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Adsorption of Fe(III) on The Biosorbent from Polymerization Process of Nephelium Fruit Peel Extract

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Abstract. Adsorption of Fe(III) on the biosorbent from polymerization of nephelium fruit peel extract with aldehyde was carried out under acidic conditions (pH=5). The adsorption process was carried out to determine adsorption equilibrium, kinetics study, capacity (q_e) and adsorption constants of Fe(III) adsorption on the biosorbent. The adsorption equilibrium was obtained after 10 minutes of the adsorption process. The kinetic model of Fe(III) adsorption at the pH solution condition pH=5 followed the kinetics model from Ho which is pseudo-second order with the qe value of 40.65 $mg.g^{-1}$ and the adsorption rate constant (h) of $3.33x10^3$ $mg.g^{-1}.min^{-1}$.

INTRODUCTION

Tannin compounds are polyphenol compounds extracted from plants [1]. Tannin compounds are usually found in coconut coir [2], apples, spicy red pepper and geranium [3], persimmon fruit peels [4-6], mangrove bark [7-8], acacia mangium bark [9], guava leaves [10], grapes [11]. Tannin compounds from various different types of plants require different solvents in the extraction process because the content and type of tannin in each plant is also different [12]. Tannin compounds can be applied in various fields such as pharmaceuticals for the removal of antibiotic compounds of Trimethoprim (TMP) [12], chemical fields as substitutes for phenols in phenol-formaldehyde resins [7], biosorbents of heavy metals such as cadmium (Cd) in fish sauce [13], metal biosorbent such as platinum (Pt) [6], dyestuff biosorbent [5], as an inhibitor of metal corrosion rates [10], antibacterial agents, composite of flaxs fiber for vehicles [14].

The use of tannin as metal biosorbent is one of the interesting studies considering that we often encounter water pollution due to exposure to metals so that the level of metal ions in the waters can exceed water quality standards. Tannins which are polyphenol compounds have the ability to bind metal ions in water, one of which is tannin derived from biomass by modification to form a stable polymer in the water medium. Biomass which is quite abundant as a source of tannins is the skin of *Nephelium* fruit. Nephelium is a plant originating from Southeast Asia to become one of the major regional commodities in Inodenesia. The fruit skin can be used as raw material for making biosorbent polymers for the prevention of pollution of metal ions in the waters, one of which is Fe metal ion.

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EXPERIMENT METHOD

General

Materials

Nephelium fruit peel, phormaldehide (E-Merck), NaOH (E-Merck), HCl (E-Merck), $FeCl_3 \cdot 6H_2O$ (E-Merck), Deionized water (DI water) (Bratachem).

Experimental

Polymerization of Nephelium fruit peel extract

The polymerization of nephelium fruit peel extract was carried out in two stages: the first stage was extraction of nephelium fruit powder and the second was the polymerization process with aldehyde compounds. The extraction of nephelium fruit powder is done by mixing it with 200 mL 0.2 M NaOH solution at 50 °C for 2 hours. The extraction process will produce nephelium fruit extract called tannin solution. The tannin polymerization procedure is carried out according to the research conducted by Yanti *et al*. (2018) [15]. The results of polymerization are furthermore called Nephelium Tanin Based Biosorbent (NTBB).

Adsorption of Fe(III) on the NTBB

The process of Fe(III) adsorption by NTBB was carried out by interacting between 50 mg NTBB with 50 mL of 50 ppm Fe(III) on variations in contact times 0, 10, 20, 30, 40, 50, 60, 70, 80, and 90 minutes . Solids and solutions were separated by filtration using Whatman 42 filter paper, the filtrate obtained was then analyzed by Atomic Absorption Spectrophotometer (AAS) to determine the remaining Fe(III) which was not adsorbed by NTBB. The adsorption aims to determine the equilibrium time of Fe(III) adsorption on NTBB and its adsorption kinetics model.

RESULT AND DISCUSSION

Fe(III) adsorption process in NTBB occurs in acidity conditions (pH=5) where in these conditions Fe(III) is in cationic species namely $Fe(OH)^{2+}$ and $FeOH_2^+$ [16]. The results of polymerization of rambutan fruit extract (NTBB) will produce compounds that have carboxylic (-COOH) functional groups and hydroxy (-OH) functional groups. The existence of these functional groups is indicated by the vibration of C=O and C-O from carbonyl and the vibration of O-H which is likely from hydroxy groups based on FTIR spetra [15]. This allows NTBB to be able to adsorb other compounds such as Fe metal ions. Acidity conditions (pH=5) in the adsorption process allow deprotonation of these functional groups to facilitate the process of adsorption of Fe(III) in cationic species.

Based on Fig. 1 it is known that overall adsorption equilibrium time occurs after the 10^{th} minute. Table 1 has shown that the optimum adsorption conditions occur in the 70^{th} minute with the value of adsorption capacity reaching 41.28 $mg.g^{-1}$, which was previously 40.39 $mg.g^{-1}$. However, the condition is not so significant that it can be said that the adsorption equilibrium condition has occurred during the 10^{th} minute.

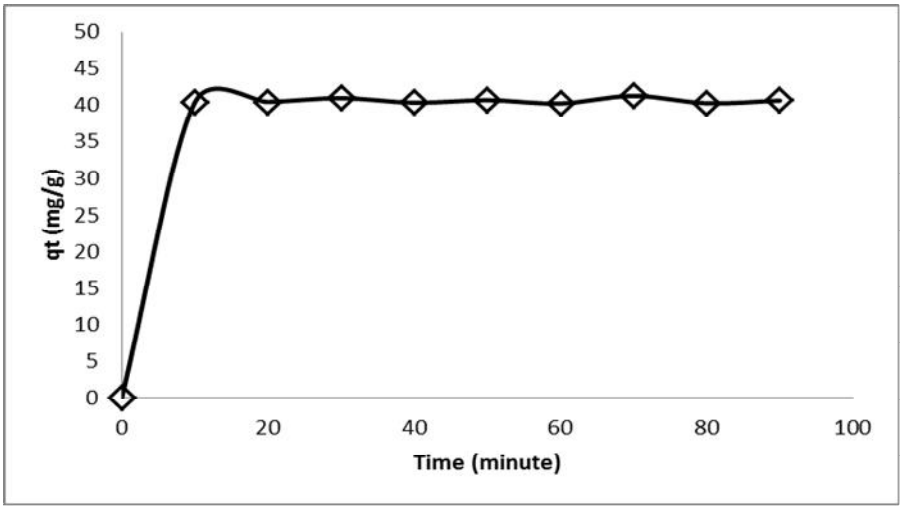

FIGURE 1. The adsorption time effect of 50 mL of 50 mg.L^{-1} Fe(III) on the 50 mg of NTBB under acidity conditions pH=5

TABLE 1. NTBB adsorption capacity of 50 mL of 50 mg.L^{-1} Fe(III) under acidity conditions pH=5

No.	Time (minutes)	q_t of Fe(III) (mg.g^{-1})
1.	0	0,00
2.	10	40.39
3.	20	40.45
4.	30	40.98
5.	40	40.35
6.	50	40.70
7.	60	40.25
8.	70	41.28
9.	80	40.28
10.	90	40.64

The kinetic model of Fe(III) adsorption in NTBB uses several kinetics models, namely the Langmuir-Hinshelwood, Santosa, Lagregreen, and Ho kinetic models. The equation of the Langmuir-Hinshelwood kinetics model is shown by eq. 1.

$$\frac{\ln \frac{C_0}{C_A}}{C_0\text{-}C_A}+K=\frac{k.t}{C_0\text{-}C_A} \quad (1)$$

Santosa kinetic model equation is shown by eq. 2.

$$\frac{\ln \frac{C_0}{C_A}}{C_A}=\frac{k.t}{C_A}+K \quad (2)$$

Where C_0 is the initial concentration of metal ions in solution (mol.L^{-1}). The value of C_A is the concentration of metal ions in solution at t (mol.L^{-1}). The value of K is the adsorption-desorption equilibrium constant (L.mol^{-1}), k is the adsorption rate constant (min^{-1}) and t is the time when adsorption (minute). The equation of Lagergreen kinetics (pseudo-first order) can be seen in eq. 3.

$$\log(q_e\text{-}q_t)=\log q_e-\left(\frac{k}{2.303}\right)t \quad (3)$$

The equation of Ho kinetics model is shown by eq. 4.

$$\frac{t}{q_t}=\frac{1}{h}+\frac{1}{q_e}t \quad (4)$$

In eq. 3 and 4 it is known that the q_e value is the adsorption capacity at equilibrium conditions ($mg.g^{-1}$), q_t is the adsorption capacity at a certain time (t) ($mg.g^{-1}$) and h is the adsorption rate constant ($mg.g^{-1}.min^{-1}$). The value of k in eq. 4 which is the Ho kinetics model (pseudo-secong order) is obtained from $h = kqe^2$ [17].

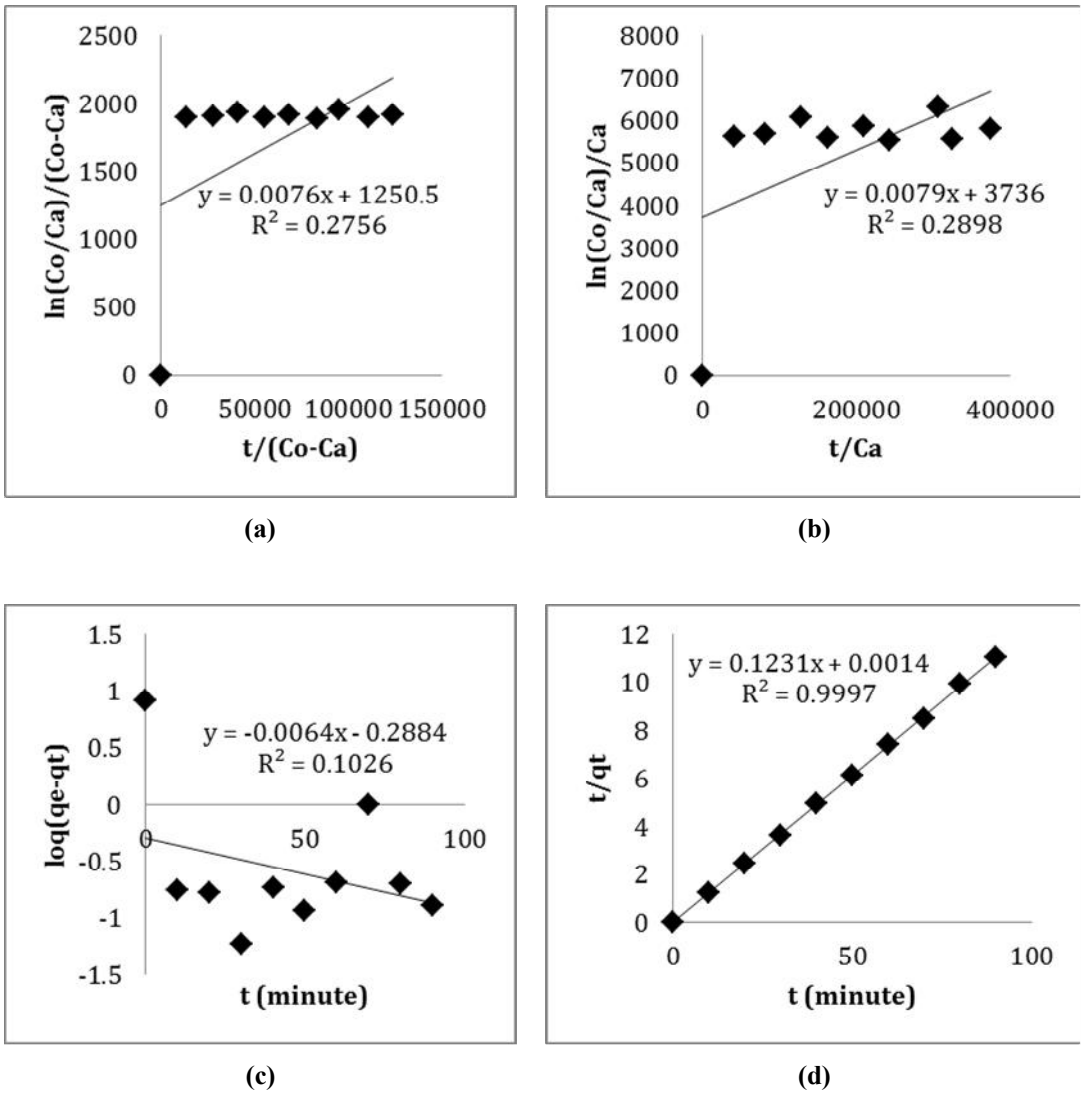

FIGURE 2. Linear plot of kinetics model for Fe(III) adsorption using NTBB by (a) Langmuir-Hinshelwood, (b) Santosa, (c) Lagergreen (d) Ho

Fig. 2 and Table 2 show that the Langmuir-Hinshelwood kinetic model is unlikely to occur because the K value of the adsorption equilibrium constant is negative, it indicates that the adsorption reaction goes to the left (reactant) or in other words the adsorption process does not occur. The kinetic model according to Santosa is also less precise because it produces a very small linear regression that is 0.2898 although the value of K which is positive allows the adsorption process to occur compared to the Langmuir-Hinshelwood kinetics model. Lagergreen's kinetic model also shows very small linear regression, which is 0.2037 which is very small compared to the kinetic model of Ho with a linear regression value which is close to 1 which is 0.9997.

TABLE 2. The results of calculation of Fe(III) adsorption kinetics by NTBB using various kinetics models

No.	Kinetics model	Kinetics parameters				
		R^2	k	K	h	q_e
1.	**Langmuir-Hinshelwood**	0.2756	$7.60x10^{-3}$ (min^{-1})	$-1.25x10^{3}$ ($L.mol^{-1}$)	-	-
2.	**Santosa**	0.2898	$7.90x10^{-3}$ (min^{-1})	$3.74x10^{3}$ ($L.mol^{-1}$)	-	-
3.	**Lagergreen**	0.2037	$1.89x10^{-2}$ (min^{-1})	-	-	2.73 ($mg.g^{-1}$)
4.	**Ho**	0.9997	2.02 ($g.mg^{-1}.min^{-1}$)	-	$3.33x10^{3}$ ($mg.g^{-1}.min^{-1}$)	40.65 ($mg.g^{-1}$)

Based on Fig. 2 and Table 2 shows that the kinetic model of Fe(III) adsorption on NTBB follows the kinetic model of Ho which states that the adsorption kinetics of metal ions are pseudo-second orders. The q_e value for Fe(III) adsorption is 40.65 $mg.g^{-1}$ and this is close to the true value of q_e at adsorption equilibrium, which is 41.28 $mg.g^{-1}$. Therefore, the pseudo-second order kinetics are the kinetics that are most likely to occur in Fe(III) adsorption with NTBB because the value is close to the actual value compared to other kinetics models.

CONCLUSIONS

The adsorption equilibrium was obtained after 10 minutes of the adsorption process. The kinetic model of Fe(III) adsorption at the pH solution condition pH=5 followed the kinetics model from Ho which is pseudo-second order with the q_e value of 40.65 $mg.g^{-1}$ and the adsorption rate constant (h) of $3.33x10^{3}$ $mg.g^{-1}.min^{-1}$.

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