide Derivative of Calix[4]arene Supported by Spectroscopic Studies". *Microchemical Journal*. **142** : 377-384. [10.1016/j.microc.2018.07.001](https://doi.org/10.1016/j.microc.2018.07.001).
- [9] K. T. A. Priyanga, Y. S. Kurniawan, and L. Yuliati. (2021). "Evaluation of C-arylcalix[4]resor-cinarenes as novel adsorbent materials: Effect on the nitro substituent on the Au(III) adsorption". *ChemistrySelect*. **6** (21): 5366-5373. [10.1002/slct.202101067](https://doi.org/10.1002/slct.202101067).
- [10] A. M. Omer, R. Dey, A. S. Eltaweil, E. M. A. El-Monaem, and Z. M. Ziora. (2022). "Insights into Recent Advances of Chitosan-Based Adsorbents for Sustainable Removal of Heavy Metals and Anions". *Arabian Journal of Chemistry*. **15** (2): 103543. [10.1016/j.arabjc.2021.103543](https://doi.org/10.1016/j.arabjc.2021.103543).
- [11] A. B. Junaidi, I. Kartini, and B. Rusdiarso. (2009). "Chitosan Preparation with Multistage Deacetylation of Chitin and Investigation of Its Physicochemical Properties". *Indonesian Journal of Chemistry*. **9** : 369-372. [10.22146/ijc.21500](https://doi.org/10.22146/ijc.21500).
- [12] D. C. S. Alves, B. Healy, L. A. A. Pinto, T. R. S. Cadaval, and C. B. Breslin. (2021). "Recent Developments in Chitosan-Based Adsorbents for the Removal of Pollutants from Aqueous Environments". *Molecules*. **26** (3): 594. [10.3390/molecules26030594](https://doi.org/10.3390/molecules26030594).
- [13] R. Permana and J. Juniarto. (2021). "Potential Use of Modified Derivative of Chitin and Chitosan on Precious Metal Recovery: A Review". *Journal of Materials Science Research and Reviews*. **7** : 14-24.
- [14] Y. S. Kurniawan, K. T. A. Priyanga, P. A. Krisbiantoro, and A. C. Imawan. (2021). "Green Chemistry Influences in Organic Synthesis: A Review". *Journal of Multidisciplinary Applied Natural Sciences*. **1** (1): 1-12. [10.47352/jmans.v1i1.2](https://doi.org/10.47352/jmans.v1i1.2).
- [15] G. K. Moore and G. A. F. Robert. (1980). "Determination of the Degree of N-Acetylation of Chitosan". *International Journal of Biological Macromolecular*. **2** (2): 115-116. [10.1016/0141-8130\(80\)90040-9](https://doi.org/10.1016/0141-8130(80)90040-9).
- [16] F. Li, C. Bao, J. Zhang, Q. Sun, W. Kong, X. Han, and Y. Wang. (2009). "Synthesis of Chemically Modified Chitosan with 2,5-Dimercapto-1,3,4-thiodiazole and Its Adsorption Abilities for Au(III), Pd(II), and Pt(IV)". *Journal of Applied Polymer Science*. **113** (3): 1604-1610. [10.1002/app.30068](https://doi.org/10.1002/app.30068).
- [17] H. Shariffard, F. Z. Ashtiani, and M. Soleimani. (2012). "Adsorption of Palladium and Platinum from Aqueous Solutions by Chitosan and Activated Carbon Coated with Chitosan". *Asia-Pacific Journal of Chemical Engineering*. **8** (3): 384-395. [10.1002/apj.1671](https://doi.org/10.1002/apj.1671).
- [18] T. G. Asere, S. Mincke, K. Folens, F. V. Bussche, L. Lapeire, K. Verbeken, P. V. D. Voort, D. A. Tessema, G. D. Laing, and C. V. Stevens. (2019). "Dialdehyde Carboxymethyl Cellulose Cross-linked Chitosan for The Recovery of Palladium and Platinum from Aqueous Solution". *Reactive and Functional Polymers*. **141** : 145-154. [10.1016/j.reactfunctpolym.2019.05.008](https://doi.org/10.1016/j.reactfunctpolym.2019.05.008).
- [19] K. Fujiwara, A. Ramesh, T. Maki, H.

- Hasegawa, and K. Ueda. (2007). "Adsorption of Platinum(IV), Palladium(II) and Gold(III) from Aqueous Solutions onto L-lysine Modified Crosslinked Chitosan Resin". *Journal of Hazardous Materials*. **146** (1–2): 39-50. [10.1016/j.jhazmat.2006.11.049](https://doi.org/10.1016/j.jhazmat.2006.11.049).
- [20] L. Zhou, J. Liu, and Z. Liu. (2009). "Adsorption of Platinum(IV) and Palladium (II) from Aqueous Solution by Thiourea-modified Chitosan Microspheres". *Journal of Hazardous Materials*. **172** (1): 439-446. [10.1016/j.jhazmat.2009.07.030](https://doi.org/10.1016/j.jhazmat.2009.07.030).
- [21] A. Ramesh, H. Hasegawa, W. Sugimoto, T. Maki, and K. Ueda. (2008). "Adsorption of Gold(III), Platinum(IV) and Palladium(II) Onto Glycine Modified Crosslinked Chitosan Resin". *Bioresource Technology*. **99** (9): 3801-3809. [10.1016/j.biortech.2007.07.008](https://doi.org/10.1016/j.biortech.2007.07.008).
- [22] S. Y. Bratskaya, A. Y. Ustinov, Y. A. Azarova, and A. V. Pestov. (2011). "Thiocarbamoyl Chitosan: Synthesis, Characterization and Sorption of Au(III), Pt (IV), and Pd(II)". *Carbohydrate Polymers*. **85** (4): 854-861. [10.1016/j.carbpol.2011.04.008](https://doi.org/10.1016/j.carbpol.2011.04.008).
- [23] M. L. Arrascue, H. M. Garcia, O. Horna, and E. Guibal. (2003). "Gold Sorption on Chitosan Derivatives". *Hydrometallurgy*. **71** (1–2): 191-200. [10.1016/S0304-386X\(03\)00156-7](https://doi.org/10.1016/S0304-386X(03)00156-7).
- [24] Y. Kanai, T. Oshima, Y. Baba. (2008). "Synthesis of Highly Porous Chitosan Microspheres Anchored with 1,2-Ethylenedisulfide Moiety for The Recovery of Precious Metal Ions". *Industrial & Engineering Chemistry Research*. **47** (9): 3114-3120. [10.1021/ie070235k](https://doi.org/10.1021/ie070235k).
- [25] E. Guibal, N. V. O. Sweeney, T. Vincent, and J. M. Tobin. (2002). "Sulfur Derivatives of Chitosan for Palladium Sorption". *Reactive and Functional Polymers*. **50** (2): 149-163. [10.1016/S1381-5148\(01\)00110-9](https://doi.org/10.1016/S1381-5148(01)00110-9).
- [26] M. Ruiz, A. Sastre, and E. Guibal. (2002). "Pd and Pt Recovery using Chitosan Gel Beads. I. Influence of The Drying Process on Diffusion Properties". *Separation Science and Technology*. **37** (1–2): 2143-2166. [10.1081/SS-120003506](https://doi.org/10.1081/SS-120003506).
- [27] P. Chassary, T. Vincent, J. S. Marcano, L. E. Macaskie, and E. Guibal. (2005). "Palladium and Platinum Recovery from Bicomponent Mixtures using Chitosan Derivatives". *Hydrometallurgy*. **76** (1–2): 131-147. [10.1016/j.hydromet.2004.10.004](https://doi.org/10.1016/j.hydromet.2004.10.004).
- [28] S. G. Kou, L. M. Peters, and M. R. Mucalo. (2021). "Chitosan: A Review of Sources and Preparation Methods". *International Journal of Biological Macromolecules*. **169** : 85-94. [10.1016/j.ijbiomac.2020.12.005](https://doi.org/10.1016/j.ijbiomac.2020.12.005).