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The Adsorption Process of Nitrite and Nitrate Content from Fertilizer Plant Liquid Waste of PT. PIM by Using Activated Carbon from Coffee Waste

¹*Mariana, ¹Mahidin, ¹Farid Mulana

¹Department of Chemical Engineering, Faculty of Engineering, Syiah Kuala University, Darussalam, Banda Aceh 23111, Indonesia;

*Corresponding Author: mariana_hasyim@yahoo.com

Abstract

Waste from fertilizer plant that containing much nitrites and nitrates is very dangerous when discharge to aquatic ecosystems. The existence of excess nitrites and nitrates content in liquid waste can cause the death of aquatic organisms. Recently, the fertilizer industry is treating excessive amount of nitrites and nitrates by using a neutralization process and aeration (called as KPPL Unit). However the treatment is not considered effective and safe for the environment. Alternative methods that can be used to decrease nitrites and nitrates content is adsorption process by using biomaterial with some advantages including low cost, high adsorption capacity, utilization of waste cake and environmental friendly. The carbon content in coffee can be used as an bioadsorbent to decrease nitrites and nitrates contained in fertilizer waste. In this study, bioadsorbent was activated by using HCl where it is expected to increase the adsorption capacity. This study includes the preparation of bioadsorbent from coffee waste with a variety of process variables to form activated carbon that has a high reactivity and to be applied as biosorbent to treat the wastewater outlet of KPPL Unit of PT. PIM. This research is expected to contribute to the process of separation of nitrites and nitrates from liquid waste which is the most important issue in the plant that must be addressed. Process variable is includes stirring time, pH, amount of adsorbent (g), and the concentration of the adsorbate. The results showed that the highest adsorption efficiency reached 88.9% and the adsorption capacity reached 28.5 mg/g. The process adsorption in this study followed the model of Isotherm Freundlich that assumes the physical adsorption process, with the largest R^2 value for nitrite of 0.841 and for the largest R^2 for nitrate of 0,862. While adsorption capacity for nitrite (n) as much as $4,81 \times 10^{-3}$ and for nitrate (n) $1,54 \times 10^{-3}$ and constant (Kf) for nitrite of $2,42 \times 10^{-6}$ and for nitrate (Kf) of $2,61 \times 10^{-4}$

Keywords: coffee grounds waste, activated carbon, nitrite, nitrate and freundlich isotherms

Introduction

PT. Pupuk Iskandar Muda Aceh has been done wastewater management in their factory by using neutralization and aeration process. Some physical chemistry and biological processes have been used to remove nitrite and nitrate dissolved in drinking water and wastewater. However the current performed treatment is considered not sufficiently effective and safe for the environment, especially in the handling of high levels of urea in wastewater. Aeration was performed to release a number of ammonia contained in the effluent into the air. Although the content of ammonia in the water outlet of KPPL unit are below the permitted quality standards of KepMen LH No. 51 Year 2004 (nitrat < 0,008 ppm, nitrat < 10 ppm) but when discharged continuously it will accumulate and exceed the quality standards mainly on the outlet KPPL location just before it has spread. Therefore, it is required an appropriate advanced processing methods to reduce the content of ammonia, nitrites and nitrates from KPPL outlet of fertilizer industrial wastewater. But here the researchers focused on decreasing levels of nitrites and nitrates in the wastewater due to nitrate compounds cause several diseases, especially for babies, causing a condition known as methemoglobinemia, also called as blue baby syndrome (Ogata, et al., 2014). And nitrite excess will lead to a decreased ability of marine biota to bind O_2 . Additionally, high nitrite compounds will also interfere with the process of spending nitrite compounds from the body of marine life (Trobos, 2007).

Coffee grounds are cheap and easily available materials and can be used to reduce levels of ammonia, nitrite and nitrate in the effluent. Coffee grounds including organic materials that can be made into activated carbon for use as an adsorbent or absorbent material (Sugiharto, 1987). Activated carbon is

a porous solids produced from carbonaceous material by heating at high temperatures. The previous study mentioned that the activated carbon from coffee grounds could adsorb up to 99.43% iron ions and able to adsorb the mercury reached 99% (Lubis and Nasution, 2002). In this study, the coffee grounds are used as materials for activated charcoal. Furthermore, activated carbon is used to lower levels of nitrites and nitrates in the wastewater of fertilizer industry outlet.

Methods

Experiments was conducted as follows: (1) preparation of activated carbon biosorbent from coffee waste; and (2) the process of adsorption of nitrite and nitrate using a batch process.

Preparation of activated carbon

Coffee waste dried under the sun and then soaked in a solution of 0.1 M HCl for 48 hours. And drained, then washed with distilled water to pH neutral. Coffee waste that have been activated then put in oven to reduce the moisture content, then the material is inserted into muffle furnace at a temperature of 350°C for 3.5 hours. Sieved using a sieve 80-100 mesh and after the activating process is finished the coffee grounds are stored in a desiccator.

Absorption of nitrate and nitrite using batch process

Liquid waste of fertilizer industry as much as 100 mL was contacted with activated carbon as much as 0.2 grams with size of 80-100 mesh at various stirring time. The wastewater before and after contacted with adsorbents was measured the nitrite nitrate levels by using spectrophotometry.

Results and Discussion

The ability of activated carbon from the coffee dregs to adsorb and accumulate waste can be seen from the total concentration of nitrate and nitrite as well as ammonia contained in the waste water. Figure 1 shows that the longer the time, adsorption efficiency will be higher, but in this study it was apparent that the saturation point of the adsorbent in which the saturation point here is that activated carbon can no longer adsorb waste (pores of carbon binds nitrite nitrate and ammonia at the optimum concentration). With the increasing concentration of waste then the percentage removal of nitrite and ammonia nitrate will decrease. In this study, we obtained the saturation point of activated carbon adsorbent to adsorb the waste is at the time of 40 minutes.

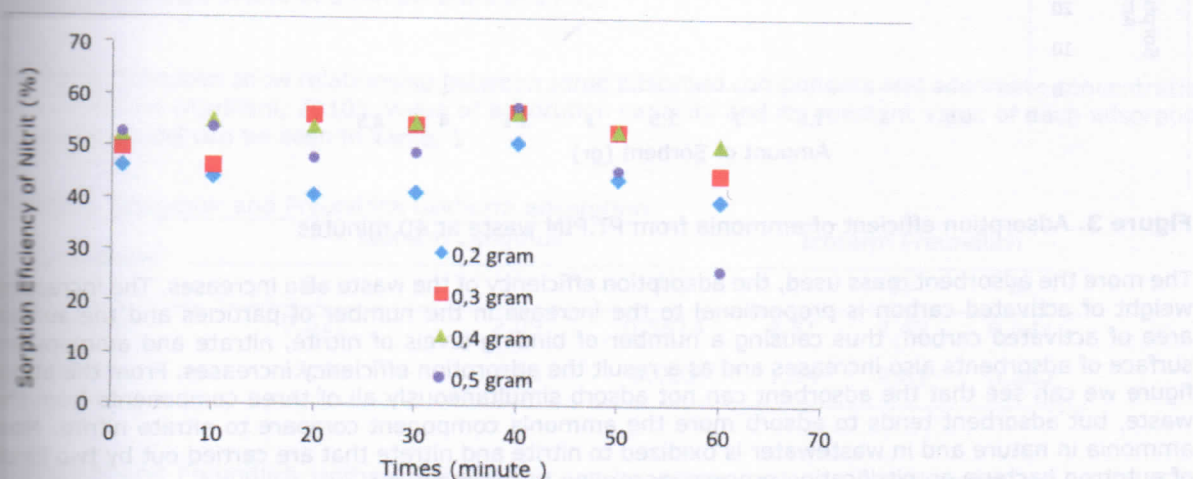


Figure 1. Effect of time toward adsorption efficiency of PT. PIM waste on various adsorbent weight

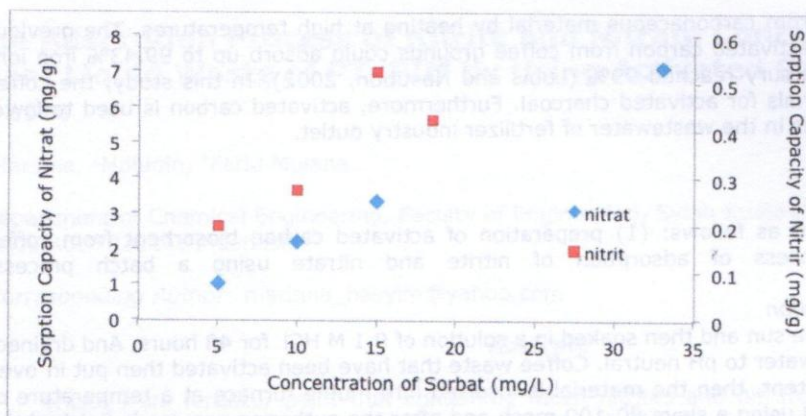


Figure 2. Effect of adsorbate concentration variations toward adsorption capacity of nitrite nitrate 40 minutes and adsorbent weight of 0.4 gram

Figure 2 shows that the adsorption capacity of nitrate and nitrite increased with increasing concentrations of the adsorbate. This is because when the concentration of adsorbate becomes high then the more the number of substances that accumulate on the surface of the adsorbent, which is caused by a substance dissolved in a solvent which is spread more, so the possibility of contact between the adsorbate and adsorbent is much greater (Syauqiah, 2011). Based on the experimental results, the adsorption capacity for nitrite with a concentration of 5 mg/L, 10 mg/L, 15 mg/L and 18.5 mg/L respectively is 0.2 mg/g, 0.275 mg/g, 0.525 mg/g, and 0.425 mg/g while for nitrate at a concentration of 5 mg/L, 10 mg/L, 15 mg/L and 33 mg/L respectively is 1.025 mg/g, 2.225 mg/g, 3.375 mg/g, and 7.125 mg/g.

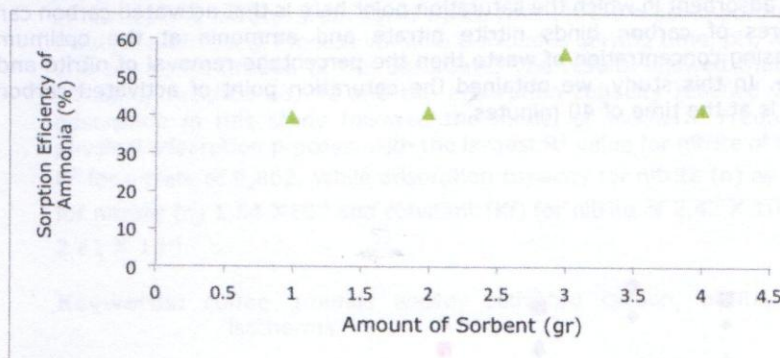
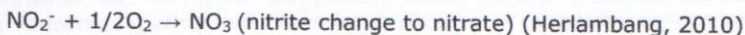
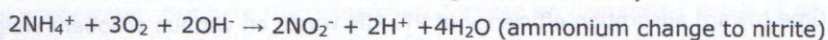
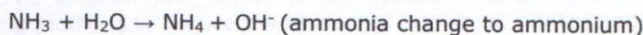


Figure 3. Adsorption efficient of ammonia from PT.PIM waste at 40 minutes

The more the adsorbent mass used, the adsorption efficiency of the waste also increases. The increasing weight of activated carbon is proportional to the increase in the number of particles and the surface area of activated carbon, thus causing a number of binding levels of nitrite, nitrate and ammonia on the surface of adsorbents also increases and as a result the adsorption efficiency increases. From the above figure we can see that the adsorbent can not adsorb simultaneously all of three components from waste, but adsorbent tends to adsorb more the ammonia component compare to nitrate and nitrite. In nature and in wastewater ammonia is oxidized to nitrite and nitrate that are carried out by two kinds of autotrophic bacteria on nitrification process, according to the reaction:



Isoterm Adsorption

To determine the adsorption isotherm on nitrate and nitrite using bio sorbents of coffee grounds, this study uses two adsorption models, namely Langmuir and Freundlich models. The models for nitrate adsorption are shown in Figures 3 and 4. Analogies are also made to the adsorption of nitrite.

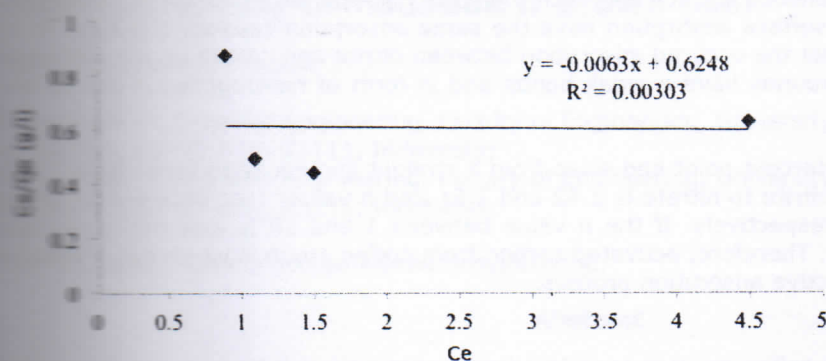


Figure 4. Langmuir isotherm adsorption on nitrate adsorption by using activated carbon produced from coffee waste at a temperature of 27°C

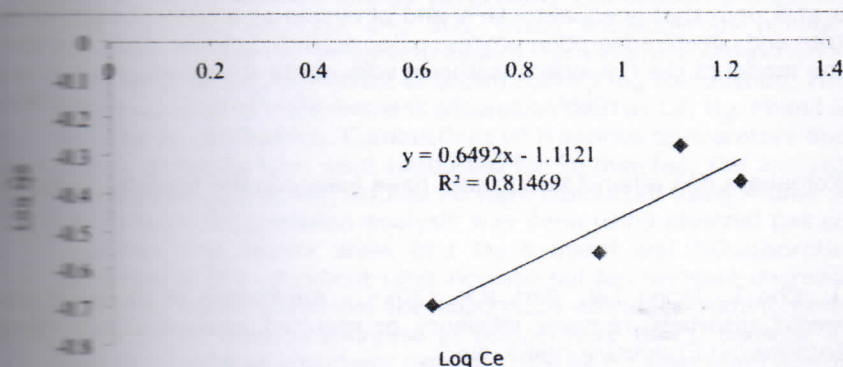


Figure 5. Freundlich isotherm adsorption on nitrate adsorption by using activated carbon produced from coffee waste at a temperature of 27°C

Isotherm adsorption show relationship between some adsorbed components and adsorbate concentration at equilibrium (Apriliani, 2010). Value of adsorption capacity and its constant value of each adsorption isotherm model can be seen in Table. 1

Table 1. Langmuir and Freundlich isotherm adsorption

Component	Isotherm Langmuir			Isotherm Freundlich		
	q_m	K_L	R^2	n	K_F	R^2
nitrite	0,027	2,09	0,5614	4,81	2,42	0,841
nitrate	-2,56	1,61	0,003	1,54	2,61	0,862

Langmuir and Freundlich isotherm adsorption can be determined by understanding the value of R^2 . Nitrite and nitrate adsorption isotherms using activated carbon produced from coffee grounds at 27°C followed the equation that has a value of R^2 correlation close to 1. According to Table 1 it can be seen that the value of R^2 on the adsorption of nitrate and nitrite that is approaching value of 1 is the Freundlich isotherm with R^2 of 0.8421 for nitrite and 0,862 for nitrates. So it can be concluded that the adsorption of nitrite and nitrate at 27°C followed Freundlich isotherm equation.

Freundlich isotherm equation assumes that the active sites on the surface of the adsorbent is a heterogeneous, where the active sites, energy and the type of bonding that occurs is not the same. and multilayer adsorption occurs on the surface of the adsorbent. Freundlich isotherm assume that on all sites of the adsorbent, surface adsorption process will occur under the given conditions. Freundlich isotherm is not able to estimate their sides on the surface capable of preventing adsorption at equilibrium is reached and there are only a few active side are capable of adsorbing molecules dissolved.

Freundlich isotherm assume that interaction is in physics and Freundlich isotherm also explained that the adsorbent having a heterogeneous surface and each molecule has a different adsorption potential, where not all of the adsorbent surface adsorption have the same adsorption capacity (Ma'rifat, et al, 2014). So it can be described that the occurred adsorption between nitrite and nitrate on the surface of activated carbon from coffee grounds have a weak bonds and in form of heterogeneous due to less uniform of adsorbent surface.

Kf and n is obtained from the intercept point and slope from a straight line equation from above figure where each value obtained for nitrite to nitrate is 2.42 and 2.61 and n values that obtained for nitrite and nitrate is 4.81 and 1.54, respectively. If the n value between 1 and 10 is assumed as a good adsorbent (Dhanakumar, 2007). Therefore, activated carbon from coffee grounds which has a value of n = 4.81 and 1.54 show an effective adsorption process.

Conclusions

Activated carbon produced from coffee grounds tend to adsorb more ammonia component compare to nitrite and nitrate components with adsorption efficiency as much as 56%. The highest adsorption capacity of nitrite was obtained at concentration of 15 ppm that is equal to 0.525 mg/g and of nitrate at a concentration of 33 ppm that is equal to 7.125 mg/g. The highest adsorption efficiency of nitrite was obtained at concentrations of 5 ppm that is equal to 16% and of nitrate at a concentration of 10 ppm that is equal to 88.9%. Nitrite and nitrate adsorption process using activated carbon produced from coffee grounds tend to follow the model of the Freundlich isotherm with nitrite R^2 values of 0.841 and nitrate R^2 value of 0.862.

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