THE FEASIBILITY OF SAGO BARK (*Metroxylon sagu*) IN Cu(II) REMOVAL: BATCH AND FIXED BED COLUMN EVALUATION

S. Fauzia¹, H. Aziz², D. Dahlan³ and R. Zein^{1,*}

¹Laboratory of Analytical Environmental Chemistry, Department of Chemistry,
Andalas University, 25163, Indonesia

²Laboratory of Physical Chemistry, Department of Chemistry,
Andalas University, 25163, Indonesia

³Laboratory of Material and Structure, Department of Physics,
Andalas University, 25163, Indonesia

*E-mail: rzein@sci.unand.ac.id

ABSTRACT

The present study examines the ability of sago bark to remove Cu(II) ions in solution which was a solid waste from sago starch industry. The optimum condition utilizing batch experiment for Cu(II) sorption was achieved at pH 5, agitation speed 100 rpm, adsorbent mass 0.1 g, temperature 298 K, 800 mg/L of initial concentration in contact time 30 minutes with adsorption capacity 16.47 mg/L. Cu(II) removal showed a good agreement with Langmuir, Freundlich and Tempkin isotherm model. The kinetic data confirmed that Cu(II) sorption followed pseudo-second-order model. The thermodynamic parameters revealed that the adsorption process was exothermic. Fixed bed column evaluation revealed that the best condition reached at 2 mL/min of flow rate with 9 cm bed depth. The breakthrough curve was suited to Thomas and Yoon-Nelson models. HNO₃ 0.01 M gave better performance as a desorbing agent and adsorption capacity decreased after 3 adsorption-desorption cycles.

Keyword: Adsorption, Batch, Column, Cu(II), Sago Bark

© RASĀYAN. All rights reserved

INTRODUCTION

The industrial process is discharged waste containing heavy metals. These metals contribute to environmental damage. The United Nations World Water Development stated that the amount of waste discharged to water bodies was 2 million tons of waste.¹ Copper (Cu(II)) is one of the heavy metals that is abundance in the earth's crust. Therefore, the occurrence of copper in the environment is both naturally and due to human activities. Human activities such as electroplating, herbicide, metal production, phosphate fertilizer production and paper industry are discharged an amount of copper to the air, water and soil. This metal ion can be accumulated or reacted to form a dangerous compound. Cu(II) is able to evoke some diseases to human body such as nausea, diarrhea, coma and death. That is why the level of Cu(II) in the drinking water level is limited by 1.3 mg/L.^{2,3} Due to its hazardous effect, the number of investigations has been conducted to overcome heavy metal wastewater. Adsorption is a common technique that has employed to remove heavy metals in wastewater. The adsorption technique can be done in two ways, the batch system and fixed-bed column system. The batch system gives information related to equilibrium and kinetic. Unfortunately, this system cannot be applied for industrial purpose but fixed-bed column. In the fixed-bed column, the waste flows continuously lead to gradient concentration that improves mass transfer and promotes adsorption efficiency.^{4,5} The adsorption technique is preferred because it is easy operation, high efficiency, low-cost and regeneration ability.⁶ The low-cost comes from the utilization of biomass or agricultural waste as adsorbent to remove heavy metals such as barley straw ash⁷, stem tree of soybean⁸, *nypa fruticans* merr shell⁹, activated carbon from oak leaves¹⁰ and date palm

dead leaflets,¹¹ curry tree carbon,¹² watermelon peel,¹³ rice husk,¹⁴ tree sawdust, natural and activated fluorapatite,¹⁵ zeolite,¹⁶ eggshell and sugarcane bagasse.¹⁷ These adsorbents consist of lignocellulosic which has pores, carboxylic and hydroxyl functional group playing a role in metal ion removal.¹⁸ Most of the adsorbents mentioned above came from agricultural or household waste. This waste would bring up another issue if it was not properly treated. Thus, the utilization of agricultural or household waste as an adsorbent will add more value toward them. Sago (*Metroxylon sagu*) is a plant that is used as raw material for starch production or livestock feed. These activities remain its bark as a waste that is not fully utilized. The bark has fiber that consists of lignin associated with the hemicelluloses.¹⁹ These compounds contain several functional groups that will support the adsorption of heavy metal. It expects to overcome both heavy metal in wastewater and sago bark itself as agricultural waste. The previous research which has been conducted in Pb(II) and Cr(VI) removal utilizing sago bark as the adsorbent confirmed the existence of pores, carbonyl and hydroxyl functional group that were one of the main requirements of biomass to be used an adsorbent. The result indicated that the ability of sago bark as an adsorbent was quite promising with adsorption capacity for Pb(II) and Cr(VI) removal 31.43 mg/g and 61.73 mg/g, respectively.^{20,21} Thus, the research aim is to evaluate the equilibrium and kinetics of chemically activated sago bark in Cu(II) removal using the batch system and investigated its feasibility in industrial purpose by following fixed-bed column system.

EXPERIMENTAL

Adsorbent Preparation

Sago (*Metroxylon sagu*) bark was obtained from the local area of West Sumatra, Indonesia. Sago bark was cut up into small pieces and washed with distilled water. Then, it was dried under the sunshade to remove water. The dried pieces of sago bark were powdered and sieved using into the particular size by a manual sieve (Retsch milling and Sieving). Later the powder of sago bark was chemically activated by HNO₃ 0.01 M for 2 hours. The powder was rinsed until the pH is neutral. Then, let it dried for further use.^{20,21}

Adsorbent Characterization

The morphology of adsorbent was studied by Scanning Electron Microscopy (SEM, Hitachi S-3400N). The sago bark powder was placed on the sample holder and coated by gold particle using ion sputtering method. Then, the surface morphology was scanned at 10 kV with 1000 times magnification. The functional group existed in sago bark was observed by Fourier Transform Infra-Red (FTIR, Unican Mattson Mod 7000). Whereas, the chemical composition was analyzed using X-ray Fluorescence Spectroscopy (XRF, PANalytical Epsilon 3).

Batch Study

The Batch study was carried out at the various experimental conditions. 10 mL of Cu(II) solution, which the pH and concentration were varied within the range (2-7) and (20-1000 mg/L), contact time (5-90 minutes), different temperature (25-45 °C) at adsorbent mass 0.1 g. After the adsorption process was over, the supernatant and adsorbent were separated by Whatman filter paper No. 42. The concentration of Cu(II) remained was measured using Atomic Absorption Spectrophotometer (AAS, AA240). Error bar represented the standard deviation.

Fixed Bed Column Study

The fixed-bed column study was conducted in a glass column (15×1 cm i.d.) by varying flow rate (2-6 mL/min) and bed depth (3-9 cm/0.5-1.5 g) with pH and concentration optimum obtained from batch system, 160 µm of particle size at room temperature. The effluent concentration was analyzed every five minutes using AAS and the breakthrough curve was plotting against Ce/Co vs time (t).

Regeneration Study

The repeatability of sago bark as adsorbent was investigated using HNO₃ with concentration 0.1 M and 0.01 M as a desorbing agent. In the batch system, the regeneration study was conducted by contacting 10

mL of Cu(II) solution with an adsorbent at the optimum condition from the batch study. Meanwhile, for the fixed bed column study, the desorbing agent was streamed through the bed in the column. Later the Cu(II) concentration was determined by AAS.

RESULTS AND DISCUSSION

Sago Bark Characterization

The FTIR spectra of sago bark before and after adsorption were reported in Fig.-1. A band at 3421.10 cm^{-1} corresponding to O-H stretching was shifted to 3422.62 cm^{-1} after Cu(II) sorption (figure 1a) The peak at 1636.26 cm^{-1} , shifted to 1637 cm^{-1} represented a C=O (carbonyl) group. Whereas, the peak within the range of $1000\text{--}1200\text{ cm}^{-1}$ assigned to C-O stretching or C-N stretching.²⁰⁻²³ The SEM image indicated that the surface of sago bark changed due to the adsorption process. The pore has disappeared because the adsorbate has attached to the adsorbent surface (Fig.-2a and b). Based on the previous research²¹, the sago bark pore radii was $24,904\text{ Å}$ and the hydrated ionic radii of Cu(II) was 4.19 Å . It explained that the feasibility of Cu(II) ion to trap in the sago bark pore. Along with the pore surface, the chemical composition of sago bark has changed as well. This proof that the Cu(II) has reacted with the sago bark not only physically (trap in the pore) but also chemically through complexation, ion exchange or electrostatic force because Cu(II) has 1.90 of electronegativity that supported electrostatic interaction.^{24,25}

Fig.-1: FTIR spectrum of Sago Bark (a) Before Adsorption^{20,21}, (b) Cu(II) Uptake

Fig.-2: SEM Morphology of Sago Bark (a) Before adsorption^{20,21}, (b) Cu(II) Uptake

Table-1: The Chemical Composition of Sago Bark

Before Adsorption ²¹		After Adsorption	
Compound	Concentration (%w/w)	Compound	Concentration (%w/w)
Ca	16.10	Ca	15.97
K	7.81	K	1.88
MgO	9.12	MgO	11.09
SiO ₂	39.47	SiO	40.00
CaO	10.84	CaO	10.03
K ₂ O	4.79	K ₂ O	1.06
Al ₂ O ₃	9.77	Al ₂ O ₃	6.53
Cu	0.042	Cu	5.34

Batch Adsorption Study

Effect pH

The pH_{pzc} and metal solution pH affects the surface charge of adsorbent and the speciation of the metal ion itself. The adsorption of Cu(II) onto sago bark achieved the peak when the pH of the solution was 5 (Fig.-3). Whereas at the pH above 5, the H_3O^+ ion gradually decreased and OH^- ion slightly increased. The high concentration of OH^- ion caused the formation of metal ions precipitation such as $Cu(OH)_2$. Thus, the metal ions could not interact with the active site properly.^{3,13,26} The previous study found that the pH_{pzc} of sago bark was 5.^{20,21} Therefore above this pH, the sago bark surface possesses positively charged²⁷. The positively charged of sago bark surface result in a repulsive force between the cation and the adsorbent. Moreover, at the lower pH the competition between H^+ and the metal ion to occupy the active site increase. Therefore, the adsorption capacity was smaller at the lower pH. In reverse, when the pH of the metal solution was higher than pH_{pzc} the adsorbent surface was negatively charged.²⁸ Although It caused an attraction force between adsorbent and cation increase, it leads to metal precipitation as well.²⁹

Kinetic Study

Figure-4 described the effect of contact time on the adsorption capacity of sago bark towards Cu(II) removal. Cu(II) sorption onto sago bark reached equilibrium after 30 minutes. At the initial stage, there are a number of vacant surfaces available so that metal ion is quickly adsorbed. Subsequently, the longer Cu(II) ion contacts with sago bark the less vacant surface remains to be occupied by Cu(II) ion. Later, the adsorption capacity comes down due to the saturation of adsorbent remarked by no significant changes in adsorption capacity after 30 minutes.^{3,27} Thus, 30 minutes of contact time was selected for further use.

Pseudo-first order, pseudo-second order and Webber-Morris intraparticle diffusion equations were employed to study the kinetic mechanism of Cu(II) sorption on sago bark. The pseudo first-order equation was described by the following equation (Eq.-1):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

Where k_1 was pseudo first-order constant (min^{-1}). q_e and q_t were the adsorption capacity (mg/g) at equilibrium and at the time t (minutes). Pseudo-second order was expressed as (Eq.-2):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

Where k_2 was pseudo-second order constant ($\text{g.mg}^{-1} \text{min}^{-1}$). Webber-Morris intraparticle diffusion given by using equation (Eq.-3):

$$q_t = k_{id} \sqrt{t} + C \quad (3)$$

Where K_{id} was intraparticle rate diffusion constant ($\text{mg/g min}^{1/2}$) and C was intercept giving information about the boundary layer thickness.³⁰

According to Table-1, the kinetic mechanism of Cu(II) sorption was well described by pseudo second-order model with q_e 1.4384 mg/g and determination coefficient 0.9996 (Fig.-5). It confirmed that the adsorption process of Cu(II) occurred chemically. The Webber Morris model indicated that Cu(II) sorption on to sago bark was monolayer at the initial stage and later the multilayer process begins to happen that's why the adsorption at the static state and decrease due to the saturation of functional group.^{31,32}

Fig.-3: pH Effect on Adsorption Capacity of Sago Bark on Cu(II) Sorption at Initial Concentration of 20 mg/L , 0.1 g Sorbent, 100 rpm of agitation rate in 60 Minutes.

Fig.-4: Contact Time Effect on Adsorption Capacity of Cu(II) Sorption onto at pH 5, initial Concentration of 20 mg/L , 0.1g Adsorbent, 100 rpm of Agitation Rate

Fig.-5: Kinetic Adsorption of Sago Bark for Cu(II) Sorption (a) Pseudo- First Order, (b) Pseudo- Second Order, (c) Intraparticle Diffusion

Initial Concentration effect and Adsorption Isotherm

As seen in Fig.-6, the adsorption Cu(II) ions rose as the concentration of metal ion increased from 20 mg/L to 800 mg/L with adsorption capacity of 16.47 mg/L. The adsorption process took place faster at the initial stage because the availability of vacant surface was sufficient to bind the metal ions either chemically or physically.³³ When the concentration of metal ions went up, the active site/the amount of adsorbent mass remained the same. Therefore, the adsorption capacity declined due to the saturation of the active site.³⁴ The isotherm adsorption was evaluated by Langmuir, Freundlich and Tempkin isotherm models. Langmuir isotherm model was calculated by the following equation (Eq.-4):

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max} \cdot K_L} + \frac{C_e}{Q_{\max}} \quad (4)$$

Where C_e and q_e were concentration (mg/L) and adsorption capacity (mg/g) at equilibrium, respectively. K_L was equilibrium adsorption constant (L/g), and $q_{\max}$ adsorption capacity maximum (mg/g). Freundlich isotherm model was described by (Eq.-5):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

Where K_F was Freundlich constant (L/g) and $1/n$ was adsorption intensity. The $1/n$ index within the range of $0.1 < 1/n < 1$ indicated a favourable adsorption process.

Whereas, Tempkin model was expressed by the following equation (Eq.-6):

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (6)$$

Where R was gas constant (8.314 J/mol.K), T was absolute temperature (K). K_T was equilibrium binding constant (L/g) and b was Tempkin constant relating to the enthalpy of adsorption (J/mol).³²

Fig.-6: Initial Concentration Effect Cu(II) Sorption onto Sago Bark at pH 5, with 0.1 g Sorbent, 100 rpm of agitation rate for 30 Minutes

The isotherm model evaluation showed that Cu(II) sorption onto sago bark was properly described by Langmuir, Freundlich and Tempkin model indicated by determination coefficient (figure 7). Langmuir isotherm model revealed that the adsorption capacity of sago bark was 16.47 mg/g. The adsorption intensity ($1/n$) pointed out that the adsorption of Cu(II) onto sago bark was favorable ($1/n=0.3557$) with K_F 1.6815 L/g. Meanwhile, enthalpy of adsorption obtained from Tempkin was 1.071 kJ/mol. It could be assumed that the adsorption of Cu(II) onto sago bark was monolayer at the initial stage than through multilayer adsorption at the next stage². According to the heat of adsorption, Cu(II) sorption onto sago bark followed physical adsorption reaction through van der Waal's interaction or trap in the pore.³²

Temperature Effect and Thermodynamic Evaluation

Effect of temperature on Cu(II) sorption was shown in figure 8. The adsorption capacity of sago bark increased as the temperature increased due to the collision between adsorbate and adsorbent.³⁰ This pointed out that the active site contained in the sago bark was able to resist up to 45 °C. The higher temperature might harm the organic matter inside the adsorbent. The thermodynamic parameters were evaluated by following the Van't Hoff equation (Eq.-7 to 9):

$$\Delta G^0 = -RT \ln K_l \quad (7)$$

$$\ln K_l = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

Table-2: Isotherm Constant for Adsorption Cu(II) onto Sago Bark

Adsorbate	Langmuir isotherm			Freundlich isotherm			Tempkin isotherm		
	$q_{\max}$ (mg/g)	K_L (L/g)	R^2	$1/n$	K_F (L/g)	R^2	b (kJ/mol)	$\ln K_T$	R^2
Cu(II)	16.47	0.0191	0.9686	0.3557	1.6815	0.9108	1.071	0.155	0.9271

Fig.-7: Isotherm Adsorption of Sago Bark for Cu(II): (a) Langmuir Model, (b) Freundlich Model, (c) Tempkin Model

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (9)$$

Where K_L was equilibrium constant related to Langmuir constant. R was gas constant (8.314 J/mol K). T was absolute temperature (K), ΔH° , ΔS° and ΔG° were enthalpy (kJ/mol), entropy (kJ/mol K) and free energy (kJ/mol), respectively.

Based on data presented in table 3, the enthalpy (ΔH°) was -62.0423 kJ/mol and the entropy (ΔS°) was -0.2312 kJ/mol K. These things showed that Cu(II) sorption onto sago bark was exothermic process and a rise in disorder. Whereas, the free energy (ΔG°) for the Cu(II) sorption was positive reflected unspontaneous reaction. The same phenomenon has been reported by previous research.^{28,35}

Table-3: Thermodynamic Parameters of Cu(II) Sorption

T(K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)
298	6.8820	-62.0423	-0.2312
308	9.1949		
318	11.5078		

Adsorption-Desorption Cycles

Adsorption-desorption cycles were carried out to evaluate the efficiency of sago bark after several times of use. HNO_3 0.1 M and 0.01 M were employed as a desorbing agent for sago bark.^{20,21} The process was repeated for three times.³⁶ Figure 9 described that the adsorption capacity of sago bark changed after three times adsorption-desorption cycles. The adsorption capacity at the first cycle was 1.9894 mg/g with HNO_3 0.1 M and 1.9891 mg/g with HNO_3 0.01 M. After the third cycles, the adsorption capacity was 1.8581 mg/g with HNO_3 0.1 M and 1.8601 mg/g with HNO_3 0.01 M. This fact indicated that the adsorption capacity did not significantly change after three times adsorption-desorption cycles. But both desorbing agents provided a different effect. Figure 9 exhibited that HNO_3 0.01 M gave better performance after three times adsorption-desorption cycles. Therefore, HNO_3 0.01 M was employed for further work. Table-6 presented the adsorption capacity of other adsorbents to remove Cu(II) ion in aqueous solution.

Fig.-8: Temperature Effect of Cu(II) Sorption onto Sago Bark at pH 5, Initial Concentration 10-50 mg/L, 0.1g of Adsorbent Dose, 30 Minutes of Contact Time at 100 rpm

Fixed Bed Column Evaluation

The breakthrough curve of Cu(II) sorption was investigated at optimum condition obtained from the batch system (pH 5 and 800 mg/L of Cu(II) concentration) with different flow rate and bed depth. Figure-10 revealed that the higher flow rate made bed saturation faster. At 2 mL/min of flow rate, the exhaustion time was 10 minutes. As the flow rate increased up to 6 mL/min, the exhaustion time declined to 5 minutes. Table-4 indicated that the adsorption capacity of sago bark at 6 mL/min was 17.08 mg/g and 14.31 mg/g at 2 mL/min. It pointed out that the adsorption capacity was higher at the higher flow rate but it shortened the exhaustion. In reverse, the variation of bed depth provided a different result. When bed depth was 9 cm, the exhaustion time was 15 minutes. Unfortunately, the lower bed depth shortened the exhaustion time to 5 minutes. At the lower flow rate, the metal ion was able to diffuse to the active site inside the adsorbent properly. It has sufficient time to react with the active site so that the concentration of a metal ion in effluent decreased. Extending the bed depth would give time to Cu(II) ion to interact with the active site and delay the breakthrough and exhaustion time. Thus, the volume of waste treated enhanced.^{4,18} The adsorption-desorption cycles were conducted using HNO_3 0.01 M as a desorbing agent. As seen in Table-4, the exhaustion time declined after three times adsorption-desorption cycles. There was no different time between the first and the second cycles. It reached the equilibrium after 15 minutes. After the third cycles, the exhaustion time reduced from 15 minutes to 10 minutes. It pointed out that HNO_3 0.01 M was suited as a desorbing agent that did not harm the active site inside of sago bark after three times adsorption-desorption cycles. This result exhibited that sago bark could be regenerated and reused for several times. The data was executed using Thomas and Yoon-Nelson models. The parameters of these model were listed in Table-5. Thomas model indicated that q_0 increased as the flow rate increased and decreased when the bed depth increased. The determination coefficient revealed that the breakthrough curve of Cu(II) sorption on sago bark followed Yoon-Nelson and Thomas model at flow rate 2 mL/min and 9 cm of bed depth. Yoon-Nelson showed that the 50 % breakthrough declined when the flow rate increased. Whereas, the increase in bed depth could extend the 50 % breakthrough time of sago bark.

Fig.-9: Adsorption-Desorption Cycles of Sago Bark

Fig.-10: Breakthrough Curve of Cu(II) Sorption onto Sago Bark at Different (a) Flow Rate, (b) Bed Depth

Table-4: Adsorption Capacity of Sago Bark at Different Flow Rate and Bed Depth

Metal Ion	Flow Rate (mL/min)	Bed Depth (cm)	t_b (min)	t_c (min)	AER (g/L)	EBRT (s)	BV	MTZ (cm)	Ce (mg/L)	q_{total} (mg)	m_{total} (mg)	q_e (mg/g)	RE (%)
Cu(II)	2	6	1	10	50	12.73	0.42	5.4	284.5	14.31	20	14.31	71.55
	4	6	1	5	50	12.73	0.85	4.8	364	12.72	20	12.72	63.60
	6	6	1	5	33.33	12.73	1.27	4.8	430.67	17.08	30	17.08	59.33
	2	3	1	5	50	25.47	0.85	2.4	364	6.36	10	12.72	63.6
	2	6	1	10	50	12.73	0.42	5.4	284.5	14.31	20	14.31	71.55
	2	9	1	15	50	8.49	0.28	8.4	336	19.92	30	13.28	66.4
Adsorption-desorption cycles													
Cycle 1	2	9	1	15	50	12.73	0.42	8.4	38.67	22.84	24	15.22	95.16
Cycle 2	2	9	1	15	50	12.73	0.42	8.4	106.66	20.8	24	13.86	86.66
Cycle 3	2	9	1	10	75	12.73	0.42	8.1	131	13.38	16	8.92	83.62

Table-5: Thomas and Yoon-Nelson Model Parameters at Different Flow Rate and Bed Depth for Cu(II) Sorption

Flow Rate (mL/min)	Z (cm)	Thomas			Yoon-Nelson		
		K_{TH} (L/mg.min)	q_0 (mg/g)	R^2	K_{YN} (min ⁻¹)	τ (min)	R^2
2	6	3.98×10^{-4}	6.70	0.7935	0.3185	4.20	0.7935
4	6	1.56×10^{-3}	20.94	0.7393	1.2490	6.53	0.7393

6	6	3.69×10^{-4}	16.15	0.7156	0.2955	3.36	0.7156
2	3	4.40×10^{-4}	10.63	0.7113	0.2932	3.14	0.8014
2	6	3.98×10^{-4}	6.70	0.7935	0.3185	4.20	0.7935
2	9	1.35×10^{-3}	8.13	0.9199	0.743	9.33	0.8392

Table-6: Adsorption Capacity of Other Adsorbents in the Batch System

Adsorbent	Q (mg/g)	Reference
Agroindustry residues		²⁸
Bark	5.96	
Bagasse	8.22	
Bark+Bagasse	7.81	
Granular Activated Carbon	7.03	³⁷
<i>Sargassum fusiforme</i>	7.69	³³
<i>Acacia nilotica</i>	9.76	⁶
Andean sachachi	9.69	³
Sago Bark	16.47	Present Study

CONCLUSION

Based on this research, it could be concluded that Cu(II) removal using sago bark reached optimum condition at pH 5, initial concentration 800 mg/L, adsorbent mass 0.1 g, 100 rpm of agitation speed for 30 minutes with adsorption capacity 16.47 mg/L at room temperature. The equilibrium in the batch system followed Langmuir, Freundlich, and Tempkin isotherm models. The adsorption of Cu(II) onto sago bark was well-described by pseudo-second order and overcame exothermic reaction. Meanwhile, in fixed-bed column system, the breakthrough curve was properly explained by Thomas and Yoon-Nelson model at the lower flow rate (2 mL/min) and the higher bed depth (9 cm). The regeneration using HNO₃ 0.01 M, revealed the repeatability of sago bark after three times adsorption-desorption cycles.

ACKNOWLEDGMENT

This work was supported by Ministry of Research, Technology and Higher Education of the Republic Indonesia [award number: 324/SP2H/LT/DPRM/IX/2016 and 059/SP2H/LT/DPRM/IV/2017]. The authors wish to express their gratitude to Prof. Piotr Konieczka (Gdansk University of Technology, Poland) for the suggestion.

REFERENCES

1. M. Sulyman, J. Namiesnik, and A. Gierak, *Polish Journal of Environmental Studies*, **26**(2), 479(2017), DOI:10.15244/pjoes/66769
2. R. Ali, K. Rao, and A. Khatoon, *Groundwater for Sustainable Development*, **2–3**, 42(2016), DOI:10.1016/j.gsd.2016.05.004
3. B. Kumar, K. Smita, E. Sánchez, C. Stael, and L. Cumbal, *Ecological Engineering*, **93**, 152(2016), DOI:10.1016/j.ecoleng.2016.05.034
4. M. Shanmugaprasanth, and V. Sivakumar, *Journal of Environmental Management*, **164**, 161(2015), DOI:10.1016/j.jenvman.2015.08.034
5. M.A. Martín-Lara, G. Blázquez, M. Calero, A.I. Almendros, and A. Ronda, *International Journal of Mineral Processing*, **148**, 72(2016), DOI:10.1016/j.minpro.2016.01.017
6. T. P., and S. T., *International Journal of Research in Chemistry and Environment*, **4**(4), 52(2014),
7. M. Arshadi, M.J. Amiri, and S. Mousavi, *Water Resources and Industry*, **6**, 1(2014), DOI:10.1016/j.wri.2014.06.001
8. Harmiwati, Salmariza, D. Kurniawati, I. Lestari, Z. Chaidir, R. Desmiarti, and R. Zein, *ARPN Journal of Engineering and Applied Sciences*, **12**(18), 5258(2017).
9. N. Nazaruddin, R. Zein, E. Munaf, and J. Jin, *Journal of Chemical and Pharmaceutical Research*, **6**(12), 370(2014).
10. M. Sulyman, J. Namiesnik, and A. Gierak, *Polish Journal of Environmental Studies*, **23**(6), 2223(2014), DOI:10.15244/pjoes/26764
11. M. Sulyman, J. Namiesnik, and A. Gierak, *Engineering and Protection of Environment*, **19**(4), 611(2016), DOI:10.17512/ios.2016.4.14

12. P.L. Prabha, S.A.F. Rani, B. Jayalakshmi, T. Ramachandramoorthy, T. Nadu, T. Nadu, and T. Nadu, *World Journal of Pharmacy and Pharmaceutical Sciences*, **5(3)**, 1543(2016).
13. N.E. Wanja, P.J. Murungi, P. Ahmed, H. Ali, and P.R. Wanjau, *International Journal of Science and Research (IJSR)*, **5(8)**, 671(2016), DOI:10.21275/ART2016929
14. N.E.M. Yahaya, I. Abustan, M.F. Pakir, M. Latiff, O.S. Bello, and M.A. Ahmad, , *International Journal of Engineering and Technology*, **11(1)**, 186(2011).
15. R.E.K. Billah, Y. Elyamani, Y. Rakhila, M. Agunaou, and A. Soufiane, *Rasayan Journal of Chemistry*, **12(1)**, 347(2019), DOI:10.31788/RJC.2019.1215078
16. A.R. Utami, S. Sugiarti, and P. Sugita, *Rasayan Journal of Chemistry*, **12(2)**, 650(2019), DOI:10.31788/RJC.2019.1222056
17. W.P. Putra, K. Azlan, siti N.M. Yussoff, C.F. Ishak, A. Mohamed, N. Hashim, and I.M. Isa, *Journal of Encapsulation and Adsorption Sciences*, **4**, 25(2014), DOI:10.4236/jeas.2014.41004
18. Z.Z. Chowdhury, S.B.A. Hamid, and S.M. Zain, *Bioresources*, **10(1)**, 732(2015).
19. D.S. Awg-Adeni, S. Abd-Aziz, K. Bujang, and M.A. Hassan, *African Journal of Biotechnology*, **9(14)**, 2016(2016).
20. S. Fauzia, H. Aziz, D. Dahlan, and R. Zein, *AIP Conference Proceedings*, **2023(020081)**, 1(2018), DOI:10.1063/1.5064078
21. S. Fauzia, H. Aziz, D. Dahlan, J. Namiesnik, and R. Zein, *Desalination and Water Treatment*, **147**, 191(2019), DOI:10.5004/dwt.2019.23577
22. W.J. Liu, F.X. Zeng, H. Jiang, and X.S. Zhang, *Chemical Engineering Journal*, **170(1)**, 21(2011), DOI:10.1016/j.cej.2011.03.020
23. L.D. Hafshejani, S.B. Nasab, R.M. Gholami, M. Moradzadeh, Z. Izadpanah, S.B. Hafshejani, and A. Bhatnagar, *Journal of Molecular Liquids*, **211**, 448(2015), DOI:10.1016/j.molliq.2015.07.044
24. J.J. Salazar-Rabago, and R. Leyva-Ramos, *Journal of Environmental Management*, **169**, 303(2016), DOI:10.1016/j.jenvman.2015.12.040
25. S. Shakoar, and A. Nasar, *Groundwater for Sustainable Development*, **7**, 30(2018), DOI:10.1016/j.gsd.2018.03.004
26. S. Najiah, M. Yusoff, A. Kamari, W.P. Putra, C.F. Ishak, A. Mohamed, N. Hashim, and I. Isa, *Journal of Environmental Protection*, **5**, 289(2014), DOI:10.4236/jep.2014.54032
27. Z. Wang, F. Shen, D. Shen, Y. Jiang, and R. Xiao, *Journal of Environmental Sciences*, **53**, 293(2016), DOI:10.1016/j.jes.2016.05.017
28. D. Schwantes, A. Celso, G. Jr, A.J. Miola, G. Ferreira, M. Gonçalves, D. Santos, E. Ariel, and V. Leismann, *Acta Scientiarum*, **37(3)**, 409(2015), DOI:10.4025/actascitechnol.v37i3.26809
29. S. Rani, M. Bansal, K. Kaur, and S. Sharma, , *Rasayan Journal of Chemistry*, **12(3)**, 1247(2019), DOI:10.31788/RJC.2019.1235171
30. R. Ahmad, R. Kumar, and S. Haseeb, *Arabian Journal of Chemistry*, **5(3)**, 353(2012), DOI:10.1016/j.arabjc.2010.09.003
31. F. An, R. Wu, M. Li, T. Hu, J. Gao, and Z. Yuan, *Reactive and Functional Polymers*, **118**, 42(2017), DOI:10.1016/j.reactfunctpolym.2017.07.005
32. S.K. Bozbaş, and Y. Boz, *Process Safety and Environmental Protection*, **103**, 144(2016), DOI:10.1016/j.psep.2016.07.007
33. S. Huang, and G. Lin, *Journal of Environmental Health Science and Engineering*, **13(21)**, 1(2015), DOI:10.1186/s40201-015-0180-4
34. N.J. Hamadi, A.A. Mohammed, and A.H. Ali, *International Journal of Engineering Sciences and Research Technology*, **3(7)**, 245(2014).
35. C. Hu, P. Zhu, M. Cai, H. Hu, and Q. Fu, *Applied Clay Science*, **143**, 320(2017), DOI:10.1016/j.clay.2017.04.005
36. N.A. Fathy, S.T. El-Wakeel, and R.R. Abd El-Latif, *Journal of Environmental Chemical Engineering*, **3(2)**, 1137(2015), DOI:10.1016/j.jece.2015.04.011
37. S. Almohammadi, and M. Mirzaei, *Advances in Environmental Technology*, **2**, 85(2016), DOI:10.22104/aet.2016.392

[RJC-5444/2019]