Equilibrium and Kinetic Studies of Lead Adsorption on Activated Carbon Derived from Mangrove Propagule Waste by Phosphoric Acid Activation

Widi Astuti, Rizki Agus Hermawan, Hariono Mukti, Nurul Retno Sugiyono

Abstract—The removal of lead ion (Pb^{2+}) from aqueous solution by activated carbon with phosphoric acid activation employing mangrove propagule as precursor was investigated in a batch adsorption system. Batch studies were carried out to address various experimental parameters including pH and contact time. The Langmuir and Freundlich models were able to describe the adsorption equilibrium, while the pseudo first order and pseudo second order models were used to describe kinetic process of Pb^{2+} adsorption. The results show that the adsorption data are seen in accordance with Langmuir isotherm model and pseudo-second order kinetic model.

Keywords—Activated carbon, adsorption, equilibrium, kinetic, Pb^{2+}, mangrove propagule.

I. INTRODUCTION

THE disposal of heavy metals into the water body is an important source of water pollution. Heavy metal is recognized as ecotoxicological hazardous substances because unlike organic pollutants, heavy metals will not degrade into harmless end products and affects the production and quality of the crops and aquatic products. They threaten the health and life of animals and human beings through the food chain [1], [2]. Lead is one of the most toxic heavy metals. It can accumulate in human bodies and causes abnormal calcium metabolism and immune disorders [2]. Numerous physicochemical and biological methods have been used to remove lead in wastewater, including ion exchange [3], reverse osmosis [4], nanocomposite membrane [5] and adsorption [6]-[8]. Among these, adsorption is one of the effective techniques that was extensively used for the removal of lead from household and industrial wastewater due to simplicity of design and easy to operate [2], [9]. The most generally used adsorbent is activated carbon, which is used to remove lead by electrostatic attraction of lead ions to various surface oxygen-containing functional groups [8], [10]-[12]. One of the advantages of activated carbon is the existence of large specific surface areas and large porous volumes to adsorb high quantity of pollutants. Another advantage is their low cost when the activated carbon is synthesized from waste materials [10].

In this study, mangrove propagule (MP) waste is transformed into activated carbon useful for removal of lead ion from aqueous solutions. The adsorption properties in terms of adsorption capacity were described. The effect of several parameters including pH of solution, contact time, dose of adsorbent, dye concentration was evaluated and discussed. The equilibrium and kinetic data have been analyzed using various adsorption isotherm and kinetic models.

II. MATERIAL AND METHODS

A. Adsorbate

Analytical grade $Pb(NO_3)_2$ purchased from Merck was used as the adsorbate without further purification. Stock solution was prepared by dissolving accurately weighed amount of $Pb(NO_3)_2$ in distilled water. The required concentrations of lead solutions were prepared by serial dilutions in distilled water.

B. Carbonization

The MP was washed with distilled water and dried in an oven at 105 °C for 24 hours to remove the moisture content. The dried sample was crushed and sieved. The fractions with particle size less than 0.149 mm was used for experiments. Carbonization was achieved by heating in an electric furnace to a temperature of 400, 500 and 600 °C for 4 hours.

C. Microwave-Induced Activation Process

The chemical activation of the char was carried out by using H_3PO_4 as an activating agent. The char was impregnated with 20, 40, and 60% phosphoric acid (H_3PO_4) with impregnation ratios of 1:7 (w/w) for 24 h. Furthermore, the sample was filtered, washed until the pH was around 7 and dried in an oven at 110 °C to constant weight. Activated carbon was further characterized and used to adsorb Pb^{2+} in a batch adsorption. The FTIR spectra of char before and after activation process were recorded using an FTIR technique (Perkin Elmer, USA) by the KBr pellet method. The spectrum was scanned in the range of 400 to 4000 cm^{-1} wavenumbers. The photomicrography of the exterior surface of char and activated carbon was obtained by SEM (JEOL, Japan).

D. Adsorption Studies

Approximately 0.5 g of MP char or activated carbon was put into an Erlenmeyer filled 50 mL of Pb^{2+} solution (concentration of 10-500 mg.L^{-1}). The pH was adjusted with

W. Astuti is with the Chemical Engineering Department, Semarang State University, Semarang 50229, Indonesia (corresponding author to e-mail: widi_astuti@mail.unnes.ac.id).

R.A. Hermawan, H. Mukti, and N.R. Sugiyono are students at the Chemical Engineering Department, Semarang 50229, Indonesia (e-mail: agushermawan.unnes@gmail.com, muktihariono@gmail.com, rulle2bix@gmail.com).

base or acid to an appropriate pH (pH range of 3-9). The Erlenmeyer contained the mixture was placed in a waterbath at 26 °C and shaken mechanically at 120 rpm for 0-180 minutes. After specified contact times, suspended solid was filtered and the filtrate was analyzed for residual Pb^{2+} using atomic absorption spectroscopy (Perkin Elmer, USA).

E. Adsorption Isotherm

To evaluate the adsorption capacities of MP activated carbon, batch adsorption test was conducted for the adsorption of Pb^{2+}. The amount of Pb^{2+} adsorbed per unit weight of adsorbent at equilibrium (q_e, mg.g^{-1}) was calculated using the equation as follows [13]:

$$q_e = \frac{(C_o - C_e)v}{m} \qquad (1)$$

where v (L) is the volume of Pb^{2+} solution and m (g) is the dry weight of the adsorbents.

The experimental isotherm data were interpreted by Langmuir and Freundlich isotherm models. The Langmuir model indicates surface homogeneity of adsorbent and hints towards the conclusion that the surface of adsorbent is made up of small adsorption patches which are energetically equivalent to each other in respect of adsorption phenomenon [14]. This model can be expressed as (2) and rearranged to the linear form of this model is given by (3) as follows [9]:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (2)$$

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_e} \frac{1}{C_e} \qquad (3)$$

where C_e (mg.L^{-1}) is the equilibrium concentration of Pb^{2+} on the solution, K_L (L.mg^{-1}) is the Langmuir constants related to the affinity of the binding sites and energy of adsorption, and q_{max} (mg.g^{-1}) is the maximum adsorption capacity related to monolayer coverage. The higher the K_L value, the higher the affinity of the binding sites. A plot of $1/q_e$ versus $1/C_e$ should yield straight line if Langmuir isotherm is obeyed by the adsorption equilibrium. The value of q_{max} and K_L can be calculated from the intercept and slope of the graphed line, respectively.

The Freundlich equation indicates a surface heterogeneity of the adsorbent since the presence of energetically heterogeneous adsorption sites. In this case, adsorbent surface is divided into small heterogeneous adsorption patches having similar adsorption properties [9]. The Freundlich isotherm is described by (4) where K_F (mg$^{1-1/n}$ L$^{1/n}$g^{-1}) and n are the Freundlich equilibrium constants which can be determined from the plot of log q_e versus log C_e on the linear form of Freundlich equation, as can be seen in (5). The higher value for K_F, indicates the higher affinity for adsorbate, and the value of the empirical parameter n indicates favorable adsorption.

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (4)$$

$$\log q_e = \log K_F + n \log C_e \qquad (5)$$

F. Adsorption Kinetics

In order to clarify the adsorption kinetics of Pb^{2+} onto activated carbon, pseudo-first order and pseudo second order kinetic models were applied to the experimental data. The pseudo-first order equation by Lagergren is given as:

$$\frac{d_{q_t}}{dt} = k_f(q_e - q_t) \qquad (6)$$

where q_e and q_t are the amounts of Pb^{2+} adsorbed at equilibrium (mg.g^{-1}) and at time t (mg.g^{-1}), respectively, k_f is the rate constant of pseudo-first order model (min^{-1}), and t is the time (min). After definite integration by applying the initial conditions q_t = 0 at t = 0 and q_t = q_t, the equation becomes:

$$\ln(q_e - q_t) = \ln q_e - k_f t \qquad (7)$$

The plots of ln (q_e−q_t) versus t should yield straight line if pseudo-first order model is obeyed by the adsorption kinetic. The constants were obtained from the slope and intercept. The pseudo-second order equation is expressed as:

$$\frac{d_{q_t}}{dt} = k_s (q_e - q_t)^2 \qquad (8)$$

where k_s is the rate constant of pseudo-second order model (g.mg^{-1}.min^{-1}). After integrating (8) for boundary conditions q_t = 0 at t = 0 and q_t = q_t at t = t, the following form of the equation can be obtained:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \qquad (9)$$

The plots of t/q_t versus t should yield straight line if pseudo-second order model is obeyed by the adsorption kinetic. The constants were obtained from the slope and intercept.

III. RESULTS AND DISCUSSION

A. Characterization of Char and Activated Carbon

Fourier-transform infrared (FT-IR) spectroscopy is used for identifying surface functional groups which are capable of adsorbing Pb^{2+} ions. The FT-IR spectra of char and activated carbon are shown in Fig. 1. For char, it can be seen that there is a band from 3300 to 3600 cm^{-1}, which indicates the presence of carboxylic acid (RCOOH) and alcohol (ROH) groups [15]. A peak at approximately 1450 cm^{-1} is the unsaturated stretching of C—C bonds ascribed to aromatic C=C vibrations [15]. FTIR spectra of the activated carbons show a number of changes. Peak indicating the existence of hydroxy groups disappeared, while peak indicating C-C bond shifts from 1450 to 1520 cm^{-1}. The new peak at 1250–1170 cm^{-1} may be ascribed to the stretching mode of hydrogen-bonded P=O, O—C stretching vibrations in the P—O—C linkage and P=OOH [15].
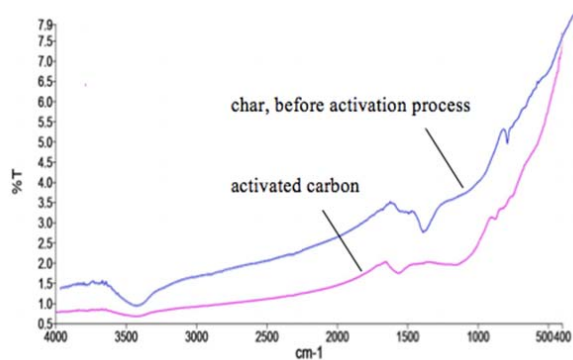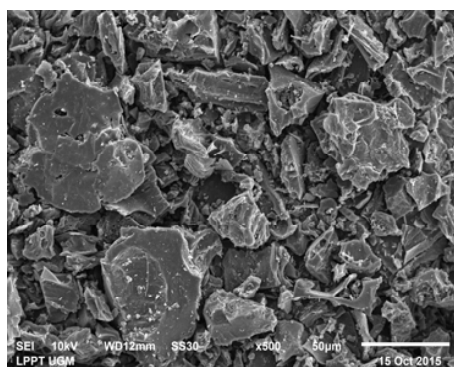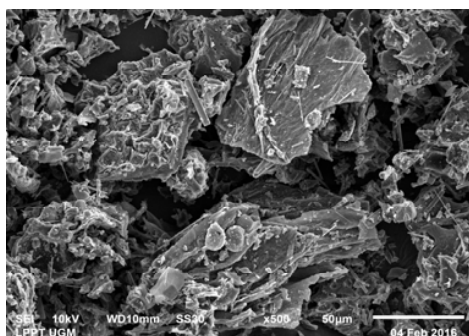
Fig. 1 FT-IR spectra of char and activated carbon

(a)

(b)

Fig. 2 SEM micrograph of MP (a) char and (b) activated carbon

SEM micrographs of char and activated carbon are shown in Fig. 2. Before activation process, pore structure of char is covered by impurities and tar. The impurities decrease after activation process, so the pores open. In this process, H_3PO_4 has two important functions, promotes the pyrolytic decomposition of the initial material, and promotes the formation of the cross-linked structure. Moreover, H_3PO_4 allows the development of both micropores and mesopores in the activated carbon [15].

The application of carbonization to an impregnated material further accelerates thermal degradation and the volatilization process. This leads to pore development and increases the surface area. The BET surface area of char is 187.18 m^2/g while that of activated carbon is 267.45 m^2/g. It can be concluded that H_3PO_4 activation causes the increase in specific surface area.

B. Adsorption of Pb^{2+}

Fig. 3 shows that MP activated carbon prepared by H_3PO_4 60% and carbonation process at 600 ^oC can adsorb Pb^{2+} higher than the others. It is caused by the existence of P=O, P—O—C and P=OOH groups as adsorption sites.
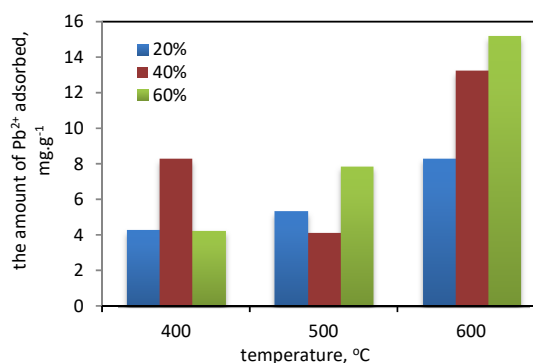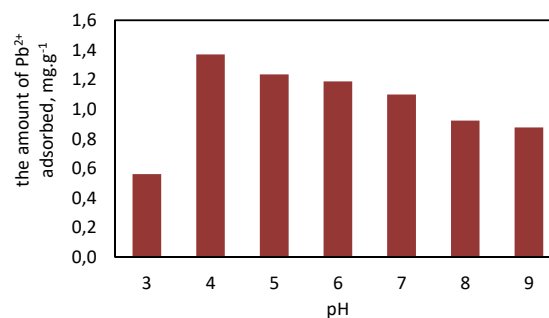

Fig. 3 The effect of H_3PO_4 concentration and carbonation temperature toward Pb^{2+} adsorbed

Fig. 4 Effect of pH on the removal of Pb^{2+} by activated carbon using H_3PO_4 60% solution and carbonation temperature of 600 ^oC (condition: adsorbent dose = 0.5 g/50 mL solution, contact time = 180 min, T = 26 ^oC, initial concentration = 100 mg.L^{-1})

Fig. 4 shows the influence of pH values on the amount of Pb^{2+} adsorbed by the activated carbon. As seen there, the amount of Pb^{2+} adsorbed increase with the increasing of pH values until after an optimal value the amount of Pb^{2+} adsorbed declines. The reason may be the protonation of carboxyl groups on the activated carbon at low pH values [2]. The increase of solution pH leads to decrease of positively charged species, and surface tends to acquire negative charge. As the adsorbent surface is negatively charged, the increase of electrostatic attraction between positively charged adsorbate species and negatively charged adsorbent particles leads to the increase of Pb^{2+} adsorption. The existence of hydroxyl ions in solution may also participate in the adsorption competition. It causes the decrease of the amount of Pb^{2+} adsorbed at higher pH values. The decrease in adsorption beyond pH 5 is due to

the formation $PbOH^+$ at pH of 5-7 and $Pb(OH)_2$ at pH more than 7. Therefore, pH 4 was selected to be the optimum pH for further studies.

Results depicted in Fig. 5 clearly describe that the adsorption of Pb^{2+} onto the activated carbon reached equilibrium in 180 min. Adsorption first followed linear rising in which instantaneous, extremely fast uptake takes place and then a stationary state was observed. This is due to the fact that a large number of vacant surface sites are available for adsorption during initial stage, and after a lapse of time the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Based on these results, an equilibrium time of 180 min was chosen for further experiments.
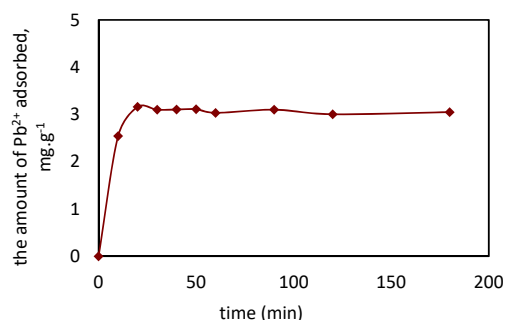

Fig. 5 Effect of contact time on the removal of Pb^{2+} by activated carbon using H_3PO_4 60% solution and carbonation temperature of 600 °C (condition: adsorbent dose = 0.5 g/50 mL solution, pH = 4, T = 26 °C, initial concentration = 100 mg.L^{-1})

Fig. 6 shows that the percentage Pb^{2+} adsorbed increases with the increase of Pb^{2+} concentration and remain constant after equilibrium reached. The initial concentration provides an important driving force to overcome all mass transfer resistance of Pb^{2+} between aqueous and solid phase. Hence, higher initial concentration of Pb^{2+} will enhance the adsorption process.
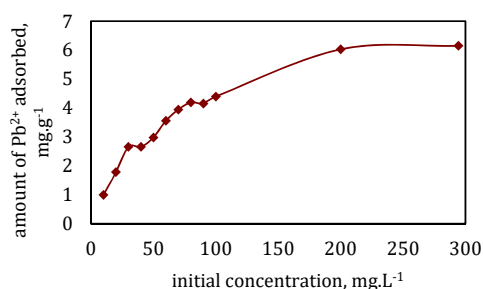

Fig. 6 Effect of initial concentration on the removal of Pb^{2+} by activated carbon using H_3PO_4 60% solution and carbonation temperature of 600 °C (condition: adsorbent dose = 0.5 g/50 mL solution, pH = 4, T = 26 °C, contact time = 180 min)

C. Adsorption Isotherm

The adsorption isotherm revealed the specific relation between the concentration of the adsorbate and its adsorption degree onto adsorbent surface at a constant temperature. The analysis of the adsorption isotherm data by fitting them to different adsorption isotherm model that can be used for design purpose [14]. In the present study, Langmuir and Freundlich isotherm models were applied to describe the adsorption equilibrium. Figs. 7 and 8 show the Langmuir ($1/q_e$ versus $1/C_e$) and Freundlich (log q_e versus log C_e) plot, respectively, for the removal of Pb^{2+} by activated carbon. The data was analysed by two correlation coefficients. The linear R^2 coefficients for linearised plots described in Figs. 7 and 8 are 0.9539 for Langmuir isotherm and 0.8783 for Freundlich isotherm (Table I).
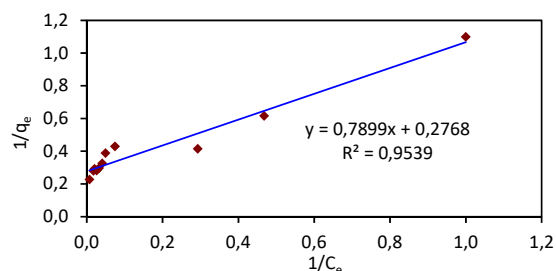

Fig. 7 Langmuir isotherm plots for the removal of Pb^{2+} by activated carbon using H_3PO_4 60% solution and carbonation temperature of 600°C (temperature = 26 °C, contact time = 180 min)
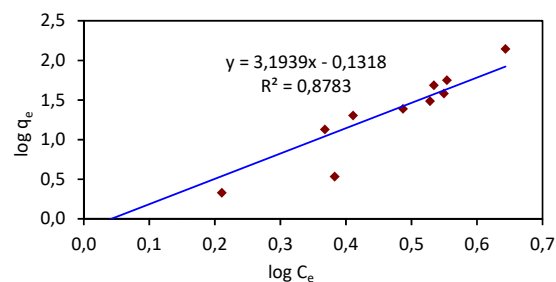

Fig. 8 Freundlich isotherm plots for the removal of Pb^{2+} by activated carbon using H_3PO_4 60% solution and carbonation temperature of 600 °C (temperature = 26 °C, contact time = 180 min)

TABLE I
ISOTHERM CONSTANTS FOR Pb^{2+} ADSORPTION ONTO ACTIVATED CARBON

constants	linear	nonlinear
Langmuir model		
K_L	0.8059	0.3005
q_{max}	4.4823	3.8032
R^2		0.9724
SSE	0.9539	0.8443
SAE		2.5454
Freundlich model		
K_F	15.707	1.3019
$1/n$	0.996	3.8117
R^2		0.9032
SSE	0.8783	2.4812
SAE		4.0542

The nonlinear R^2 values are based on the actual deviation between the experimental points and the theoretically predicted data points and are a better correlation of experimental data. The nonlinear correlation coefficients for

the Langmuir and Freundlich isotherm analyses are presented in Table I. In this case, Langmuir equation represents a better fit of experimental data than Freundlich equation due to the correlation coefficient for the Langmuir isotherm is closer to unity than Freundlich isotherm. The values of parameters for Langmuir and Freundlich isotherms are given in Table I.

Due to the inherent bias result from linearisation, two different error functions of nonlinear regression were employed to evaluate the isotherm constants including the sum of the square of the errors (SSE) and the sum of the absolute errors (SAE), as shown by (10) and (11), respectively.

$$\sum_{i=1}^{n}\left(q_{e,calc} - q_{e,meas}\right)_i^2 \qquad (10)$$

$$\sum_{i=1}^{n}\left|q_{e,calc} - q_{e,meas}\right|_i \qquad (11)$$

The values of two error measurements were presented in Table I. These values show that the Langmuir isotherm best fits for Pb^{2+}-activated carbon system. This is the same as predicted by R^2 analysis.

D. Adsorption Kinetic

The experimental data were tested with pseudo-first order and pseudo-second order kinetic models in order to understand the kinetics of Pb^{2+} removal using activated carbon as an adsorbent.

Pseudo-First Order Model. Pb^{2+} adsorption kinetics onto activated carbon was tested with the pseudo-first order model by plotting $\ln(q_e - q_t)$ versus t. It was found that calculated q_e value was not suitable with the experimental values with R^2 values of 0.8608.

Pseudo-Second Order Model. Adsorption kinetics model of Pb^{2+} onto activated carbon was also tested with the pseudo-second order kinetic model by plotting t/q_t versus t. The calculated q_e values show a very good agreement with the experimental values with R^2 values exceeding 0.999. This indicates that the pseudo-second order kinetics model describes well Pb^{2+} removal using activated carbon under study with the value of k_s 0.0092 and q_e 126.58.

IV. CONCLUSION

In this study, adsorption of Pb^{2+} on activated carbon has been investigated. The data obtained through this work support the statement that the activated carbon is an effective low cost adsorbent for the removal of Pb^{2+} in aqueous solution. The sorption of Pb^{2+} is heavily dependent on pH, contact time and concentration of Pb^{2+}. Maximum removal of Pb^{2+} on activated carbon occurs at pH 4. The adsorption data are seen in accordance with Langmuir isotherm model and pseudo-second order kinetic model.

ACKNOWLEDGMENT

REFERENCES

[1] A. M. A. Al-Haidapy, F. H. H. Zanganah, S. R. F. Al-Azawi, K. I. Khalili, A. H. Al-Dujaili, "A study on using date palm fibers and leaf base of palm as adsorbents for Pb(II) ions from its aqueous solution," *Water, Air, & Soil Pollution,* vol.214, 2011, pp.73-82.

[2] C. Duan, N. Jhao, X. Yu, X. Zhang, J. Xu, "Chemically modified kapok fiber for fast adsorption of Pb^{2+}, Cd^{2+}, Cu^{2+} from aqueous solution," *Cellulose,* vol.20, 2013, pp.849-860.

[3] W. Yang, Q. Tang, J. Wei, Y. Ran, L. Chai, H. Wang, "Enhanced removal of Cd(II) and Pb(II) by composites of mesoporous carbon stabilized alumina," *Applied Surface Science,* vol.369, 2016, pp.15-223.

[4] N. Abdullah, R. J. Gohari, N. Yusof, A. F. Ismail, J. Juhana, W. J. Lau, T. Matsuura, "Polysulfone/hydrous ferric oxide ultrafiltration mixed matrix membrane: preparation, characterization and its adsorptive removal of lead (II) from aqueous solution," *Chemical Engineering Journal.* vol.289, 2016, pp.28-37.

[5] N. Ghaemi, S. Zereshki, S. Heidari, "Removal of lead ions from water using PES-based nanocomposite membrane incorporated with polyaniline modified GO nanoparticles: performance optimization by central composite design," *Process Safety and Environmental Protection*, vol.11, 2017, pp.475-490.

[6] X. Huang, M. Pan, "The highly efficient adsorption of Pb(II) on grapheme oxides: a process combined by batch experiments and modeling techniques," *Journal of Molecular Liquids.* vol.215, 2016, pp.410-416.

[7] W. Astuti, W. Martiani, A. I. Khair, "Competitive adsorption of Pb^{2+} and Zn^{2+} ions from aqueous solutions by modified coal fly ash," *AIP Conference Proceedings*, vol.1818, 2017, pp.020007-1–020007-6.

[8] W. Astuti, R. A. Hermawan, H. Mukti, N. R. Sugiyono, "Preparation of activated carbon from mangrove propagule waste by H_3PO_4 activation for Pb^{2+} adsorption, *AIP Conference Proceedings*, vol.1788, 2017, pp.030082-1–030082-5.

[9] W. Astuti, T. Sulistyaningsih, M. Maksiola, "Chemically modified kapok sawdust as adsorbent of methyl violet dye from aqueous solution," *Jurnal Teknologi*, vol.78(9), 2016, pp.35-42.

[10] L. Largitte, T. Brudey, T. Tant, P. C. Dumesnil, P. Lodewyckx, "Comparism of the adsorption of lead by activated carbons from three lignocellulosic precursors," *Microporous and Mesoporous Materials*, vol.219, 2016, pp.265-275.

[11] T. Brudey, L. Largitte, C. Jean-Marius, T. Tant, P. C. Dumesnil, P. Lodewyckx, "Adsorption of lead by chemically activated carbon from three lignocellulosic precursors," *Journal of Analytical and Applied Pyrolysis*, vol.120, 2016, pp.450-463.

[12] M. E. Goher, A. M. Hassan, I. A. Abdel-Moniem, A. H. Fahmy, M. H. Abdo, S. M. El-Sayed, "Removal of aluminium, iron and manganese ions from industrial waste using granular activated carbon and amberlite IR-120H," *Egyptian Journal of Aquatic Research*, vol.41, 2015, pp.155-164.

[13] W. Astuti, T. Sulistyaningsih, M. Maksiola, "Equilibrium and kinetics of adsorption of methyl violet from aqueous solutions using modified ceiba pentandra sawdust," *Asian Journal of Chemistry*, vol.29(1), 2017, pp.133-138.

[14] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, "Removal of cadmium (II) from aqueous solutions by adsorption using meranti wood," *Wood Sci Technol*, 2012, vol. 46, pp. 221-241.

[15] S. Yorgun, D. Yildiz, "Preparation and characterization of activated carbons from Paulownia wood by chemical activation with H_3PO_4," *Journal of the Taiwan Institute of Chemichal Engineers*, 2005, vol. 53, pp. 122-131.