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Removal of artificial iron ions using activated carbon from sago pith waste

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ABSTRACT

In the present day, the industry is growing rapidly. Every process in the industries brings out pollution. Heavy metals, especially iron ions have contaminated water resources due to industrial activity. The high concentration of iron ions is dangerous for human life. To solve this issue an activated carbon from sago pith waste was developed to remove iron ions from industrial wastewater represented by artificial iron solution. The objective of this research is to measure the adsorption capacity of sago pith waste activated carbon (SPWAC) for treating artificial iron solution. The adsorbent was carbonized at 300 °C and 80 min. Further, it was activated by citric acid 0.1 M. The treated iron solution was analyzed by condutometer to examine the iron content. Subsequently, the functional groups of SPWAC were tested via Fourier Transform Infra-Red (FTIR). The result indicates that the SPWAC can reject iron ions of more than 80 % with an iron ions concentration of 1.81 mg/L at 60 min and 300 rpm. While, FTIR analysis show alkenes, carbonyl, and hydroxyl groups are present in SPWAC. The iron ions concentration in treated water is below the allowable threshold (0.3 mg/L) based on World Health Organization (WHO) guidelines for drinking water. Therefore, the SPWAC is promising technology to be applied for treating industrial wastewater.

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1. Introduction

Fe is a symbol of iron which is a chemical element. Industrial activities such as the utilization of pesticides, metals leaching from waste dumps, runoff, landfill, acid mine drainage, smelting, and foundries generate heavy metal pollution. It negatively impacts soil, water, and air ecosystems. Not only from industrial activities but high iron is also found in peat water or wetland water as well [1–12]. Iron excess can be harmful to human bodies because it has high solubility that can easily be absorbed in the body [13]. Even at low concentrations, heavy metals can be a threat to living creatures [14]. This has been a challenge in many developing countries in decreasing human exposure to heavy metals in the water.

Several methods have been attempted to remove the iron content. It included zero-valent iron (ZVI), electro-coagulation, oxidation, ion exchange, lime softening, membrane separation, and adsorption [15–26]. Membrane is advance technology which widely for metal or organic removal in water [27–49]. Meanwhile, adsorption is recognized as the most effective method to remove the heavy metal because it is easy to operate and simple design, and more convenience [50]. In recent years, there is an improvement in the use of renewable materials as adsorbents for heavy metal rejection in water. Several natural adsorbents such as Juniper bark and wood [51], rice bran [52], sugarcane bagasse [53], orange peel [54], pomelo peel [55], and potato peel [56] have been reported to adsorb heavy metals.

Sago waste is mainly produced from starch processing [57]. Sago (*Metroxylon sagu Rott.*) can be easily found in the wetland area where other crops cannot grow without improved soil and drainage [58]. The distribution of sago has spread around Southeast

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Asia (Malaysia, Indonesia, Philippines, Thailand) and northwestern Melanesia (Solomon island and Papua New Guinea). Indonesia has 2.3 million ha (51 % of the sago area in the world) [59]. It has been consumed by humans and animals as sago starch. However, about 50 % of the sago palm is not extracted [60]. Yamamoto [60] fabricates a charcoal briquette, biodegradable foam, and ethanol from sago pith waste. This is a reason to find another alternative that can reuse sago pith waste with high economic value and minimize environmental damage.

Sago pith waste which is lignocellulosic biomass can be a promising material for activated carbon fabrication [61]. Activated carbon in particular is a very flexible material as it can be easily tailored with appropriate chemical and physical treatments [62]. A prior study has studied sago waste as a biosorbent using H_2SO_4 and $(NH_4)_2S_2O_8$ activation [63]. But these activating agents have difficult accessibility in rural areas and complex preparation. Therefore, the present paper reports the adsorption capacity of sago pith waste activated carbon (SPWAC) using citric acid for treating industrial wastewater. It is because citric acid contains a carboxylic functional group and is abundant [64]. Carboxyl is negatively charge. Fe ions will be more easily attached to the carboxyl functional group because of its positively charged surface. The effect of carboxyl in adsorption has reported in another study[65].

The objective of this study is to measure the adsorption capacity of sago pith waste activated carbon (SPWAC) for treating artificial iron solution. Majority of studies use pseudo-first order (PFO) and pseudo-second order (PSO) models to describe adsorbent kinetics. The SPWAC can provide low-cost material with simple fabrication to remove iron from an aqueous solution.

2. Materials & method

2.1. Materials

In this experiment, sago waste was collected from the sago industry located in Sungai Tabuk sub district-Banjar district, South Kalimantan Province, Indonesia, $Fe_2(SO_4)_3$ powder to make an artificial iron solution of 10 ppm, distilled water, 0.1 M citric acid ($C_6H_8O_7$), conductivity meter (Lutron CD-4301, Taiwan) as well as furnace and oven.

2.2. Sago pith waste activated carbon fabrication

Sago pith waste undergoes a washing and drying process under the sun to remove dirt. Next, the sago pith meshed. Carbonaceous sago pith waste (CSPW) is made by meshing sago pith waste. It is then followed by a calcination process for 80 min at 300 °C in air condition to remove ash, water content, and volatiles. The CSPW was sifted to 120 mesh and dried. Citric acid was added (0.1 M) and stirred for 2 h. It is dried again at 100 °C for 2 h to obtain Sago pith waste activated carbon (SPWAC). Finally, distilled water was used to wash SPWAC until pH is neutral and dried in an oven for 2 h at 80 °C. Fourier Transform Infrared (FTIR) was tested to characterize the SPWAC.

2.3. Batch adsorption and kinetic studies

An adsorption study was performed using a batch process to obtain kinetic data. $Fe_2(SO_4)_3$ was diluted in distilled water to make a 10 ppm artificial iron solution. After that, 0.1 mg SPWAC was mixed into an artificial iron solution and stirred at room temperature for 60 min. During the adsorption process, the solution conductivity was observed to determine Fe concentration [66]. After all, the suspension was filtrated using a vacuum filter to separate the adsorbent from the solution and final conductivity was measured. The Fe removal efficiency and Fe adsorbed at equilibrium (q_e) were calculated using the equation below:

$$Feremoval(\%) = \frac{(C_i - C_e)}{C_i} \times 100\% \quad (1)$$

$$q_e = \frac{(C_i - C_e)}{w} \times V \quad (2)$$

Where C_i is initial concentration of Fe ion (mg/L), C_e is concentration of Fe ion at equilibrium condition (mg/L), w is weight of adsorbent used (g) and V is volume of Fe solution (L). The kinetic adsorption of Fe ion was observed using Pseudo First Orde (PFO) and Pseudo Second Orde (PSO) models [67–69]. PFO and PSO models can be written as:

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{k_2 q_t^2} \times \frac{1}{q_e} \quad (4)$$

Where k_1 is PFO constant (s^{-1}), k_2 is PSO constant (g/mg s) and t is adsorption time (min).

3. Results and discussions

3.1. Fourier Transform Infrared (FTIR)

Fig. 1 depicts the difference between sago pith waste and sago pith waste activated carbon (SPWAC) based on Fourier Transform Infrared (FTIR). The FTIR is operated within 4000–600 cm^{-1} wavelength numbers. FTIR works by identifying functional groups. Alkenes (C=C) and carbonyls (C=O) are found at 1639 and 1733 cm^{-1} for sago pith waste, while at 1629 and 1716 cm^{-1} for SPWAC. It is noteworthy that the C=O drastically increases after sago pith waste is turned into SPWAC with citric acid addition. Citric acid as organic acid will enhance adsorption capacity because several new sites are created on the SPWAC. Carboxyl from citric acid donates a proton (H +) and transforms a negatively charged car-

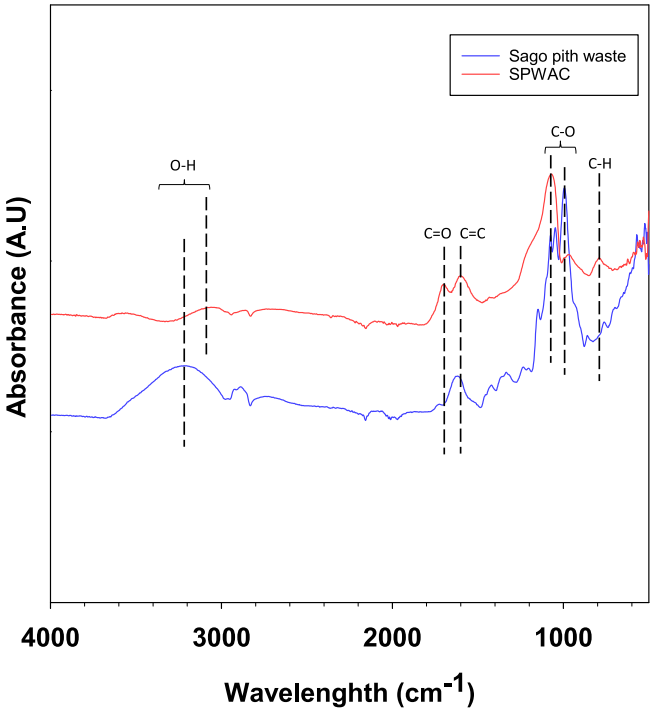

Fig. 1. FTIR of sago pith waste and sago pith waste activated carbon (SPWAC).

boxyl group [70]. The absorption bands at 817 cm^{-1} for SPWAC and 767 cm^{-1} for sago pith waste attributed to alkenes (C—H). This is in line with a study by Skoog, et al. [71], C—H appears at 995–675 cm^{-1}. C—H was also observed in sago waste activated carbon with the addition of phosphoric acid and potassium hydroxide [72]. As mentioned before, the peaks at 1718 and 1753 cm^{-1} corresponded to C=O groups. The spectra around 3152 and 3256 cm^{-1} are indicative of O—H (hydroxyl) groups. The O—H is related to lignin, cellulose, and hemicellulose content [73]. Carboxylic acids (R-COOH) are formed from carbonyl and hydroxyl [74]. The absorption bands of C—O are shown at 1092 cm^{-1} for SPWAC and 1005 cm^{-1} for sago pith waste. Identical absorbance bands were also observed in a previous study by Al-Swaidan and Ahmad [75]. As shown from all the functional groups in Fig. 1, it can be concluded that the SPWAC has more carbon than sago pith waste.

3.2. Adsorption

The adsorption effect of SPWAC on the artificial iron solution can be seen in Fig. 2. The rate of adsorption is high at the initial 10 min. It indicates the majority of iron adsorption occurred during the times. It is probably caused by a high Fe ion concentration at the initial condition that leads to massively Fe ion mass transfer into the abundant unoccupied active site[69]. Then, the rate of adsorption drastically decreases at 20 – 60 min due to the high concentration of Fe(III) ion at the surface and adsorbent pore, especially on active sites. It causes the adsorbent becomes saturated and loses its ability to Fe(III) ion adsorption. In addition, it shows the adsorbent reaches maximum adsorption capacity at 10 ppm of Fe(III) ion concentration. Moreover, it proves that the adsorption process depends on time, therefore contact time has an essential role [76].

In this study, the highest removal efficiency is obtained more than 80 %. This result is better than previous researches [77,78]. Comparison to other studies with different activating agent can be shown in Table 1. Activating agent may influence the adsorption performance by modifying surface area of adsorbent [79]. This condition denotes the potential of SPWAC to be applied for treating water with iron content. However, comprehensive studies are still required for implementing the adsorbent in the scale-up case, especially its interaction with another metal ion and dye.

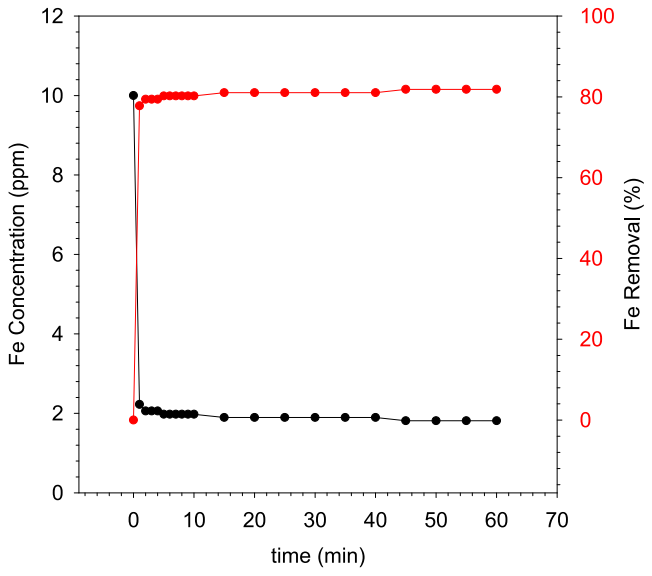

Fig. 2. Remain concentration of Fe ions and percent of Fe ions removal.

3.3. Kinetic studies

Pseudo-first order (PFO) and pseudo-second order (PSO) kinetic were used to identify which model fitted well to the adsorption data. The data was obtained from various sampling times. The parameters of the models and calculated data are illustrated in Table 2.

Fig. 3 shows the correlation between the PFO model and experimental data. It is clear evidence that the model does not fit Fe(III) adsorption experimental data. The PFO model is firmly related to an un-equilibrium state that describes a slow and steady adsorption rate due to a few active sites in the adsorbent. It also elucidates that at the initial stages of adsorption, the active sites are nearly zero due to the high concentration of adsorbate at the initial stage [84]. Thus, based on PFO characteristics, the present study shows the concentration of adsorbate is relatively low. Meanwhile, the unoccupied active site is abundant. Its characteristics belong to the PSO model. Generally, the PSO model has several conditions before it can be applied such as the final stages of adsorption, abundant active sites and, low concentration of adsorbate. In this research, the PSO model is fitted well to adsorption experimental data. The same result and pattern are found in previous researches [67,77,85]. Moreover, the kinetic constant and correlation coefficients (R2) of PSO are higher than PSO. It indicates the kinetic adsorption of Fe(III) is better described by the PSO model [67].

PSO model characteristics is a good kinetic model to explain about rapid adsorption that occurred at the initial stages of the Fe(III) adsorption process. It is related to the abundant active site that appears compared to adsorbate concentration in artificial solution. This condition drives the adsorbate to adsorb at the active site massively.

4. Conclusion

The study of characteristic and kinetic models of SPWAC during the adsorption process was conducted. It found that the SPWAC has been created successfully via carbonization and chemical activation procedures. FTIR analysis shows that the active sites have formed by citric acid via chemical activation. It was proven by increasing C=O absorbance intention. In addition, PSO kinetic model fits well with adsorption experiment data. It has also confirmed that abundant active sites appear on the adsorbent. The adsorbent exhibit a good performance with a removal efficiency of more than 80 %. Therefore, the SPWAC promises to be applied for treating industrial wastewater.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Muthia Elma reports article publishing charges was provided by Lambung Mangkurat University. Muthia Elma reports a relationship with Lambung Mangkurat University that includes: employment. Muthia Elma has no patent pending.

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Table 1
Comparison of heavy metal rejection using different biomass and activating agent.

Adsorbent type	Rejection (%)	Solution	Activating agent	References
Sago pith waste	81	Iron solution	$C_6H_8O_7$	This work
Sago	95	Mercury solution	H_2SO_4 and $(NH_4)_2S_2O_8$	[63]
Robusta coffee waste	65.4	Iron content in peat water	HCL	[80]
Mango peel	84	Iron in Batik wastewater	H_2SO_4	[81]
Albizia lebbeck seed	87	Lead solution	HCL	[82]
Banana Peel Activated Carbon (BPAC)	61	Chopper and chromium in textile waste solution	NaOH	[83]

Table 2
Parameters of the kinetic model for PFO and PSO at equilibrium time (60 min), ambient temperature and pH 5.

Models	Constant (k)	Equilibrium (q_e)	Adjusted R^2
PFO	0,0853(s^{-1})	81,87 (mg/g)	0.7638
PSO	8.6355 (g/mg.s)	81,58 (mg/g)	0.9999

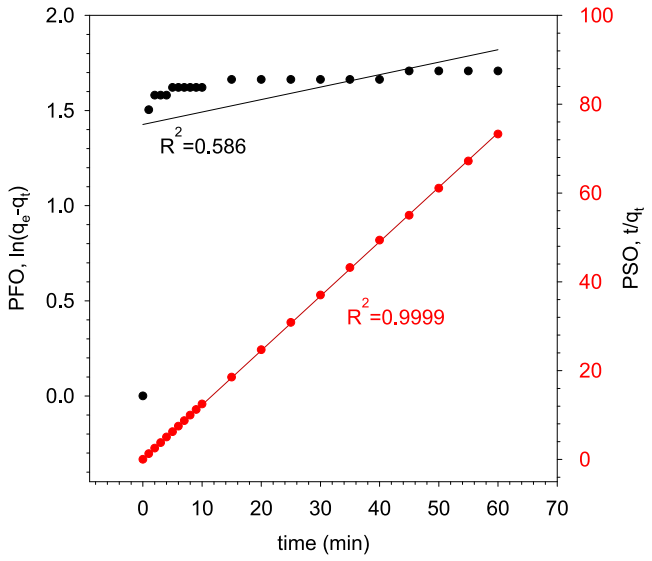

Fig. 3. PFO vs PSO kinetic models.

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