The Ability of Coconut Shell Biochar Originated from Highland Area to Remove Nutrients from Agricultural Wastewater

Tivany Edwin[1], Puti Sri Komala[2], Mas Mera[3], Zulkarnaini[4]
{tivany@eng.unand.ac.id[1], putisrikomala@eng.unand.ac.id[2], masmera@eng.unand.ac.id[3]}

Environmental Engineering Department of Andalas University, Kampus Unand Limau Manis-Padang, Indonesia[1,2,4], Civil Engineering Department of Andalas University, Kampus Unand Limau Manis- Padang, Indonesia[3]

Abstract. Nutrient removal in wastewater before disposal into water bodies. One of the common adsorption materials is biochar, which can be made from coconut shells. Coconut shells also grow in the highlands, which are also utilized as agricultural areas. This study was performed to test the ability of biochar to remove ammonium, nitrate, and phosphate in a batch adsorption experiment. The results show a maximum ammonium, nitrate, and phosphate adsorption capacity using highland coconut shell biochar of 5.45, 4.85 and 6.57 mg/g, respectively. The best-fit isotherm that describes the ammonium, nitrate and phosphate adsorption process is the Langmuir isotherm. The best-fit adsorption kinetics are Pseudo 1st order. The results of this study indicate the potential of coconut shells from the highlands to remove nutrients from wastewater.

Keywords: Adsorption, biochar, coconut shell, highland.

1 Introduction

Ammonium, nitrate and phosphate as nutrients present in agricultural waste due to excessive use of fertilizers [1]. The accumulation of nutrients in water bodies can cause eutrophication. To remove them, wastewater treatment is required before it enters the water body. Adsorption is one method that is known to be economical and can remove nutrients from wastewater. One of the adsorption materials that can be used is biochar.

Biochar can be made with a variety of raw materials such as agricultural waste. Coconut shell is one of the wastes found in tropical countries, which is difficult to decompose. Coconut shells have the potential to be processed into biochar and are traditionally produced by the community using barrels. Nutrient removal using biochar has previously been studied by Zou et al. [2] and Konneh et al. [3]. However, the biochar is in powder form. The use of biochar in powder form will make it difficult for its application to treat agricultural waste water with a heavy flow, because it can be potentially clogged.

The highland region is an area of agricultural intensification in West Sumatra, Indonesia. In this area, there is also a generation of coconut shell waste that is processed into biochar by the local community. However, coconut shells that grow in the highlands have slightly different

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components than those of coconuts that grow in the lowlands. The use of local materials for wastewater treatment will be very beneficial.

For this reason, this study was conducted to analyze the ability of coconut shell biochar from one of the intensive agricultural areas in the West Sumatra-Indonesia region, in the coarse form to remove nitrates from agricultural wastewater. It is expected that the results of this study will be useful as an alternative to agricultural wastewater treatment.

2 Methodology

The study was performed using coconut shell biochar originated from highland are, in coarse form of 1 cm in size. Nitrate removal was tested by batch adsorption method with initial nitrate concentrations of 10, 20, 40 and 80 mg/L and observed every hour for 6 hours, with three replications. Each experiment was conducted in triplicate with 5g biochar in each 100 mL sample [4]. Nitrate artificial solution used potassium nitrate, ammonium used ammonium chloride, and phosphate used potassium dihydrogen phosphate. The ability of coconut shell biochar to remove nitrate was also tested using real agricultural wastewater.

The adsorption capacity was calculated using Equation 1. In this study, Feundlich isotherm (Equation 2) and Langmuir isotherm (Equation 3) along with adsorption kinetics consisting of a Pseudo 1st order model (Equation 4), and Pseudo 2nd order (Equation 5) were also calculated [5].

$$q = \frac{(C_0 - C_t)V}{m} \qquad (1)$$

Where q is adsorption capacity, C_o is the initial nitrogen or phosphate concentration, C_t is the nitrogen or phosphate concentration at time t (mg/L), V is the solution volume (L), and m is the dry weight of the biochar (g).

$$x/m = K_f (C_e)^{1/n} \qquad (2)$$

Where K_f as Freundlich constant (l/g) and n as adsorption capacity and adsorption intensity, x/m as the amount of phosphate adsorbed onto 1 g adsorbent under equilibrium conditions (mg/g), C_e as the contaminant concentration at equilibrium (mg/L).

$$q = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (3)$$

Where q as the adsorption capacity of nutrients(mg/g), K_L as Langmuir constants, q_m is maximum adsorption capacity of nutrients (mg/g), and C_e as the concentration of contaminant at equilibrium (mg/L), *a,b*.

$$q_t = q_e\left[1 - \exp\left(-k_{1p} t\right]\right. \qquad (4)$$

Where q_t is the adsorption capacity at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), k_{1p} is the pseudo first-order rate constant (h^{-1}), and t is the contact time (h).

$$q_t = \frac{K_{2p} {q_e}^2 t}{1 + K_{2p} {q_e}^2 t} \qquad (5)$$

Where q_t is the adsorption capacity at time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g), K_2p stands for the second-order rate pseudo-constant (g/mg/h), and t is the contact time (h).

3 Results

During the experiment, dissolved oxygen (DO) and pH were observed which are presented in **Figure 1** and **Figure 2**. The pH ranges during the ammonium, nitrate and phosphate removal experiments were 5.98-6.57; 6.86-7.06 and 5.56-6.34, respectively. While DO during the ammonium, nitrate, and phosphate removal experiments were 4.4-6.1 mg/L; 4.5-5.4 mg/L and 4.7-6.6 mg/L, respectively. pH values are getting lower as the initial concentration increases in the ammonium and phosphate removal experiments. this is due to the parent solution in the experiment is acidic.

The adsorption capacity of biochar based on the initial concentration of ammonium, nitrate and phosphate is shown in **Figure 3**. The adsorption capacity of ammonium, nitrate and phosphate tends to be the same, but the highest among them is the adsorption capacity of phosphate.

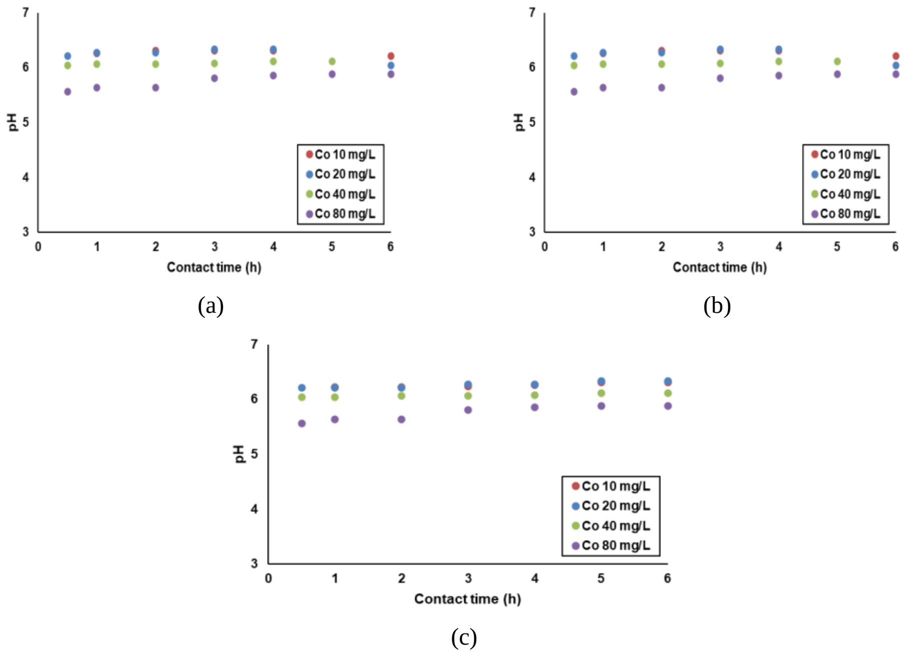
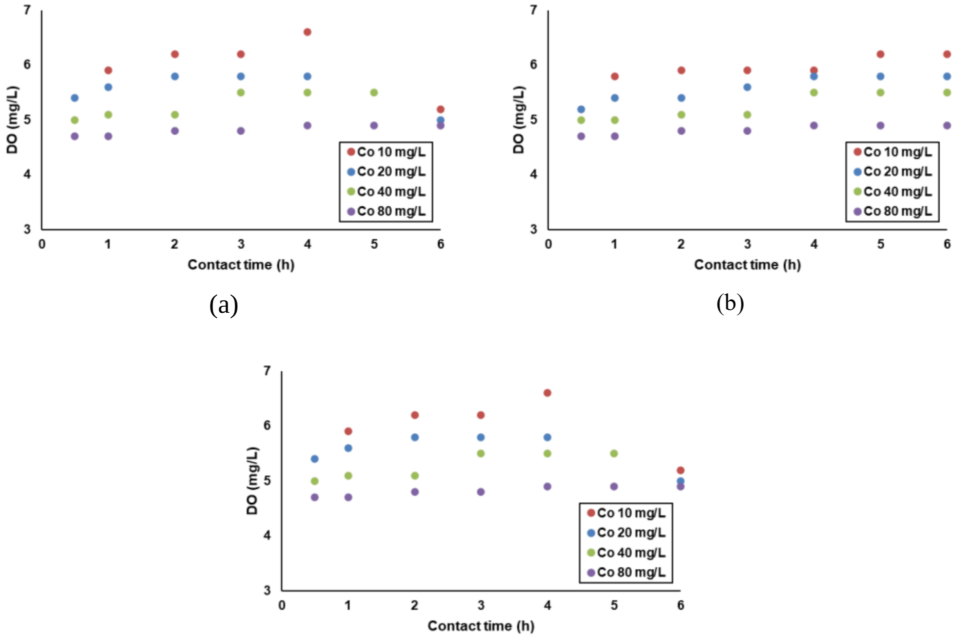


Fig. 1. pH level of the experiments in the removal of (a) ammonium, (b) nitrate and (c) phosphate.



(a) (b) (c)

Fig. 2. Dissolved oxygen level of the experiments in the removal of (a) ammonium, (b) nitrate and (c) phosphate.

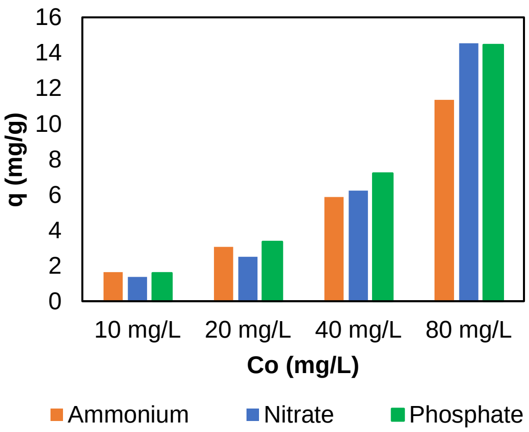


Fig. 3. Adsorption capacity in different nutrient's initial concentration

The maximum adsorption capacity of biochar on ammonium, nitrate and phosphate removal, as well as the Langmuir and Freundlich isotherm constants from the experiment, is presented in Table 1. The maximum adsorption capacity of biochar is higher for phosphate than the other nutrients in this study at 6.67 mg/g. Followed by the maximum capacity of ammonium is 5.85 mg/g and nitrate is 4.85 mg/g. Research by Zou et al. [2] showed the maximum adsorption capacity of ammonium using coconut shell biochar in powder form in the range of 12.80-15.50 mg/g and nitrate of 78.1 mg/g. Research by Konneh et al. [3] showed the maximum adsorption capacity of nitrate with powdered coconut shell biochar of 12.97 mg/l. The results of other studies show a maximum adsorption capacity that is more satisfactory than this study. However, the form of biochar used in this study is coarse, which causes the biochar surface area to be smaller than the powder form, thus reducing the sites for adsorption on the biochar surface. However, powdered biochar is not always applicable, sometimes the use of a coarse form will be beneficial to overcome clogging in the filter.

Regarding the adsorption isotherms, from the R^2 values that are almost close to 1, the Langmuir isotherm model appears to be the most suitable to describe the adsorption of ammonium, nitrate, and phosphate using coconut shell biochar from this plateau.

The Langmuir model describes monolayer adsorption, assuming that adsorption occurs on a certain number of adsorption sites, each site is occupied by one adsorbate molecule, all sites are equal, and there is no interaction between adsorbed molecules [6]. Whereas the Freundlich Model represents non-ideal adsorption, with multiple adsorption sites and heterogeneous surfaces. It is based on the assumption that active binding sites are occupied first, and the binding ability decreases as the site occupation increases [7].

In the Langmuir isotherm, where qm (mg/g) is the maximum mass of contaminant adsorbed per unit weight of adsorbent when the surface is completely covered by a monolayer of contaminant ions. K_L (l/mg) is the Langmuir constant associated with the affinity of the binding sites on the surface adsorbent to the contaminant ions, Whereas, the Freundlich isotherm, K_f and n are Freundlich constants, indicating adsorption capacity and adsorption intensity, respectively. A value of n>1 indicates a favourable adsorption process [8].

Table 1: Adsorption isotherm of the study.

Removal of	Langmuir			Freundlich		
	q_m(mg/g)	K_L	R^2	n	K_F	R^2
Ammonium	5.45	2.21	0.84	2.71	2.60	0.87
Nitrate	4.85	8.70	0.78	3.46	3.36	0.52
Phsophate	6.67	1.96	0.87	2.03	3.46	0.79

Table 2: Adsorption kinetic for the removal of ammonium, nitrate, and phosphate.

Removal of	Pseudo 1st order			Pseudo 2nd order		
	K (/jam)	q_e (mg/g)	R^2	K (/jam)	q_e (mg/g)	R^2
Ammonium	1.70	0.36	0.85	0.02	5.20	76.34
Nitrate	1.13	0.39	0.73	0.00014	49.61	69.11
Phsophate	0.31	1.71	0.96	0.001	19.54	77.39

The results of adsorption kinetics are shown in Table 2. From the R^2 values, it appears that all materials for adsorption for the removal of ammonium, nitrate and phosphate using biochar obtained from the highlands are more suitable to be described by the Pseudo 1st order model.

This indicates that the adsorption rate is proportional to the concentration remaining in the solution. Comparison of the picture of adsorption capacity vs time obtained with the models for nitrate, ammonium and phosphate adsorption [9], [10].

4 Conclusions

Coconut shell biochar from the highlands has the potential to remove ammonium, nitrate and phosphate from wastewater. The maximum adsorption capacity of biochar from the highest is against phosphate > ammonium > nitrate. Langmuir isotherm is more appropriate to describe the adsorption process that occurs. While the adsorption kinetics that matches the nutrient removal in this study is the Pseudo 1st order model.

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