JFCN
JOURNAL OF FOOD, CULINARY, AND NUTRITION
RESEARCH ARTICLE

Study of Pectin Capability to Adsorb Cd(II) In Aqueous Solution and Its Selectivity with Zn Mineral

Meiliana, Mellia Harumi*
Department of Food Technology, Soegijapranata Catholic University, Semarang, Indonesia
**Corresponding author, email: mellia@unika.ac.id*

ABSTRACT
The polluted environment leads to food chain contamination and risk to human health. As an eco-friendly adsorbent, pectin has been studied to adsorb Cd(II) and other heavy metal ions effectively. It has the potential to prevent heavy metal ions absorption but might interfere mineral absorption during the digestive process. This research aimed to analyze the ability of pectin to adsorb Cd(II) ions in multi metal solutions at stomach condition (pH 2) and small intestine condition (pH 6) with competition to other mineral Zn as essential nutrient. About 0.2 grams of pectin was dispersed into multi metal solution 32 ppm of Cd(II) and 1 ppm of Zn(II) in pH 2 and 6. Metal ions were analyzed using Atomic Absorption Spectroscopy (AAS). The result proved that pectin can adsorb 0.32 ppm (29.03%) of Zn(II) and 13.8 ppm (38.87%) of Cd in pH 2. Pectin was more selective to adsorb Zn(II) in pH 6 where minerals were absorbed. This analogue result also provided distribution coefficient (D) which lead to the increasing of pectin selectivity towards Zn(II) with increasing of pH. The very high performance of pectin was selective for Cd in pH 2 $\alpha_{Cd/Zn}$ of 1.55.

KEYWORDS: *Pectin, Cd(II), Zn(II), Adsorption*

Introduction

The massive industrial growth and improper waste management have caused heavy metal pollution. Heavy metals could be produced by electronic waste (Ni, Au, Ag) and illegal mining (Pb, Cd, and Hg). High concentration of heavy metal ions generally damages both aquatic and terrestrial organism (Harumi et al., 2019). In agriculture, accumulation of high concentration in fertilizer and water contaminate crop products will impact to the human health (Briffa, Sinagra, & Blundell, 2020; Vardhan, Kumar, & Panda, 2019). Living in such polluted environment, marine bivalve molluscs such as scallops and oysters contain heavy metal ions and are considered as a potential biomonitor for heavy metal contamination in the marine ecosystem (Singh & Gupta, 2021). Scallops filter particles from water and can accumulate Cadmium (Cd) from sediment and harmful substances. Hence, they become the indicator of environmental contamination from cadmium (Khan et al., 2015). Cadmium is a highly toxic pollutant and human could accumulate up to 30 mg of Cd in 50 years old. This leads to the serious accumulation in human and animal metabolic from food chain (Mezynska & Brzoska, 2018; Hezbullah et al., 2016).

Both conventional methods and novel treatment strategies are needed for removal of heavy metals in order to prevent adverse health effects (Vardhan, Kumar, & Panda, 2019). Previous studies have been conducted several methods to remove heavy metal ions such as sedimentation, ion exchange, filtration, and biosorption. Biosorption are considered as effective, simple, and eco-friendly method. Pectin as one of the bio-sorbent to adsorb heavy metal ions such as Pb^{2+}, Cd^{2+}, Zn^{2+}, Hg^{+} (Wang et al., 2019). As water-soluble fiber, pectin could be obtained from banana, orange, and other fruit peels which have higher

Received: 27/04/2022
Accepted: 22/05/2023
Published: 07/03/2024

concentration than its flesh (Tuhuloula et al., 2013). Pectin is the most interesting polysaccharides with low cost adsorbent, renewable nature, and abundance. Plant based, such as fruit peel and pulp, sugar beet, sunflower heads are the sources of pectin (Lessa et al., 2017). Biopolymer such as pectin has high capabilities for adsorption process and be a promising adsorbent extracted from agricultural waste (Shahrin et al., 2021). Hydroxyl, carboxyl, and methoxy are main active groups in pectin which can be used to bind heavy metal ions. To improve the adsorption properties, many materials have been modified to imropve physicochemical properties of pectin ability for heavy metal adsorption. For example, to obtain better properties of Pb(II) ions adsorption, pectin-based microspheres were prepared by adding different proportions of active carbon (Wang et al., 2021).

Hastuti and Totiana (2017) have synthesized pectin from carrot peel to adsorb Pb(II) ions and obtained the maximum adsorption in pH 6 with the main functional group is carboxyl. The main constituent of pectin is galacturonic acid polymer which has strong influence in adsorption process. -COO- groups has negatively charged that can be interacted with positively charged of heavy metal ions (Arifiyana and Devianti, 2021). Adsorption is based on the interaction between -OH and -COOH functional groups with pectin surface. However, interaction between pectin surface and heavy metal ions may occur with electrostatic interaction, chelation, or ion exchange (Wang et al., 2019). Metal ions has specific charge such as cation or anion in every pH conditions. pH is an important parameter that influence physical-chemical process of adsorption. Characteristic of metals and active sites on the surface of materials depend on this parameter (Lopez et al., 2021). At low pH, carboxyl groups will be protonated and decrease metal ions binding activity (Wang et al., 2019). Souhoka et al (2021) conducted adsorption process using pectin extraction from cocoa to adsorp Cd(II) ions and found the optimum adsorption is in pH 11. In the other hand, different surface material also give different optimum of pH. Adsorption of Cd(II) using Bio-charcoal from Durian Barks give the optimum pH of adsorption is pH 7 (Napitupulu et al., 2018). The optimum pH condition for Cd removal using pectin beads in several research is in acid condition range from pH 3-4 (Lessa et al., 2017). This pH condition leads to the possible study for effectiveness and selectivity of pectin as bio-sorbent of Cd(II) and its competition with Zn as essential mineral at different pH in human metabolic such as stomach and small intestine.

Materials and Method

Materials

Pectin commercial from citrus peel used in this study was low methoxyl (CP Kelco GENU). This study used all reagents in analytical grade from Merck Co Inc. (Germany). The multi metal solutions of Cd(II) and Zn(II) were made from 1000 ppm of Cd and $ZnCl_2$. HCl and NaOH 0.1 M were also prepared to make pH condition for multi metal solutions. Concentration of Cd(II) and Zn(II) in sample were analyzed using Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer).

Instrumentation

This research used Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer).

Procedure

Multi metal solutions were prepared by dissolved Zn and Cd in aqueous solutions into 5 and 32 ppm. The solutions were made in pH 2 and 6 condition, according to the model condition for stomach and small intestine in human metabolic (Koziolek et al., 2014). The amount of 5 ppm of Zn and 32 ppm of Cd were determined based on the common research of Zn and Cd contamination in scallops in Semarang Area. About 0,2 g of pectin was added and shaked 37 °C for 3h 150 rpm. The mixture was then centrifuged for 10 minutes 2000 rpm. Analyte and solid were filtrated, and solid phase were dried in oven 150 °C for 24 h. Dry solid phase was furnaced 550 °C for 8 h followed by dissolved in HNO_3 5 mL 25% before AAS analysis.

Results and Discussion

Adsorption of Cd(II) and Zn(II) in Various pH

Table 1. displays the adsorbed of Cd(II) and Zn(II) in pectin surface. Based on trends given in Table 1, it can be seen that there were correlations between pH conditions and the ability of pectin as adsorbent to adsorb Cd(II) and Zn(II) in multi metal solutions. The ability of pectin in metal adsorption based is supported by the presence of carboxyl group (-COOH) as functional group which has paired electron to make an interaction with positive charge of metal. The amount of methoxyl was influenced by esterification process. The more the methoxyl groups, the more optimal of pectin adsorption will be. The adsorption was conducted using 2 replications.

Table 1. Adsorption of Cd(II) and Zn(II) in pectin at pH 2 and 6.

Metal	Initial Concentration (ppm)	Adsorption (ppm)	Adsorption (%)
	pH 2 condition		
Cd	35.50	13.8	38.87
Zn	1.09	0.32	29.03
	pH 6 condition		
Cd	32.90	11.43	34.73
Zn	1.11	0.49	44.34

In acid condition (pH <4), the ability pectin to adsorp Zn(II) ions get decrease and will increase with increasing of pH condition. Adsorbent tends to be positively charged due to protonation process (Ekowati et al., 2019) and could not interact with Zn^{2+} species optimally. While in pH 6, Zn still as Zn^{2+} species and will be more interacted with negatively charged of carboxyl groups due to deprotonation process (Wang et al., 2018) and possible to make chelation with metal ions. Zn adsorbed reach 44.34% in pH 6.

Based on the species distribution of Cd(II) ions, the dominant form of Cd(II) are positively charge (Cd^{2+}) in pH 2 and 6 condition (Kosolsaksakul et al., 2014) and lead to the same result of 38.87 and 34.73% respectively. In base condition, Zn(II) ions was more adsorbed than Cd(II) ions. Based on the Hard Soft Acid Base (HSAB) theory, COO- as functional group of pectin surface has hard base character and will be more interacted with Zn^{2+} as hard acid in borderline than Cd^{2+} as soft acid.

Selectivity of Cd(II) and Zn(II) in Various pH

The probability of Cd(II) to be adsorbed on the pectin surface was supported by calculating the distribution coefficient (D) of Cu and Zn at pH 2 and 6. Q is adsorption capacity (mg/g) and Ct is final concentration (ppm). Selectivity coefficient (α) is obtained from ratio between D of Cd(II) towards Zn(II) in accordance to the equation below:

$$D = \frac{Q}{C_t} \quad (1)$$

$$\alpha_{Cd/Zn} = \frac{D_{Cd}}{D_{Zn}} \quad (2)$$

Table 2. Selectivity of Cd(II) and Zn(II) in pectin at pH 2 and 6.

Metal	Q_{max}	D	α (Cd/Zn)
pH 2 condition			
Cd	1.38	0.06	1.55
Zn	0.03	0.04	
pH 6 condition			
Cd	1.14	0.05	0.67
Zn	0.05	0.08	

Distribution coefficient of Zn(II) (D_{Zn}) decreases with the increasing of pH, while Cd(II) is opposite with that. This condition proves that pectin interacts strongly and more selective to adsorb Cd(II) ions in acid conditions (stomach model) and more selective to adsorb Zn in base condition (small intestine model). The amount of selectivity coefficient (α) of Cd(II) towards Zn(II) also decreased from 1.55 in pH 2 into 0.67 in pH 6. This condition proved the main interaction between metal ions and biosorbent. At pH 2 the dominant form of Cd(II) are positively charge (Cd^{2+}) and could make interaction with carboxyl group (-COOH) as functional group of biosorbent.

Conclusion

Pectin has potential to prevent Cd(II) absorption but might interfere mineral Zn absorption during digestive process. Pectin might adsorb more Cd(II) than Zn(II) in stomach condition (pH 2). Adsorption of Zn(II) in small intestine (pH 6) might be interfered due to pectin. Further research is needed to analyze the ability of pectin to adsorb heavy metals and minerals in a continuous model of digestive and absorption system.

Acknowledgements

This research was completed in part of funding by Institute of Research and Community Service, Soegijapranata Catholic University. We thank Felix Sholeh K, Ricky, and Tobias Adriel Yaphet as research assistants of this project.

Conflict of Interest

The authors declare that there is no conflict of interest in this research.

Author Contributions

Meiliana and Mellia Harumi conducted the experiment, calculations, wrote and revised the manuscript. All authors agreed to the final version of this manuscript.

Ethical Statement

Not applicable.

References

Arifiyana, D, & Devianti, V.A. (2021). BIOSORPTION OF Fe (II) IONS FROM AQUEOUS SOLUTION USING KEPOK BANANA PEEL (*Musa acuminate*). *KPK (JURNAL KIMIA DAN PENDIDIKAN KIMIA),* 6(2), 206-214.

Briffa, J., Sinagra, E., & Blundell, R. (2020). Heavy metal pollution in the environment and their toxicological effects on humans. *Heliyon*, 6(9), e04691.

Ekowati, G. W., & Rahmayanti, M. (2019). Kajian Desorpsi Zat Warna Indigosol Blue Dari Adsorben Humin Hasil Isolasi Tanah Gambut Riau, Sumatera. *Analit: Analytical and Environmental Chemistry*, 4(2), 68-75

Harumi, M., Santosa, S.J., & Nuryono. (2019). Recovery of Au(III) from printed circuit board waste by chitosan/SiO2 coated on iron sand magnetic material, *Mater. Today: Proc.*, 19, 1101–1110

Hastuti, B., & Totiana, F. (2017). GREEN ADSORBENT OF PECTIN FROM CARROT PEEL AND ITS APPLICATION AS REMOVAL OF PB(II). *International Journal of Advances in Science Engineering and Technology*, 5(4), 4-7.

Hezbullah, M., Sultana, S., Chakraborty, A.R., & Patwary, M.I. (2016). Heavy metal contamination of food in a developing country like Bangladesh: An emerging threat to food safety. *J. Toxicol. Environ. Heal. Sci.*, 8(1), 1–5

Khan, N.V., Vinh, T.D., kubo, K., Kinh, K.T., & Vinh, D.C. (2015). Assessment Of Lead And Cadmium Contamination By Sediments And Bivalve Species From The Estuaries in Da Nang City, Vietnam. *Journal of Environmental Science for Sustainable Society*, 6, 1

Kosolsaksakul, P., Farmer, J. G., Oliver, I. W., & Graham, M. C. (2014). Geochemical associations and availability of cadmium (Cd) in a paddy field system, northwestern Thailand. Environmental Pollution, 187, 153-161.

Koziolek, M., Grimm, M., Becker, D., Iordanov, V., Zou, H., Shimizu, J., Wanke, C., Garbacz, G., & Weitschies, W. (2015). Investigation of pH and Temperature Profiles in the GI Tract of Fasted Human Subjects Using the Intellicap® System. *Journal of Pharmaceutical Sciences*, *104*(9), 2855–2863. https://doi.org/10.1002/jps.24274

Lessa, E.F., Medina, A.L., Ribeiro, A.S., & Fajardo, A.R. (2020). Removal of multi-metals from water using reusable pectin/cellulose microfifibers composite beads *Arabian Journal of Chemistry*, 13, 709–720

Lopez, L.P.C., Macena, M., Esteves, B., & Guine, R.P.F. (2021). Ideal pH for the adsorption of metal ions Cr^{6+}, Ni^{2+}, Pb^{2+} in aqueous solution with different adsorbent materials. *Open Agriculture*. 6(1), 115-123

Mezynska, M., & Brzoska, M. M. (2018). Environmental exposure to cadmium—A risk for health of the general population in industrialized countries and preventive strategies. *Environmental Science and Pollution Research*, 25(4), 3211-3232.

Napitupulu, M., Walanda, D.K., Natakusuma, Y., Basir, M., & Mahfudz. (2018). Capacity of Adsorption of Cadmium (II) Ion by Bio-charcoal from Durian Barks. *J. Surface Sci. Technol.* 34(1–2), 30-36.

Shahrin, E.W.E., Narudin, N.A.H., Padmosoedarso, K.M., Kusrini, E., Mahadi, A.H., Shahri, N.N.M., & Usman, H. (2021). Pectin derived from pomelo pith as a superior adsorbent to remove toxic Acid Blue 25 from aqueous solution. *Carbohydrate Polymer Technologies and Applications*, 2, 1-9.

Singh, P. P., & Gupta, S. M. (2021). MOLLUSCS AS BIOMONITORS OF HEAVY METAL POLLUTION: A REVIEW. *Journal of Advanced Scientific Research*, 12.

Souhoka, F.A., Tanasale, M.F.J.D.P., & Tomia, S. (2021). Pectin extraction from cocoa (*Theobroma cacao* L) pod husk and its application as cadmium (Cd) metal adsorbent. *AIP Conference Proceedings*, 2360(1).

Tuhuloula, A., Budiyarti, L., & Fitriana, A.N. (2013). Karakterisasi Pektin Dengan Memanfaatkan Limbah Kulit Pisang Menggunakan Metode Ekstraksi, *J. Konversi*, 2(1), 21–27.

Vardhan, K. H., Kumar, P. S., & Panda, R. C. (2019). A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives. *Journal of Molecular Liquids*, *290*, 111197.

Wang, E., Yan, Z., Liu, Q., Gao, J., Liu, M. & Sun, G. (2018). *Research and Development of Metal-Air Fuel Cells. In Anion Exchange Membrane Fuel Cells* (pp. 285-323). Springer, Cham.

Wang, R., Liang, R., Dai, T., Chen, J., Shuai, X., and Liu, C. (2019). Pectin-based adsorbents for heavy metal ions: A review, *Trends Food Sci. Technol.*, 91, 319–329.

Wang, R. S., Li, Y., Shuai, X. X., Liang, R. H., Chen, J., & Liu, C. M. (2021). Pectin/activated carbon-based porous microsphere for Pb^{2+} adsorption: Characterization and adsorption behaviour. *Polymers*, 13(15), 2453.

Cite this article: Meiliana, & Harumi, M. (2024). Study of Pectin Capability to Adsorb Cd(II) In Aqueous Solution and Its Selectivity with Zn Mineral. *Journal of Food, Culinary, and Nutrition*, 1(1), 27-32.