Journal of Data Analytics, Information, and Computer Science (JDAICS)
Volume 2, No 1 – Januari 2025
e-ISSN : 3032-4696

ADSORPTION OF MERCURY (II) FROM AQUEOUS SOLUTION BY CRUMB RUBBER SLUDGE: ISOTHERM AND KINETIC STUDIES

Monik Kasman[1*], Hadrah Hasan[2], Titania Eno Widyaningsih[3]
[1,2,3]University of Batanghari, Indonesia
[1]monik.kasman@unbari.ac.id, [2]hadrah.hasan@gmail.com, [3]enotitania@gmail.com

Received: 28-12- 2024	Revised: 15-01-2025	Approved: 20-01-2025

ABSTRACT

The use of two different crumb rubber adsorbent (CRS), pure crumb rubber sludge (pCRS) and modified crumb rubber sludge (mPCRS) with HNO_3 activator was investigated for the removal of Hg(II) from aqueous solution. Batch experiment was conducted to analyze the effect of adsorbent dosage and contact time on the adsorption capacities of pCRS and mCRS. Adsorption isotherm and adsorption kinetics was also analyzed to get description of the adsorption mechanism and the adsorbent properties. The Langmuir isotherm provided the best correlation with the maximum adsorption capacity was 16.00 mg/g an, 17.513 mg/g for respected to pCRS and mCRS. The kinetics studies showed that the Hg(II) for both adsorbents adsorbed rapidly which can be adjusted to the pseudo second order model. Our current study confirmed that CRS was effective adsorbent for the removal of Hg(II) from aqueous solution which followed monolayer and multilayer chemisorption
Keywords: *Adsorption, Crumb rubber sludge, Isotherm, Kinetic, Mercury*

INTRODUCTION

Adsorption is the most chosen method implemented to reduce various pollutants from wastewater due to its economical, applicable, and environmental friendly. Moreover, numerous adsorbent types have been widely used. One of them is byproduct of wastewater treatment plant (WWTP), or used to be labeled as residue. Residue WWTP was such of a sludge waste produced by biological treatment unit. Which of common method used is activated sludge system.

Recently, the management and disposal of sludge waste of industries WWTP becomes a big problem. Crumb rubber's industries WWTP for instance, deliver 32 tons a month of sludge residue for each industry to landfill (S.Sy et al, 2018). The sludge residue and the active sludge contain similar elements in the forming of microorganism. The microorganisms in sludge residue are dead or dormant due to drying condition. It also contains other contaminants that would be potential hazard to environment such as greenhouse gas emissions and water pollution (S.Sy et al, 2018).

To address these problems, we have been pioneer observing the use of crumb rubber as adsorbent to remove some heavy metals from aqueous solution for some years. It is respected to the similar reports which utilize various industries WWTP's sludge. Some of these are clarified sludge of municipal wastewater (C. Yang, et al, 2010), dairy factory (H. Benaïssa & M. A. Elouchdi, 2011), textile mills (M. Hunsom and C. Autthanit, 2013), cosmetics factory (V. M. Monsalvo, et al, 2011), palm factory (M.A.A. Zaini et al, 2013), high Mn-containing groundwater treatment sludge (S. Zhu et al, 2019), activated sludge graphene oxide composites (C. Zhao et al, 2018), coalmine dry sludge (R. Kumar et al, 2020), swine sludge (J. Liu et al, 2020), sewage sludge (J. Ifthikar *et al, 2017)* and dry activated sludge (H. Zare, 2015).

Our earlier interesting studies showed that crumb rubber industries WWTP's sludge residue (CRS) was good adsorbent either modified or unmodified. There

were three types of adsorbent, as labeled pure sludge (PS), chemically activated sludge (WS) and pyrolysis activated sludge (P600) treated some heavy metals form aqueous solution in several shaken conical flasks. The results indicated that CRS reduced Cr(VI), Cd(II) and Zn(II) (S. Sy et al, 2018), with high adsorption capacities.

The continuous studies have been conducted by observing the ability of CRS in removal of mercury. Mercury, in accordance of its nature, is the most severe toxic heavy metals. It has longer endurance, easier transferred, and easier accumulated (D. Patiño-Ruiz, 2019), (N. M. Mora Alvarez et al, 2019), (M. Arshadi, 2015). The organic and inorganic mercury can be dangerous for human health such as central nervous, reproductive, retinal nerve system, human kidney and liver (N. M. Mora Alvarez , 2018), (Y. Guo et al, 2016), (G. Tan et al, 2016).

Thus, our current study focused on the potential of CRS with modified or without modified in removal of mercury (Hg(II)) from aqueous solution. The effect of adsorbent dosage and contact time to batch adsorption experiment was investigated. The mechanism of adsorption was fitted to the Langmuir and Freundlich models. It was followed by analyzing of adsorption kinetics using first order and pseudo second order model.

RESEARCH METHODS

Crumb Rubber Adsorbent

Adsorbent was made from crumb rubber activated sludge waste of crumb rubber industry (crumb rubber sludge - CRS). It was a byproduct of biological processing unit of Wastewater Treatment Plant (WWTP) which was collected from final clarifier of WWTP of PT. Djambi Waras, Jambi City.

The preparation method refers to previous method done by [2], but raw CRS was dried longer than that of it. After sun drying, it was oven dried (Memmert UNB 300) for 8 hours in 9 days within 110^{o}C. Dried raw CRS was ground and sieved using siever merk Retsch 5657 Haun W. Germany no. 35 mesh (0.425 mm). This raw CRS – the first type was labeled the pure CRS (pCRS).

The For modified CRS (mCRS), the second type of adsorbent, pCRS was soaked in 0.01 M nitric acid (HNO_3) for 2 hours to remove impurities. The soaked pCRS was then cleansed with distilled water to the neutral pH of water. Finally, it was dried in 70^{o}C - 100^{o}C. The two adsorbents were kept in container.

Mercury(II) Aqueous Solution

The adsorption experiment of the prepared CRS adsorbent on Hg(II) ion is investigated using an aqueous solution of the metal. The stock solution of Hg(II) (1000 mg/l) was prepared by dissolving the necessary amount of $HgSO_4$ in distilled water. The stock solution was diluted to obtain standard solutions 20 mg/l of Hg(II).

Adsorption Experiment

Batch adsorption studies are carried out in five beaker glasses with 20 mg/l of Hg(II) solution filled with varying amount of adsorbent dosage (1, 2, 3, 4 and 5 g/L) under room temperature. These beakers were agitated by flocculator jar test within certain speed time (60, 100, 120, 150 and 180 RPM) for predetermined time intervals (15, 30, 45, 60 and 75 minutes). At the end of agitation, the suspensions are filtered through Whatman 42 filter paper to be analyzed for the remaining metal concentration in the sample using Atomic Absorption

Spectrophotometer GBC 932 AA. Each determination is performed in duplicate. Blank determinations are made simultaneously with samples under the same experimental conditions.

The amount of Hg(II) adsorbed per unit mass of the adsorbent was determined as the following equation:

$$Q_e = \frac{C_i - C_e}{M} V \qquad (1)$$

Where Qe is the amount of Hg(II) adsorbed per unit mass of the adsorbent (mg/g), V is the volume of the aqueous solution (L), M is the mass of the adsorbent (g); C_i and C_e are the concentration of Hg(II) in initial solution and equilibrium solution adsorbed for minute in mg/L, respectively.

RESULTS AND DISCUSSIONS

Adsorption Isotherm

The adsorbate – Hg(II) interactions with adsorbent - CRS were described with adsorption isotherm. Its mechanism provides important information about the nature and the affinity of adsorbent. It is obtained by determining the maximum adsorption capacities in equilibrium state. Then, the obtained data were analyzed by modeling using Langmuir and Freundlich models.

In the Langmuir model, adsorbent surface is expected homogeneous. Each active adsorption sites corresponds the magnitude of the adsorption energy magnitude. This site adsorbs each molecule of adsorbates. The Langmuir model is expressed by equation (2). However, the Freundlich model is the most preferred model to explain an asymmetric or heterogeneous adsorption equilibrium data with complex surface structure of adsorbent. The Freundlich model is given by equation (3).

$$Q_e = \frac{Q_o b C_e}{1 + b C_e} \qquad (2)$$

$$Q_e = K_f C_e^{\,n} \qquad (3)$$

Q_o (mg/g) and b (L/mg) are the Langmuir constants which are a measure of maximum adsorption capacity and a measure of energy, respectively. K_f $(mg/g(L/g)^{1/n})$ is the Freundlich constant, describes energy bonds occurring in process. *n* is the heterogeneity factor which represent the degree of divergence from linearity of the adsorption (T. Aprianti et al, 2017).

The Langmuir isotherm can be described by equilibrium constant, RL, which is defined as equation (4). The value of R_L indicates the shape of isotherm to be either unfavorable ($R_L > 1$) or linear ($R_L < 1$) or irreversible ($R_L = 0$).

$$R_L = \frac{1}{(1 + b C_i)} \qquad (4)$$

The illustration of two models of adsorption isotherm is shown in Fig.1. All the constants determined from the non-linear plots (Q_e vs C_e) of two models are

presented in Table 1. From Table 1, it can be seen for both adsorbents (pCRS and mCRS), the Langmuir isotherm fitted better with the experimental data and the adsorption process follows a Langmuir type ($R^2 > 0.99$) monolayer adsorption. The maximum adsorption capacity (Qo) of Hg(II) aqueous solution onto mCRS 17.513 mg/g was higher than that of pCRS 16 mg/g.

However, it was also be noticed that the R^2 for Hg(II) adsorption from Freundlich model was greater than 0.97. These results indicate that adsorption process also occurred in multilayers.

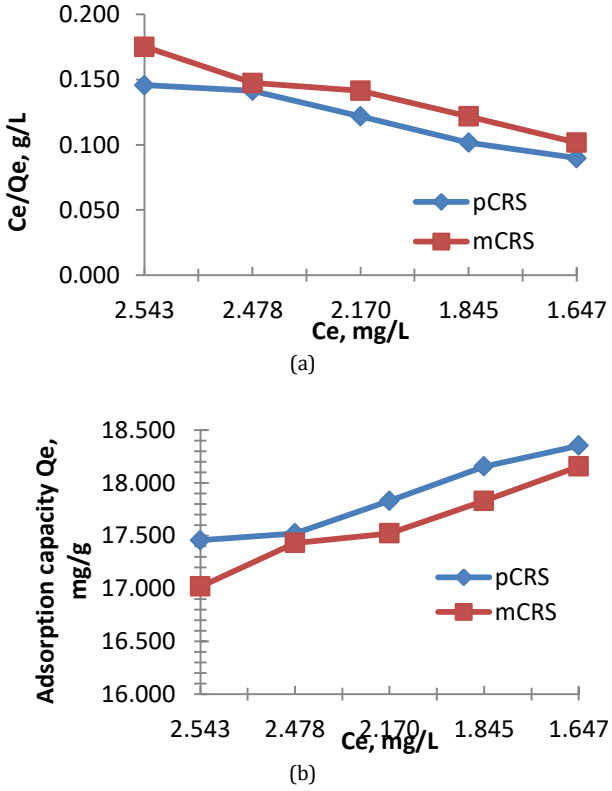

Figure 1. Adsorption isotherm of Hg(II) adsorption onto. (a) Langmuir isotherm model; (b) Freundlich isotherm model

Table 1
Adsorption isotherm model parameters for adsorption of Hg(II) onto pCRS and mCRS

Adsorbent type	Model	Parameters		R^2
pCRS	Langmuir	Qo	16.000	0.9985
		b	4.630	
		R_L	0.011	
	Freundlich	Kf	1.216	0.992
		n	1.388	
mCRS	Langmuir	Qo	17.513	1.000
		b	35.688	
		R_L	0.001	
	Freundlich	Kf	1.417	0.977
		n	1.091	

The constant of *n* calculated from the Freundlich isotherm for pCRS and mCRS was 1.388 and 1.417 respectively, in the range of favorable adsorption (n > 1). It was suggested a high adsorption strength and chemical adsorption, which was consistent with the large R_L value of the Langmuir model (R_L < 1). The two isotherm models revealed that different types crumb rubber sludge adsorbent used in this study can remove Hg(II) aqueous solution in monolayer and multilayer chemical adsorption process.

Adsorption Kinetics

Adsorption kinetics was used to control Hg(II) adsorption process rate at solid-liquid interface. Here, two familiar kinetics models - the pseudo first-order and pseudo-second-order were applied to determine the parameters of adsorption kinetics of Hg(II) adsorption onto pCRS and mCRS. The pseudo first-order and pseudo-second-order equations are expressed in equation 5 and 6 respectively.

$$Log\left(\frac{Q_e}{Q_e - Q_t}\right) = \frac{K_1}{2.303}t \quad (5)$$

$$Q_t = \frac{t}{(1/K_2 Q_e^{\,2}) + (t/Q_e)} \quad (6)$$

Where Q_t (mg/g) is the amount of adsorbed Hg(II) on the adsorbent at time t, K_1 (min^{-1}) is the rate constant of pseudo first order adsorption and K_2 (g.mg/min) is the rate constant of pseudo second order adsorption. The Qe is extrapolated from the experimental data at time t as seen in Fig.2. The representative plots were linearized to obtain the kinetic parameters. The value of Q_e and K_1 were calculated from the intercept and slope of the linear plot of log (Q_e – Q_t) versus t respectively (Fig.2(a)). The value of K_2 was calculated from slope of plot t/Q_e versus t (Fig.2 (b)).

Table 2
Kinetic model constants for adsorption of Hg(II) onto pCRS and mCRS.

Adsorbent type	Model	Parameters		R^2
pCRS	Pseudo First order	K1	0.055	0.4291
		Qe	6.769	
	Pseudo second order	K2	0.054	0.9995
		Qe	11.074	
mCRS	Pseudo First order	K1	0.053	0.299
		Qe	4.337	
	Pseudo second order	K2	0.054	0.9996
		Qe	12.034	

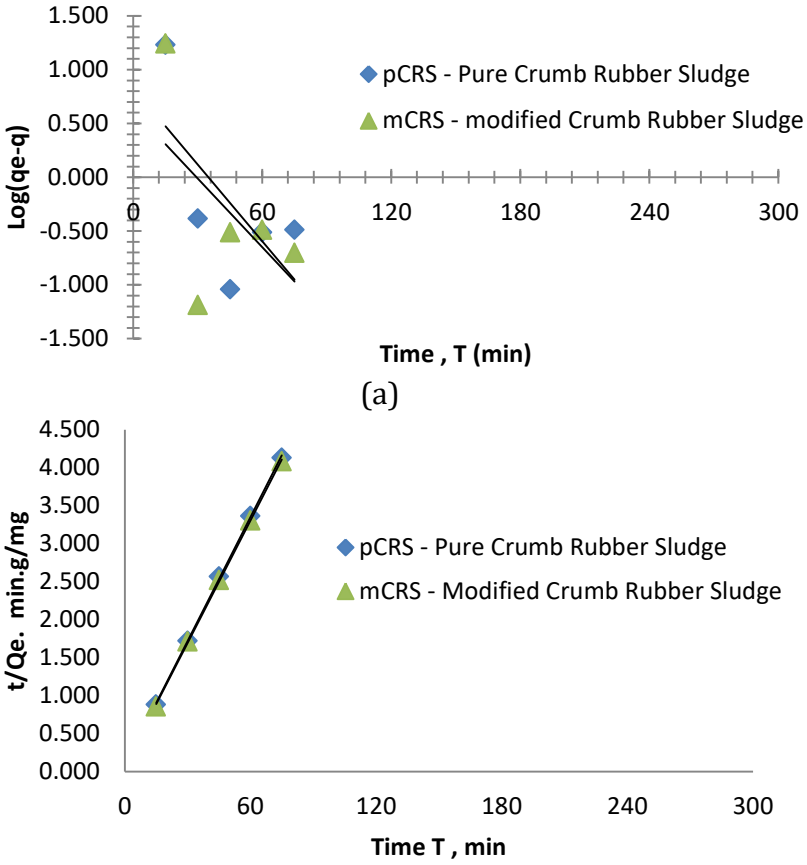

Figure 2. Adsorption kinetics of Hg(II) onto. (a) Pseudo first order model; (b) Pseudo second order model.

Table 2 provides the kinetic parameters and corresponding correlation coefficients of pseudo first order and pseudo second order model for Hg(II) adsorption kinetics. The adsorption of Hg(II) onto pCRS and mCRS was fitted better by pseudo second order model due to the R^2 values are close to 1 (0.999) (Y. Sun et al, 2017). The calculated adsorption capacities (Q_e) in pseudo second order model theoretically was close to the value of real adsorption capacities. It can be concluded that The adsorption Hg(II) onto pCRS and mCRS was following the pseudo second order model under chemisorption process control * T. Sheela et al, 2012), (Y. Fransiscus et al, 2018), (S. Pan et al, 2012).

Effect of Adsorbent Dosage

The results for adsorptive removal of Hg(II) with respect to adsorbent dosage of pCRS and mCRS are shown in Fig.3 over the range 1 – 5 g/L. From Fig.3, shows that the equilibrium adsorption capacities of Hg(II) for both adsorbents were decreased with the increasing of adsorbent dosage. It was due to the exchangeable site on adsorption surface area which is fulfilled with adsorbent pores which function as active binding sites or places for adsorption. Adsorption process begins as the attachment of pollutants contained in the adsorbate to the adsorption surface area. Then it will be absorbed in the adsorbent pores (M. Zahihi et al, 2010), (K.K. Wong et al, 2003) .

According to the results, it was concluded that the interaction between adsorbate and adsorbent highly depends on the adsorbent dosage. For both adsorbent, the adsorption removals were almost the same with the highest percentage reached on 92% and 93% for respected to pCRS and mCRS at 5 g/L of adsorbent dosage. However, the adsorption capacities were the lowest 3.69 mg/g and 3.739 mg/g for pCRS and mCRS respectively.

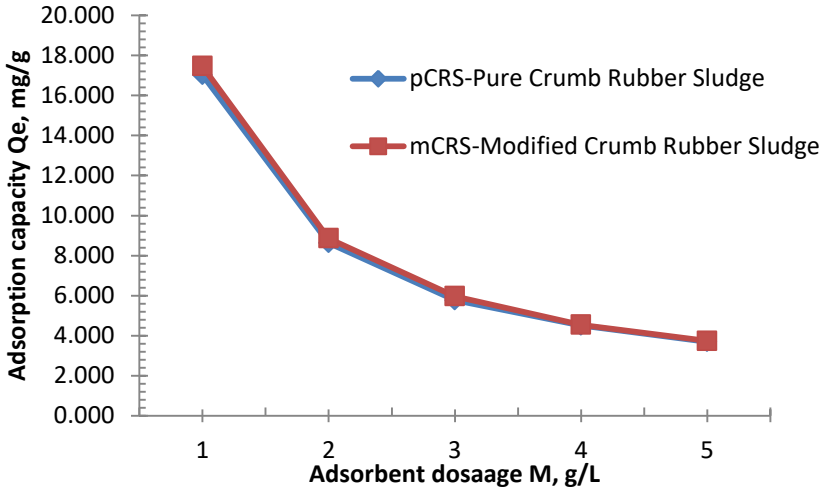

Figure 3. Effect of adsorbent dosage on Hg(II) adsorption

Effect of Contact Time

Fig.3 showed the curve plots of Hg(II) adsorption capacities versus contact time. The adsorption capacities (Qe mg/g) of Hg(II) onto pCRS and mCRS are illustrated as the trend increasing by time extending. The adsorption process increased rapidly, and being stagnant over 30 minutes. External diffusion and surface adsorption was assumed as the reason for this process (E.K. Faulconer et al, 2012). The pollutants transferred rapidly onto the adsorbent surface because the presence of free site for binding on the adsorbent surface (D.K. Mondal, 2013).

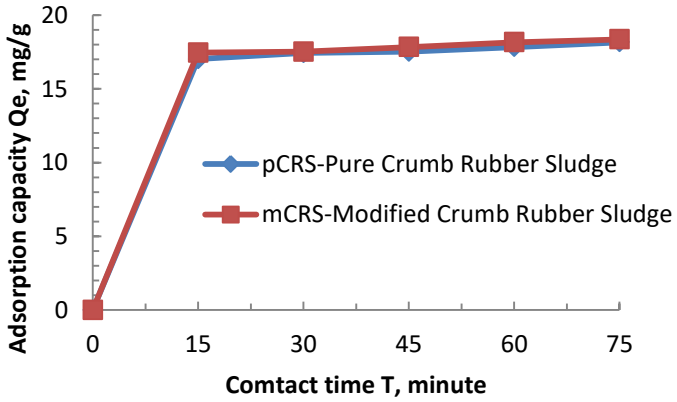

Figure 4. Effect of contact time on Hg(II) adsorption

CONCLUSION

1. The CRS, two different types, Pure Crumb Rubber Sludge (pCRS) and Modified Crumb Rubber Sludge (mCRS) have been successful in removing Hg(II) from aqueous solution at different operating condition. Chemically modified crumb rubber sludge showed slightly better in Hg(II) adsorption. Adsorption process was highly adsorbent dosage and contact time dependent.
2. The maximum Hg(II) adsorption was reached on 5 g/L adsorbent dosage. While, the adsorption capacities got higher rapidly until 30 minutes of contact time and went slow down and balance at the end of contact time process. The Hg(II) adsorption mechanism for both adsorbent follows Freundlich and Langmuir model, and pseudo second order kinetics model. The Hg(II) adsorption onto pCRS and mCRS occurred in monolayer and multilayer of chemisorption condition.

ACKNOWLEDGEMENT

This work was supported by Lembaga Penelitan dan Pengabdian Kepada Masyarakat (LPPM) Universitas Batanghari Jambi Research Assistantship – Penelitian Kompetitif (Nomor: 01/UBR – LPPM/2020).

REFERENCES

[1] S. Sy, Harmiwati, D. Kurniawati, H. Aziz, Z. Chaidir, and R. Zein, "Removal of Zinc onto Several adsorbents derived from waste activated sludge of crumb rubber industry (CRI-WAS)," *Int. J. Adv. Sci. Eng. Inf. Technol.*, vol. 8, no. 1, pp. 157–164, 2018.

[2] S. Sy, D. Kurniawati, I. Lestari, H. Harmiwati, and M. Kasman, "Pengaruh pH dan dosis adsorben dari limbah lumpur aktif industri crumb rubber terhadap kapasitas penyerapan ion Cd(II) dan Zn(II)," *J. Litbang Ind.*, vol. 8, no. 2, p. 95, 2018.

[3] C. Yang, J. Wang, M. Lei, G. Xie, G. Zeng, and S. Luo, "Biosorption of zinc(II) from aqueous solution by dried activated sludge," *J. Environ. Sci.*, vol. 22, no. 5, pp. 675–680, 2010.

[4] H. Benaïssa and M. A. Elouchdi, "Biosorption of copper (II) ions from synthetic aqueous solutions by drying bed activated sludge," *J. Hazard. Mater.*, vol. 194, pp. 69–78, 2011.

[5] M. Hunsom and C. Autthanit, "Adsorptive purification of crude glycerol by sewage sludge-derived activated carbon prepared by chemical activation with H3PO4, K2CO3 and KOH," *Chem. Eng. J.*, vol. 229, pp. 334–343, 2013.

[6] V. M. Monsalvo, A. F. Mohedano, and J. J. Rodriguez, "Activated carbons from sewage sludge. Application to aqueous-phase adsorption of 4-chlorophenol," *Desalination*, vol. 277, no. 1–3, pp. 377–382, 2011.

[7] M. A. A. Zaini, M. Zakaria, S. H. Mohd.-Setapar, and M. A. Che-Yunus, "Sludge-adsorbents from palm oil mill effluent for methylene blue removal," *J. Environ. Chem. Eng.*, vol. 1, no. 4, pp. 1091–1098, 2013.

[8] S. Zhu *et al.*, "Valorization of manganese-containing groundwater treatment sludge by preparing magnetic adsorbent for Cu(II) adsorption," *J. Environ. Manage.*, vol. 236, no. August 2018, pp. 446–454, 2019.

[9] C. Zhao *et al.*, *A novel activated sludge-graphene oxide composites for the*

removal of uranium(VI) from aqueous solutions, vol. 271, no. Vi. Elsevier B.V, 2018.

[10] R. Kumar *et al.*, "Waste sludge derived adsorbents for arsenate removal from water," *Chemosphere*, vol. 239, p. 124832, 2020.

[11] J. Liu, Z. Huang, Z. Chen, J. Sun, Y. Gao, and E. Wu, "Resource utilization of swine sludge to prepare modified biochar adsorbent for the efficient removal of Pb(II) from water," *J. Clean. Prod.*, vol. 257, p. 120322, 2020.

[12] J. Ifthikar *et al.*, "Highly Efficient Lead Distribution by Magnetic Sewage Sludge Biochar: Sorption Mechanisms and Bench Applications," *Bioresour. Technol.*, vol. 238, pp. 399–406, 2017.

[13] H. Zare, H. Heydarzade, M. Rahimnejad, A. Tardast, M. Seyfi, and S. M. Peyghambarzadeh, "Dried activated sludge as an appropriate biosorbent for removal of copper (II) ions," *Arab. J. Chem.*, vol. 8, no. 6, pp. 858–864, 2015.

[14] S. Sy, Sofyan, Ardinal, Harmiwati, M. Kasman, and R. Zein, "The ability of three types of adsorbents prepared from waste activated sludge of crumb rubber industry (CRI-WAS) for Cd(II) ion removal," *AIP Conf. Proc.*, vol. 2049, no. Ii, 2018.

[15] D. Patiño-Ruiz, H. Bonfante, G. De Ávila, and A. Herrera, "Adsorption kinetics, isotherms and desorption studies of mercury from aqueous solution at different temperatures on magnetic sodium alginate-thiourea microbeads," *Environ. Nanotechnology, Monit. Manag.*, vol. 12, no. July, p. 100243, 2019.

[16] N. M. Mora Alvarez, J. M. Pastrana, Y. Lagos, and J. J. Lozada, "Evaluation of mercury (Hg2+) adsorption capacity using exhausted coffee waste," *Sustain. Chem. Pharm.*, vol. 10, no. September, pp. 60–70, 2018.

[17] M. Arshadi, "Manganese chloride nanoparticles: A practical adsorbent for the sequestration of Hg(II) ions from aqueous solution," *Chem. Eng. J.*, vol. 259, pp. 170–182, 2015.

[18] Y. Guo, J. Deng, J. Zhu, X. Zhou, and R. Bai, "Removal of mercury(II) and methylene blue from a wastewater environment with magnetic graphene oxide: Adsorption kinetics, isotherms and mechanism," *RSC Adv.*, vol. 6, no. 86, pp. 82523–82536, 2016.

[19] G. Tan, W. Sun, Y. Xu, H. Wang, and N. Xu, "Sorption of mercury (II) and atrazine by biochar, modified biochars and biochar based activated carbon in aqueous solution," *Bioresour. Technol.*, vol. 211, no. Ii, pp. 727–735, 2016.

[20] T. Aprianti, B. D. Afrah, and T. E. Agustina, "Acid mine drainage treatment using activated carbon ceramic adsorbent in adsorption column," *Int. J. Adv. Sci. Eng. Inf. Technol.*, vol. 7, no. 4, pp. 1241–1247, 2017.

[21] Y. Sun *et al.*, "Adsorption of mercury (II) from aqueous solutions using FeS and pyrite: A comparative study," *Chemosphere*, vol. 185, no. Ii, pp. 452–461, 2017.

[22] T. Sheela, Y. A. Nayaka, R. Viswanatha, S. Basavanna, and T. G. Venkatesha, "Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles," *Powder Technol.*, vol. 217, pp. 163–170, 2012.

[23] Y. Fransiscus, R. K. Widi, G. O. Aprilasti, and M. D. Yuharma, "Adsorption of phosphate in aqueous solutions using manganese dioxide," *Int. J. Adv. Sci. Eng. Inf. Technol.*, vol. 8, no. 3, pp. 818–824, 2018.

[24] S. Pan, H. Shen, Q. Xu, J. Luo, and M. Hu, "Surface mercapto engineered

magnetic Fe3O4 nanoadsorbent for the removal of mercury from aqueous solutions," *J. Colloid Interface Sci.*, vol. 365, no. 1, pp. 204–212, 2012.

[25] M. Zabihi, A. Haghighi Asl, and A. Ahmadpour, "Studies on adsorption of mercury from aqueous solution on activated carbons prepared from walnut shell," *J. Hazard. Mater.*, vol. 174, no. 1–3, pp. 251–256, 2010.

[26] K. K. Wong, C. K. Lee, K. S. Low, and M. J. Haron, "Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions," *Chemosphere*, vol. 50, no. 1, pp. 23–28, 2003.

[27] E. K. Faulconer, N. V. H. von Reitzenstein, and D. W. Mazyck, "Optimization of magnetic powdered activated carbon for aqueous Hg(II) removal and magnetic recovery," *J. Hazard. Mater.*, vol. 199–200, pp. 9–14, 2012.

[28] D. K. Mondal, B. K. Nandi, and M. K. Purkait, "Removal of mercury (II) from aqueous solution using bamboo leaf powder: Equilibrium, thermodynamic and kinetic studies," *J. Environ. Chem. Eng.*, vol. 1, no. 4, pp. 891–898, 2013.