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Study of Equilibrium, Kinetic and Thermodynamic for Removal of Pb(II) in Aqueous Solution Using Sago Bark (*Metroxylon sago)*

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Abstract. This research investigated the ability of Sago Bark (*Metroxylon sago*) to remove Pb(II) in aqueous solution using the batch method. The adsorption of Pb(II) with Sago Bark (*Metroxylon Sago*) reached the peak at pH 5, contact time 60 minutes, initial concentration 600 mg/L, agitation rate 100 rpm, adsorbent dose 0.1 g and adsorption capacity 31.4375 mg/g. The equilibrium of adsorption revealed that Langmuir isotherm model was fitted better to describe the adsorption of Pb(II) onto Sago Bark (*Metroxylon sago*) indicated by R^2 values at 0.8908 and 0.918 for Freundlich and Langmuir, respectively. Pseudo-second order yielded a good correlation (R^2 = 0.9979) of the experimental data. While the thermodynamic study showed a spontaneous with an endothermic process. SEM micrograph and FTIR spectrum indicated that porous surface covered by Pb(II) and the wavelength number shifting of hydroxyl and carbonyl groups from 3421.10 cm^{-1} to 3423.54 cm^{-1} and from 1734.16 cm^{-1} to 1718.65 cm^{-1} supported the adsorption of Pb(II) onto Sago Bark (*Metroxylon sago*).

Keywords: Pb(II), *Metroxylon sago,* adsorption

INTRODUCTION

Industrial development in various fields has affected the environmental ecosystem. These industries discharge assorted wastes into the environment such as pesticide, dyes and metal ion [1]. Lead (Pb) is one of dangerous metal that is not degradable and can be accumulated in the living creature's body. The presence of Pb(II) in environment is due to the manufacturing of batteries, pulp and paper, printing, electroplating and so forth [1-5]. Therefore, it is necessary to remove this metal ion from the environment. Several methods have been used to reduce the heavy metals content from aqueous solution such as precipitation, electrochemical, ion exchange, membrane separation, coagulation, biological treatment etc. Unfortunately, these methods are ineffective due to the high cost and generating of another waste like precipitate or side product [6-10].

Adsorption is an alternative method of metal ion removal from aqueous solution. Adsorption is inexpensive and effective because it exploits a low-cost material to eliminate heavy metal [11-15]. Many researchers have reported a various low-cost adsorbents such as *bombax buonopozense* [1], *pongamia pinnata* tree and natural adsorbent [5], agricultural waste [2-4], coconut shell [11], algae [15], orange peel [16], clay [17], tea residue [18], coconut husk [19], household waste [20], shell and seeds of *kelengkeng* fruit [21], papaya leaves and *petai* peels [22], *nypa fruitcans* Merr shell [23], mangosteen [24] and so forth. Hence, this research aim is the utilization of sago bark (*Metroxylon sago)* which is a solid waste of sago starch from processing industry as the low-cost adsorbent to

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eliminate Pb(II) from a dilute solution. This research was carried out by batch method and the characterization of sago bark was conducted using AAS, FTIR and SEM-EDX.

MATERIALS AND METHODS

Sago (*Metroxylon sago)* barks were collected from local area of West Sumatra, Indonesia. Lead nitrate ($Pb(NO_3)_2$), sodium hydroxide (NaOH), Nitric acid (HNO_3) and distilled water. All of reagents were got from Merck, Germany. Sago barks were washed and dried. Then, it was grinded and soaked in HNO_3 0.01 M for 2 hours. The powder of sago barks were washed with distilled water to remove the acid excess. Next, it was dried to remove the water. Batch method was carried out under certain parameters such as pH, contact time, agitation rate and initial concentration. Concentration residue of metal ions was measured by AAS (AA240 Atomic Absorption Spectrophotometer). Characterization of sago bark was done by FTIR (Unican Mattson Mod 7000 FTIR) and SEM-EDX (Hitachi S-3400N).

RESULTS AND DISCUSSION

Effect of pH on Pb(II) Adsorption

pH has an effect to the functional group on the surface of biosorbent. Figure 1 shows the adsorption capacity of sago bark increased from pH 2 to 5. Optimum adsorption capacity of Pb(II) was achieved at pH 5 with adsorption capacity of 1.5049 mg/g. This phenomenon was due to the high concentration of H_3O^+ at lower pH which competes with Pb(II) for an active site on the biosorbent surface. At pH above 5, there was solvation and hydrolysis of metal ions to form soluble hydroxilated complexes that competes for an active site [2]. The occurrance of hydrated species of metal ions leads to form a precipitation of the appropriate salt that may cause the reduction of adsorption capacity [1]. Other researches that have been conducted Pb(II) removal from selected agricultural waste [2], coffee husk [4] and biomass of maize stover [5] showed the same adsorption pattern which reached the optimum condition at pH 5.

Effect of Contact Time on Pb(II) Adsorption

Contact time is the time required by the adsorbent and metal ions to interact properly. The adsorption capacity did not significantly change from 5 to 30 minutes. It revealed that the optimum contact time of sago bark was achieved at 60 minutes with adsorption capacity 1.5049 mg/g (Fig. 2). Then, it was slightly decreased after 60 minutes due to driving force and availability of the active site [3, 4]. At the beginning, the adsorption process occurred rapidly related to the availability of active sites supporting the adsorption process. As the time passed, the availability of a vacant surface decreased as the active sites bonded with Pb(II). Thus, the adsorption capacity of sago bark decreased. Other adsorbents which have been reported for the adsorption of Pb(II) such as tea leaves [6], *Pongamia pinnata* Tree Bark [7] and natural adsorbent [8] reached the equilibrium at contact time of 75 minutes, 60 minutes, and 150 minutes, respectively.

Effect of Agitation Speed on Pb(II) Adsorption

The agitation speed affected the contact time between Pb(II) and sago bark. Figure 3 shows that the optimum agitation speed was reached at 100 rpm with adsorption capacity 1.5049 mg/g. At the lower agitation speed, adsorbent was accumulated resulting in an ineffective adsorption [25]. Then, the adsorption capacity of sago bark was gradually decreased and achieved equilibrium at agitation rate 150 rpm. It could be assumed that Pb(II) has bonded with the free active site due to the low affinity toward active site. Hence, the agitation speed of 100 rpm was chosen for the optimum condition.

Effect of Temperature on Pb(II) Adsorption

Figure 4 revealed that the adsorption capacity of Pb(II) on sago bark increased from 298 to 318 K. It means the adsorbent could resist not only at room temperature but also at higher temperature. Other research has been reported

the adsorption of Pb(II) using maize stover and the result showed that the adsorption capacity decreased as the temperature increased due to releasing of Pb(II) from active site as temperature increased [5].

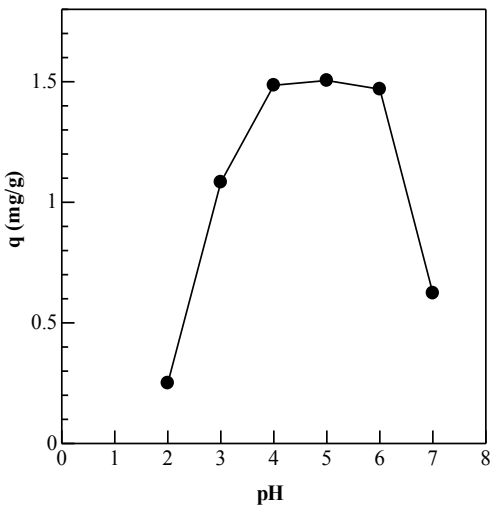


FIGURE 1. Effect of pH on the adsorption of Pb(II), initial concentration 20 mg/L, contact time 60 minutes, agitation speed100 rpm and bio sorbent mass 0.1 g.

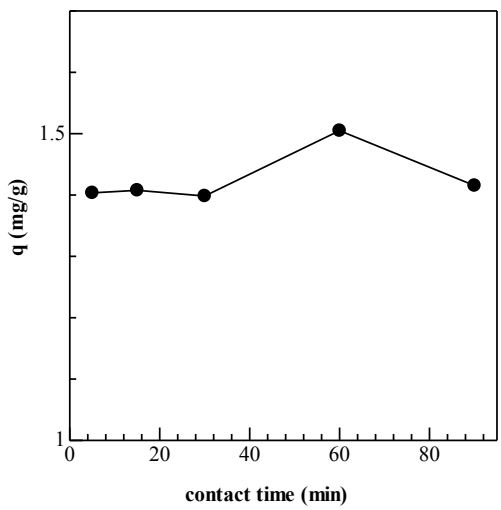


FIGURE 2. Effect of contact time on the adsorption of Pb(II), at pH 5 for Pb(II), initial concentration 20 mg/L, agitation speed 100 rpm and adsorbent mass 0.1 g.

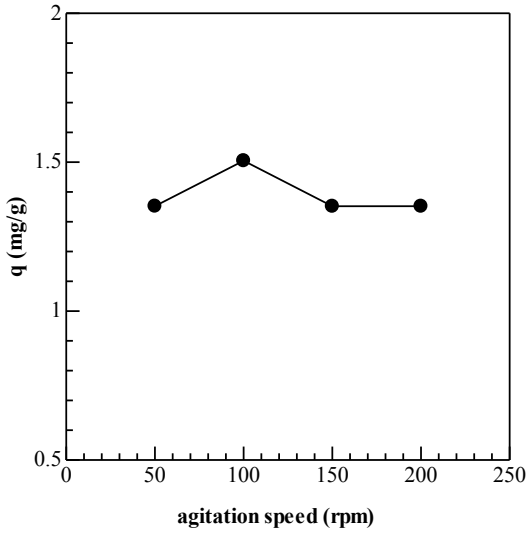


FIGURE 3. Effect of agitation speed on the adsorption of Pb(II), at pH 5 for Pb(II), initial concentration 20 mg/L, contact time 60 minutes and adsorbent mass 0.1 g.

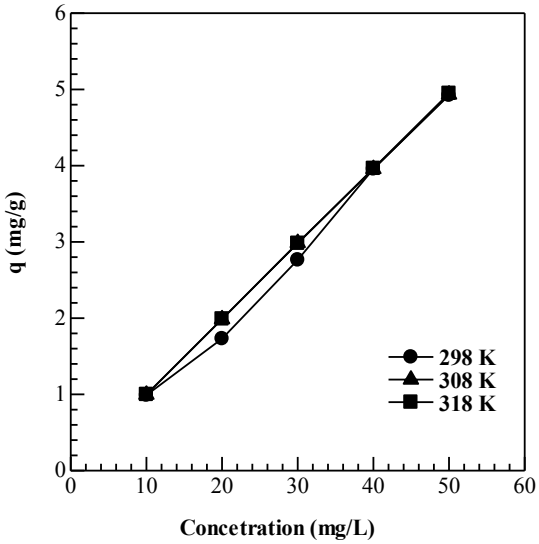


FIGURE 4. Effect of temperature on the adsorption process, at pH 5 for Pb(II), agitation speed 100 rpm, contact time 60 minutes and adsorbent mass 0.1 g

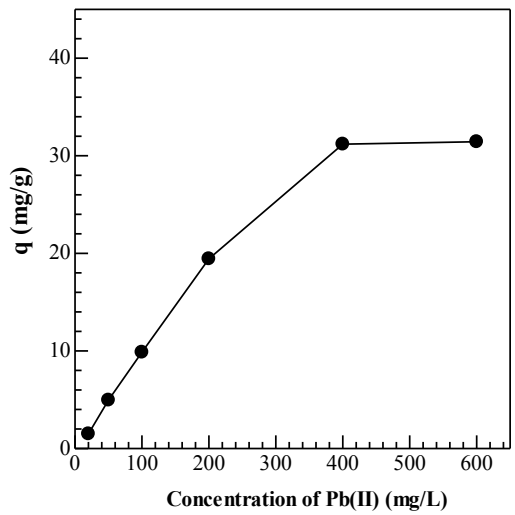


FIGURE 5. Effect of Pb(II) concentration on the adsorption process, at pH 5 for Pb(II), agitation speed 100 rpm, contact time 60 minutes and adsorbent mass 0.1 g

Effect of Initial Concentration on Pb(II) Adsorption

As seen in Figure 5, the adsorption capacity of sago bark is proportional to the initial concentration within range of 20-400 mg/L. At the lower concentration, there was enough number of active site to interact with Pb(II). As the initial concentration increased, the number of active site also decreased and became saturated. This was affected to the lowering adsorption capacity [5, 6]. As the concentration increased, the active site remained. The maximum adsorption capacity of sago bark was 31.4375 mg/g at initial concentration of 600 mg/L.

Adsorption Isotherm Model

The adsorption equilibrium was studied by Langmuir and Freundlich models. The Langmuir model was set by the following equation:

$$\frac{Ce}{qe} = \frac{1}{Qmax.KL} + \frac{Ce}{Qmax} \tag{1}$$

where Ce is the equilibrium concentration of the adsorbate (mg/L), qe is adsorption capacity at equilibrium (mg/g), Qmax and K_L are maximum adsorption capacity (mg/g), and Langmuir equilibrium constant (L/mg), respectively. Langmuir model assumed a monolayer adsorption process on homogeneous surface with limited number of identical sites and the interaction between adsorbed molecules is negligible [26]. Freundlich model was expressed by the following equation:

$$ln\, qe = ln\, K_F + \frac{1}{n} ln\, Ce \tag{2}$$

where qe is adsorption capacity (mg/g), K_F is Freundlich constant (L/mg) and 1/n is Freundlich adsorption intensity. Freundlich model indicates multilayer adsorption process [27]. Figure 6 indicates that K_L and K_F are 0.1889 L/mg and 5.9996 L/mg, respectively. The determination coefficient shows that Langmuir isotherm model (R^2 = 0.918) fits better than Freundlich isotherm model (R^2 = 0.8908) indicating that adsorption of Pb(II) onto sago bark is a monolayer.

Adsorption Kinetic

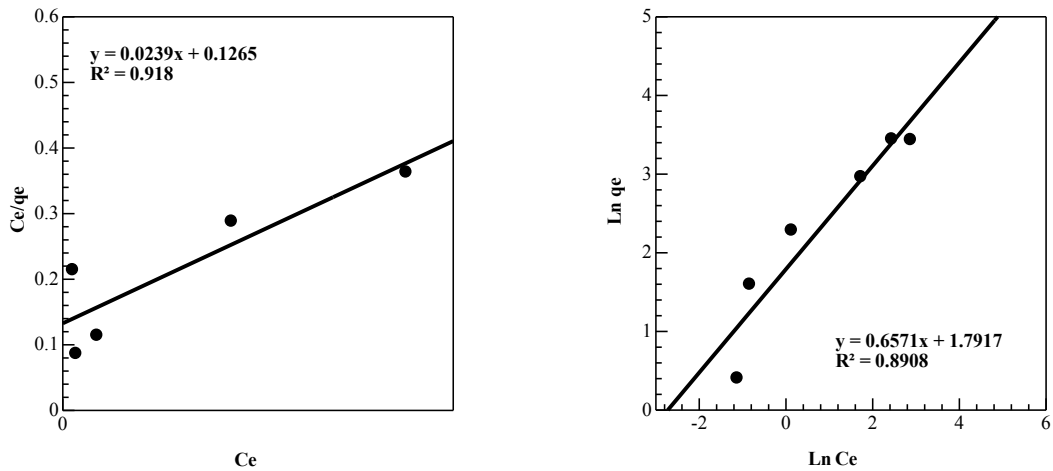
In this study, pseudo-first order and pseudo-second order kinetic were required to explain the adsorption of Pb(II) on sago bark. Pseudo-first order model was given by the following Lagergren equation [28]:

$$log(q_e - q_t) = log q_e - \frac{k_1 t}{2.303} \tag{3}$$

where q_e and q_t are adsorption capacities of sago bark at equilibrium and at t (mg/g), k_1 is pseudo-first-order kinetic constant (min^{-1}). As seen in Fig. 7a, the coefficient determination of pseudo-first order is 0.5537 and k_1 is $-1.38x10^{-3}$ min^{-1}. Meanwhile, pseudo-second order was expressed by the equation [29]:

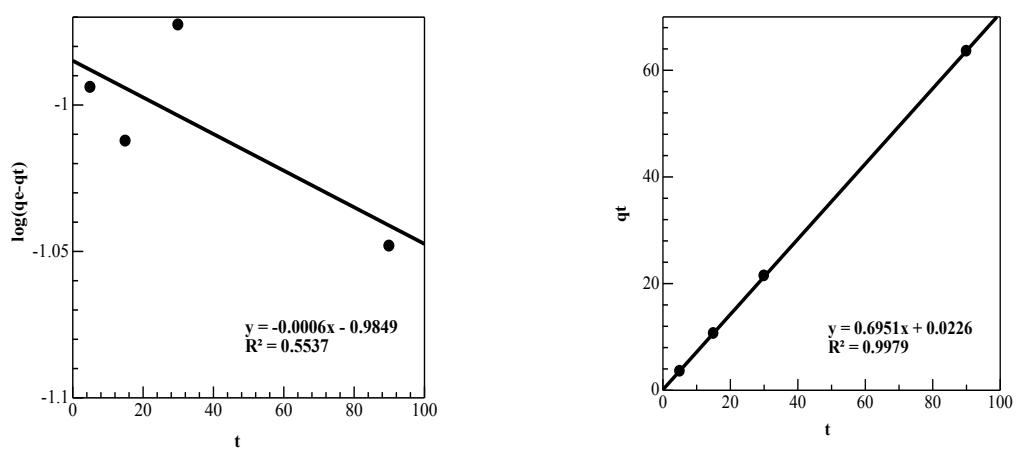
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where t is time (minutes), qt is adsorption capacity at the time (mg/g), qe and k_2 are adsorption capacity at equilibrium (mg/g) and pseudo-second order constant (g/mg.min), respectively. Figure 7b indicates that R^2 of pseudo-second order is 0.9979 and k_2 is 0.03251 g/mg.min. This result explained that adsorption of Pb(II) on sago bark obeyed the pseudo-second order kinetic and implied a chemisorption process [9-11].



(a) (b)

FIGURE 6. Adsorption isotherm of Pb(II) on sago bark (a) Langmuir (b) Freundlich

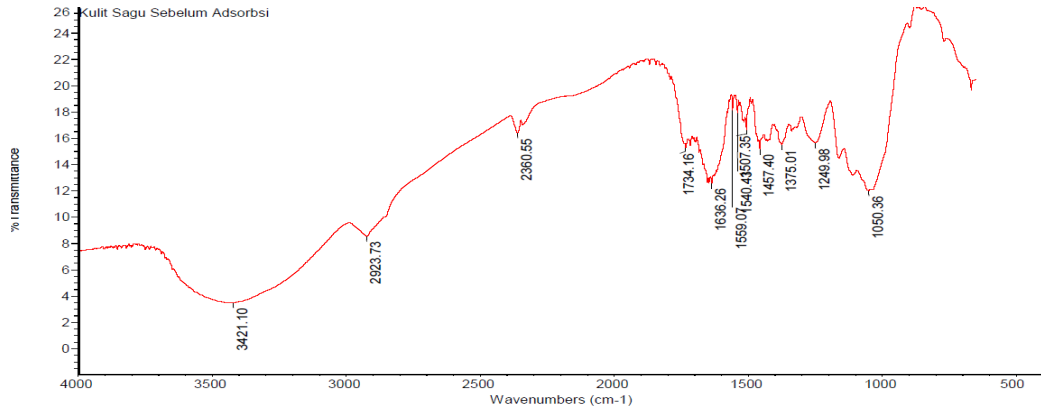


(a) (b)

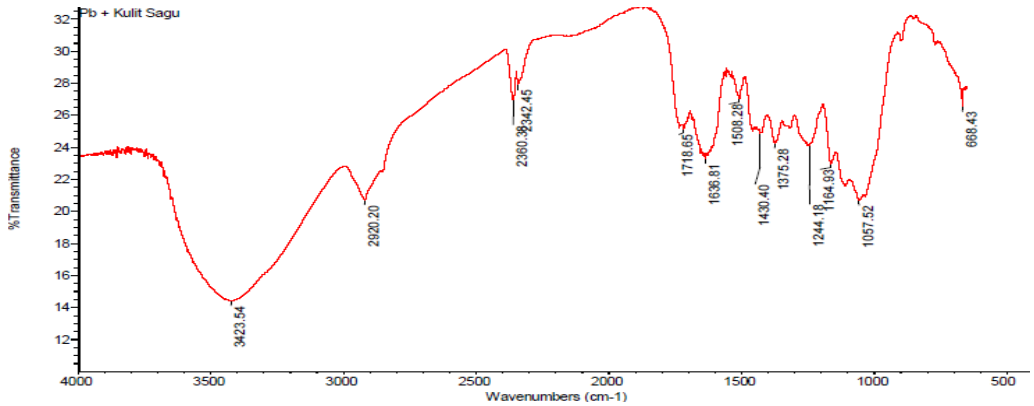
FIGURE 7. Adsorption kinetic of Pb(II) on sago bark (a) pseudo-first order, (b) pseudo-second order

TABLE 1. Termodynamic parameters of Pb(II) Adsorption on sago bark

T (K)	(kJ/mol)	(kJ/mol)	(J/mol.K)
298	-4.065	15.576	65.204
308	-4.058		
318	-5.398		

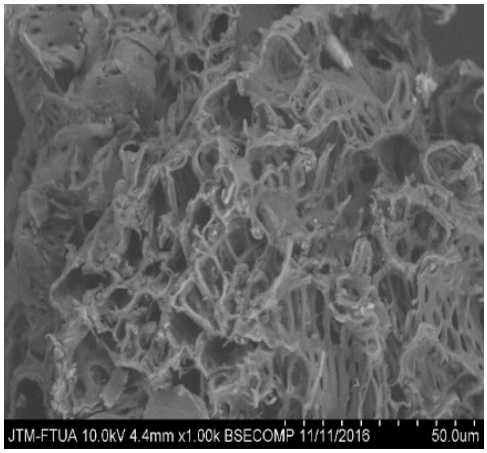


(a)

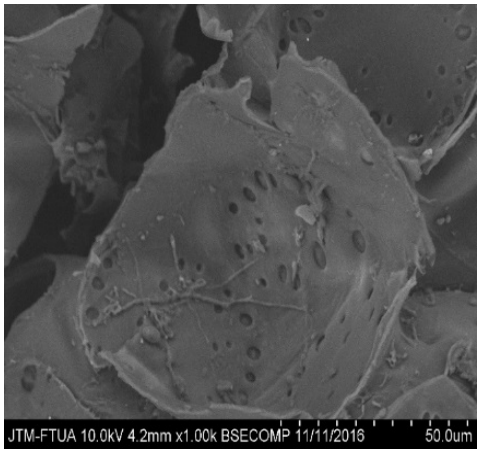


(b)

FIGURE 8. FTIR spectrum of sago bark (a) before and (b) after Pb(II) adsorption



(a)



(b)

FIGURE 9. SEM image of sago bark (a) before and (b) after Pb(II) adsorption magnification 1000 times

Thermodynamic

The thermodynamic parameters depend on temperature. The experiment was conducted within the temperature range of 298-318 K. These parameters were explained by Van't Hoff equation. As seen in Table 1, the G has a negative value indicating a spontaneous reaction. The G decreased as the temperature increased. The positive value of H (15.576 kJ/mol) described an endothermic consequence of deprotonation and diffusion process [12]. The disorder of Pb(II) adsorption increased which was indicated by the positive value of S (65.204 J/mol.K) [9, 12, 30].

Characterization of Sago Bark

Characterization of sago bark was carried out by FTIR and SEM-EDX. Figure 8 revealed functional groups exist in sago bark. The band at 3421.10 cm^{-1} was attributed to O-H (the intra-molecular H-bonded). Whereas, the band at 1734.16 cm^{-1} was C=O. After Pb(II) uptake onto sago bark, there was a shift from 3421.10 cm^{-1} to 3423.54 cm^{-1} for OH group. While, C=O group was shifted from 1734.16 cm^{-1} to 1718.65 cm^{-1}. This shift proved that the adsorption process has occurred. SEM image indicated the porous surface of sago bark. This pore supported the adsorption process of Pb(II) on sago bark shown by the smooth surface of sago bark after Pb(II) adsorption (Fig. 9).

CONCLUSIONS

Sago bark could be used as an adsorbent for Pb(II). The adsorption process followed the Langmuir isotherm model which means a monolayer adsorption. Kinetic study revealed the pseudo-second order model fits better to describe Pb(II) uptake onto sago bark. The thermodynamic suggested an endothermic reaction.

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REFERENCES

1. S. Mustapha, B. E. N. Dauda, Y. A. Iyaka, T. J. Mathew, I. A. Aliyu, and E. Y. Shaba, International Journal of Engineering and Science Invention **3**, 17 (2014).
2. S. N. M. Yusoff, A. Kamari, W. P. Putra, C. F. Ishak, A. Mohamed, N. Hashim, and I. M. Isa, J. Environ. Prot. **5**, 289 (2014).
3. S. Berhe, D. Ayele, A. Tadesse, and A. Mulu, International Journal of Scientific and Research Publications (IJSRP) **5**, 1 (2015).
4. U. Guyo, J. Mhonyera and M. Moyo, Process Saf. Environ. Prot. **93**, 192 (2015).
5. C. S. Yue, K. H. Chong, C. C. Eng, and L. S. Loh, Journal of Water Resource and Protection (JWARP) **8**, 568 (2016).
6. M. Mamatha, H. B. Aravinda, S. Manjappa, and E. T. Puttaiah, IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT) **2**, 1 (2012).
7. T. M. Elmorsi, Z. H. Mohamed, W. Shopak, and A. M. Ismaiel, J. Environ. Prot. **5**,1667 (2014).
8. S. K. Bozbaş and Y. Boz, Process Saf. Environ. Prot. **103**, 144 (2016).
9. G. Yuvaraja, N. Krishnaiah, M. V. Subbaiah, and A. Krishnaiah, Colloids Surf. B Biointerfaces **114**, 75 (2014).
10. J. N. Edokpayi, J. O. Odiyo, T. A. M. Msagati and E. O. Popoola, Sustainability **7**, 14026 (2015).
11. C. Song, S. Wu, M. Cheng, P. Tao, M. Shao and G. Gao, Sustainability **6**, 86 (2014).
12. M. H. Dehghani, D. Sanaei, I. Ali and A. Bhatnagar, J. Mol. Liq. **215**, 671 (2016).
13. B. Alawa, J. K Srivstava, A. Srivastava and J. Palsania, International Journal of Chemical Studies **3**, 03 (2015).
14. R. T. Prabha and T. H. Udayashankara, IOSR Journal of Environmental Science, Toxicology and Food Technology (IOSR-JESTFT**) 8**, 26 (2014).
15. K. Kowanga, G. O. Mauti, and E. M. Mauti, Journal of Scientific and Innovative Research **4**, 218 (2015).

16. M. S. Rajput, A. K. Sharma, S. Sharma and S. Verma, International Journal of Applied Research (IJAR) **1**, 411 (2015).
17. M. A. Etoh, D. J. D. Dina, H. M. Ngomo, and J. M. Ketcha, International Journal of Applied Research (IJAR) **1**, 793 (2015).
18. X. Yang and X. Cui, Water Resources and Industry **3**, 1 (2013).
19. I.E. Agbozu and F. O. Emoruwa, Afr. J. Environ. Sci. Technol. **8**, 239 (2014).
20. M. Kanyal, and A. A. Bhatt, J. Bioremed. Biodeg. **6**, 1 (2015)
21. D. Kurniawati, I. Lestari, S. Sy, H. Harmiwati, H. Aziz, Z. Chaidir, and R. Zein, Der Pharmama Chem. **8**, 149 (2016).
22. T. Suyono, M. A. Yuser, E. Munaf, H. Aziz, D. H. Tjong and R. Zein, J. Chem. Pharm. Res. **7**, 100 (2015).
23. N. Nazaruddin, R. Zein, E. Munaf and J. Jin, J. Chem. Pharm. Res. **6**, 370 (2014).
24. R. Zein, R. Suhaili, F. Earnestly, I. Indrawati, and E. Munaf, J. Hazard. Mater. **181**, 52 (2010).
25. B. Kumar, K. Smita, E. Sánchez, C. Stael, and L. Cumbal, Ecol. Eng. **93**, 152 (2016).
26. I. Langmuir, J. Am. Chem. Soc. **40**, 1361 (1918).
27. H. Freundlich, Phys. Chem. Soc. **40**, 1361 (1906).
28. S. Lagergren, Handlingar **24**, 1 (1898).
29. Y. S. Ho, G. McKay, Process Saf. Environ. Prot. **76**, 332 (1998).
30. L. B. L. Lim, N. Priyantha, M. H. F. Lai, R. M. Salleha, and T. Zehra, Int. Food Res. J. **22**, 1043 (2015).