EFFECT OF PH AND ADSORBENT DOSES ON MN (II) METAL ADSORPTION IN THE KALIGARANG RIVER SEMARANG CITY USING SYNTHETIC COCONUT SHELL POWDERED ACTIVATED CARBON (PAC)

Irene Nindita Pradnya*, Bayu Triwibowo, Ria Wulansarie, Ririn Hanifah, Iffat Ganjar Fadhila Prakasita

Departement of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Kampus Sekaran, Gunungpati, Semarang, 50229, Indonesia

*Email: irene.nindita@mail.unnes.ac.id

Abstract

Kaligarang River is the largest river in the Semarang, which looks clear but actually containing Mn metal above the permitted threshold. Excessive presence of Mn metal can cause problems for human being inside the brain (Parkinson's syndrome), liver, and kidneys. The aim of the study was to analyze the effect of the adsorbent dose and the pH of the solution containing Mn metal. The river water sample was tested at Tirta Moedal PDAM, Semarang; contaminated 1.075 mg/L heavy metal Mn. Based on Government Regulation No. 82 of 2001, the maximum allowable concentration of Mn in water is 0.1 mg/L. Adsorption with activated carbon is an effective method in processing Mn metal pollution. Activated carbon formed as powder from coconut shell size of 500 microns. The adsorption process was with a contact time of 90 minutes and a stirring speed of 210 rpm. The pH variables were pH 3, 7, and 12 and the adsorbent dose was 1, 5, 10 and 15 g /L. The adsorption results showed that the optimum conditions of the adsorption process occurred at pH 3 with an adsorbent dose of 15 g / L with percent absorption of Mn metal of 87.18%.

Keywords: *Activated carbon, Adsorption, Manganese*

INTRODUCTION

Kaligarang River is the largest river that flows in the middle of Semarang city. Various residents activities are found along this river, such as fishing, food industry, textile industry, iron smelting, ceramics industry, pharmacy, hospital, and landfill (Kurniawati., 2017). These activities can produce waste that will increase heavy metals pollution, BOD and COD number reserves in the waterbody and dyes contamination from textile industry. Heavy metal is one of the most dangerous pollutions that can harm the ecosystem.

The river-water sample testing, that is conducted at Tirta Moedal PDAM, Semarang City; showed that the Kaligarang River was contaminated with heavy metal Mn above the permitted threshold of 1.075 mg/L. The presence of Mn metal in a flowing river was observed due to the waste of ceramic industry, metal coating industry, drug industry, and paint industry. The toxicity, bioaccumulation also persistence of heavy metals contamination in the river and its sediment at the bottom, especially developed at high concentrations, is a serious warning. In addition, fish are located at the end of the aquatic food chain and may accumulate metals and pass them to human beings through food causing chronic or acute diseases.

Based on Government Regulation No. 82 Year 2001, the maximum permissible concentration of Mn in the waterbody is 0.1 mg / L, while the concentration of Mn metal in the Kaligarang River has reached 1.075 mg / L. Excessive presence of Mn metal can cause problems for human being, which can agglomerate inside the brain, liver, and kidneys, cause the onset of parkinsonism, and damage the central nervous system (Niemiec & Wiśniowska-Kielian, 2015).

Various attempts have been made to overcome battle of Mn metal waste in rivers, amongst are using membrane filtration (Kasim *et al.*, 2017), electrocoagulation (Ganesan., 2013), and adsorption technique (Idrees et al., 2018). The adsorption method has many advantages which the cost required is relatively cheap, efficient, practical, and also can be reused (Monteiro *et al*., 2017).

Activated carbon is an adsorbent that is often used in the adsorption process because it has many advantages that have high complexity that can adsorb high amount of molecules and are stable

ISBN 2528-5912

(Lakshmi *et al.*, 2018). Moreover, activated carbon from biomass waste has a cheap and reasonable cost that is fully supported to be developed.

Coconut shell is a potential material made from activated carbon because it contains 36.3% cellulose, 25.1% hemicellulose, and 28.7% lignin (Dhyani & Bhaskar, 2018). In addition, coconut shells also have a low ash content of 0.7%, low prices (Zhao *et al.*, 2018), have high density and high purity, also contain resources that can be renewed (*Bharadwaj*., 2007)

Activated carbon made from coconut shell has several advantages, including having a uniform pore structure distribution, having high hardness so that it is good for water purification, environmentally friendly because it comes from organic matter (Bharadwaj *et al*., 2007). Activated carbon from coconut shell also is harder, more micropores, resistant to abrasion, and has a lower ash content than coal activated carbon (Ratnoji & Singh, 2014)

Based on its size, there are several types of activated carbon, namely granules, powders, and pellets (Gamal *et al.*, 2018). Among these types, powder activated carbon has the advantages of contact surface area per unit weight greater than granular activated carbon and pellets, has better mass transfer and diffusion rates, and more homogeneous particle distribution (Schulz *et al.*, 2017), therefore our research used powdered activated carbon type. Based on the description above, the aim of this research on adsorption of heavy manganese metal (Mn) is to determine the effect of adsorbent dosage on the levels of adsorbed Mn metal and to analyze the effect of the pH of the solution on the levels of adsorbed Mn metal. An alternative technology used in dealing with heavy metal waste in the Kaligarang River is the adsorption method using powdered activated carbon from coconut shells.

METHODS

Tools and materials

The tools used in this study are digital scales, spatulas, watch glasses, measuring pipettes, ball filler, 100 mL measuring flask, 100 mL beaker, erlenmeyer, glass stirrer, filter paper, glass funnel, universal indicator, sieve tray, shakers and Atomic Absorption Spectrophotometry (AAS). While the material used is synthetic Powdered Activated Carbon (PAC) from coconut shell waste, with trademarks Haycarb, NaOH p.a., HCl p.a., aquades and $MnSO_4.H_2O$ p.a. The variables in this study were the pH 3, 7, and 12 and the adsorbent dose of 1 g / L, 5 g / L, 10 g / L and 15 g / L.

Research procedure

Active Carbon Preparation

Sifted Powdered Activated Carbon (PAC), Haycarb-trademark, using a sieve tray to obtain activated carbon with a pore size of 500 microns.

Fomulating Mn (II) solution 10.75 ppm

Ionic solution 1000 ppm Mn (II) was assembled by dissolving 0.307 grams of $MnSO_4.H_2O$ powder into 100 mL of distilled water.

Metal Mn (II) adsorption

Adsorption assessment was carried out via batch adsorption using 10.75 ppm Mn solution. 10.75 mL solution out of 1000 ppm Mn was diluted with 100 mL of distilled water to obtain 107.5 ppm Mn solution. Then 10 mL of 107.5 ppm Mn solution was diluted with 100 mL of distilled water so that a 10.75 ppm Mn solution was obtained. 0.05 grams of activated carbon was added with a solution of 50 mL $MnSO_4.H_2O$ with a concentration of 10.75 ppm. The solution is then pH adjusted by adding 1 M HCl or NaOH to adjust pH 3, 7, and 12. This pH represents acidic, neutral, and basic pH. The solution is then shaken using a shaker with a speed of 210 rpm and 90 minutes adsorption time. The solution is then filtered with filter paper to separate the filtrate from the obtained residue. This process is repeated for adsorbent doses of 5, 10, and 15 g / L.

Atomic Absorption Spectrophotometry (AAS) Test

The filtrate obtained was then tested using AAS to determine the concentration of Mn after adsorption.

RESULTS AND DISCUSSION

Effect of pH on the adsorption process

The degree of acidity or pH is an important parameter that needs to be assessed in an adsorption process. This is due to pH affects the metal ion charge and the active site charge of the adsorbent that is used (Idrees et al, 2018). The study of the pH effect on Mn (II) metals adsorption was carried out to determine the optimum pH in order to obtain the maximum adsorption results of Mn (II) metals. Mn (II) metal adsorption in this study was carried out at variations of pH 3, 7 and 12, which represented acidic, neutral and basic pH. The results of research on the effect of pH on the adsorption of Mn (II) metal are shown in Figure 1.

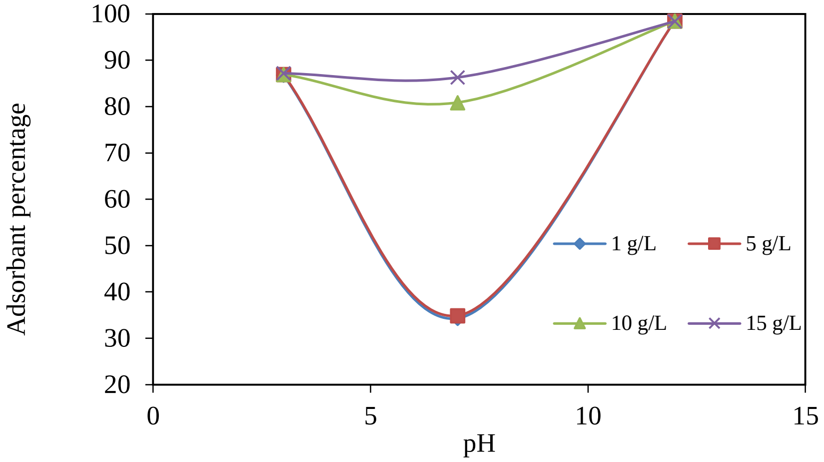

Figure 1. Effect of pH on various doses of adsorbent

Figure 1 shows the graph of the pH influence on the percentage of Mn (II) metal absorption. Mn (II) metal adsorption with activated carbon at pH 3 gives adsorption results with a percentage of 86.78%, 86.92%, 86.91% and 87.18%. Mn (II) metal adsorption with activated carbon at pH 7 gives results with a percentage of 34.33%, 34.88%, 80.85% and 86.28%. While the adsorption of Mn (II) metal at pH 12 gives the results with percentages of 98.5%, 98.43%, 98.42% and 98.4%.

The results showed the same characteristics in all four adsorbent doses where the acidic pH yielded a high percentage of adsorption, at neutral pH the percentage of adsorption decreased significantly, then the percentage of adsorption rose again with the increase in pH of the solution becoming alkaline.

Mn (II) metal adsorption under acidic conditions with a pH of 3 gives a high percentage of adsorption results at four different doses. This can be due to the pH 3, the adsorbent active site has not been protonated properly and there are not many H^+ ions that bind to the adsorbent active site so that competition between the metal ions Mn and H^+ ions to bind to the active adsorbent site does not occur significantly. This condition causes the adsorbent to absorb more Mn (II) metal because many active sites are still empty.

Adsorption test under alkaline conditions with pH 12 gives a decrease result in metal Mn (II), which is higher than acidic conditions with an average reduction percentage of 98.4%. The high loss of metal Mn (II) in solution is due to the alkaline pH, the metal ion Mn (II) in the solution experiences precipitation where the precipitate formed is filtered along with activated carbon residues during the screening process after the adsorption test.

This situation causes the level of metal Mn (II) in the solution to decrease. The occurrence of Mn (II) metal precipitation is caused by the reaction between the Mn^{2+} ion and the OH^- ion from the addition of NaOH solution. The Mn^{2+} ion will react with the OH^- ion from the NaOH solution to form a brown precipitate that does not dissolve in excess reagents. The depositional reaction equation that occurs is as follows (Leonard, 1990) :

$$Mn^{2+} + 2\,OH^- \rightarrow Mn(OH)_2\downarrow$$

ISBN 2528-5912

Precipitation of the metal Mn (II) to $Mn(OH)_2$ causes the adsorption efficiency at pH 12 to decrease because the deposits can close the pore of activated carbon so that it interferes with the adsorption process. Mn (II) metal adsorption at pH 7 shows different results, where at this pH the percentage of Mn (II) metal absorption tends to decrease. This is because at neutral pH metal ions in solution can undergo hydrolysis reactions which cause metal ions to be difficult to absorb because they are unstable (Nurafriyanti *et al*., 2017). This condition causes the absorption efficiency of metal Mn (II) at neutral pH tends to decrease.

Based on the explanation above, it can be seen that in this study the optimum absorption of Mn (II) metal using activated carbon was achieved at pH 3 and adsorbent dose of 15 g / L with an adsorption percentage of 87.18%. The results of this study are relevant to the results of previous studies conducted by (Mengistie *et al*., 2012) on the adsorption of metal Mn (II) using activated carbon from birbira leaves where the optimal adsorption results of metal Mn (II) were reached at pH 3.

Effects of Adsorbent Doses on Mn (II) Metal Adsorption

The effect of activated carbon dose on the adsorption of Mn (II) metal can be determined by the adsorption of 10.75 ppm Mn (II) solution at the optimal pH of adsorption using a variation of activated carbon mass of 1, 5, 10, and 15 g / L. Mn (II) metal adsorption is done by adding activated carbon to 50 mL of sample solution with a concentration of Mn (II) of 10.75 ppm. Adsorption was carried out with a contact time of 90 minutes at the optimum pH, namely pH 12 with a stirring speed of 210 rpm. After 90 minutes, the filtered filtrate was then analyzed the remaining metal content of Mn (II) by using Atomic Absorption Spectroscopy (AAS). The effect of activated carbon dose on the absorbed Mn (II) level is shown in Figure 2.

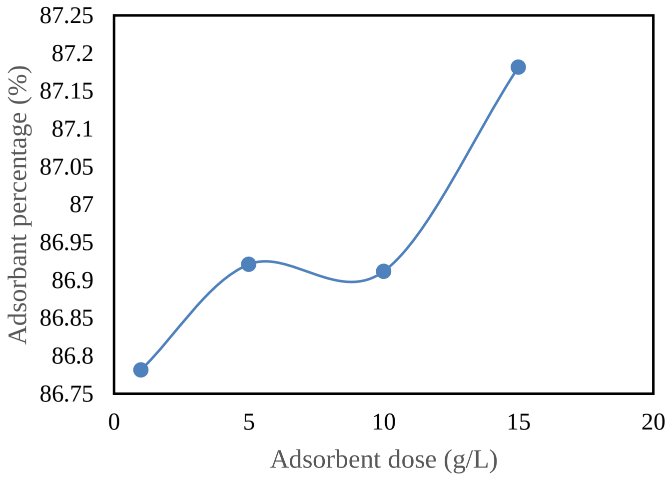

Figure 2. Effect of adsorbent dose with percent adsorbed

Figure 2 shows that the more adsorbent mass is added, the higher percent adsorption. The biggest percent absorption is obtained at the mass of the adsorbent 15 g / L that is equal to 87.18%. This is because the active site or surface area of the adsorbent increases with the increase in the adsorbent mass, so that more adsorbate is absorbed (Pandia & Warman, 2016)

CONCLUSION

The more mass of adsorbent activated carbon is added, the higher Mn (II) metal adsorption efficiency is. The highest Mn (II) metal adsorption results were achieved at adsorption using a 15 g/L adsorbent dose with an adsorption percentage of 87.18%. In addition, the highest Mn (II) metal adsorption results were achieved at pH 3 with the highest absorption percentage of 87.18%.

ACKNOWLEDGMENTS

The authors would like to thank Faculty of Engineering, Universitas Negeri Semarang for the financial support from DIPA FT UNNES.

REFERENCES

Bharadwaj, N. D., Mishra, P., Jain, R., & Uchchariya, D. (2007). Use of activated carbon of coconut shell (cocos nucifera) for reduction of chloride and hardness of water. *International Advanced Research Journal in Science, Engineering and Technology ISO*. https://doi.org/10.17148/IARJSET.2016.3815

Dhyani, V., & Bhaskar, T. (2018). A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renewable Energy*. https://doi.org/10.1016/j.renene.2017.04.035

Gamal, M. El, Mousa, H. A., El-Naas, M. H., Zacharia, R., & Judd, S. (2018). Bio-regeneration of activated carbon: A comprehensive review. *Separation and Purification Technology*. https://doi.org/10.1016/j.seppur.2018.01.015

Ganesan, P., Lakshmi, J., Sozhan, G., & Vasudevan, S. (2013). Removal of manganese from water by electrocoagulation: Adsorption, kinetics and thermodynamic studies. *Canadian Journal of Chemical Engineering*. https://doi.org/10.1002/cjce.21709

Idrees, M., Batool, S., Ullah, H., Hussain, Q., Al-Wabel, M. I., Ahmad, M., Kong, J. (2018). Adsorption and thermodynamic mechanisms of manganese removal from aqueous media by biowaste-derived biochars. *Journal of Molecular Liquids*. https://doi.org/10.1016/j.molliq.2018.06.049

Kasim, N., Mohammad, A. W., & Abdullah, S. R. S. (2017). Iron and manganese removal by nanofiltration and ultrafiltration membranes: influence of ph adjustment. *Malaysian Journal of Analytical Science*. https://doi.org/10.17576/mjas-2017-2101-17

Kurniawati, S., Nurjazuli, N., & Raharjo, M. (2017). Risiko kesehatan lingkungan pencemaran logam berat kromium heksavalen (Cr VI) pada ikan nila (*Oreochromis niloticus*) di aliran Sungai Garang Kota Semarang. *Higiene: Jurnal Kesehatan Lingkungan, 3 No 3,* 153–160. Retrieved from http://journal.uin-alauddin.ac.id/index.php/higiene/article/view/4654

Lakshmi, S. D., Avti, P. K., & Hegde, G. (2018). Activated carbon nanoparticles from biowaste as new generation antimicrobial agents: A review. *Nano-Structures and Nano-Objects*. https://doi.org/10.1016/j.nanoso.2018.08.001

Leonard, M. . (1990). Vogel's textbook of quantitative chemical analysis. 5th edn. In *Endeavour*. https://doi.org/10.1016/0160-9327(90)90087-8

Mengistie, A. A., Rao, T. S., & Rao, A. V. P. (2012). Adsorption of Mn(II) ions from wastewater using activated carbon obtained from birbira (*Militia ferruginea*) leaves. *Global Journal of Science Frontier Research Chemistry*, *12*(1), 5–11.

Monteiro, M. S., de Farias, R. F., Chaves, J. A. P., Santana, S. A., Silva, H. A. S., & Bezerra, C. W. B. (2017). Wood (*Bagassa guianensis* Aubl) and green coconut mesocarp (*Cocos nucifera)* residues as textile dye removers (Remazol Red and Remazol Brilliant Violet). *Journal of Environmental Management*. https://doi.org/10.1016/j.jenvman.2017.08.033

Niemiec, M., & Wiśniowska-Kielian, B. (2015). Accumulation of manganese in selected links of food chains in aquatic ecosystems. *Journal of Elementology*. https://doi.org/10.5601/jelem.2015.20.1.808

Nurafriyanti, N., Prihatini, N. S., & Syauqiah, I. (2017). Pengaruh variasi ph dan berat adsorben dalam pengurangan konsentrasi Cr total pada limbah artifisial menggunakan adsorben ampas daun teh. *Jukung (Jurnal Teknik Lingkungan)*. https://doi.org/10.20527/jukung.v3i1.3200

Pandia, S., & Warman, B. (2016). Pemanfaatan kulit jengkol sebagai adsorben dalam penyerapan logam Cd (II) pada limbah cair industri pelapisan logam. *Jurnal Teknik Kimia USU*.

Ratnoji, S. S., & Singh, N. (2014). A study of coconut shell - activated carbon for filtration and its comparison with sand filtration. *International Journal of Renewable Energy and Environmental Engineering*.

Schulz, M., Bünting, S., & Ernst, M. (2017). Impact of powdered activated carbon structural properties on removal of organic foulants in combined adsorption-ultrafiltration. *Water (Switzerland)*. https://doi.org/10.3390/w9080580

Zhao, X., Zeng, X., Qin, Y., Li, X., Zhu, T., & Tang, X. (2018). An experimental and theoretical study of the adsorption removal of toluene and chlorobenzene on coconut shell derived carbon. *Chemosphere*. https://doi.org/10.1016/j.chemosphere.2018.04.126