Adsorption of Metals ion with Biochar Derived from biomass waste with fixed column

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Abstract: Industrial activity has been generating wastewater and need to be treated. Biochar is a potential and low-cost adsorbent as an alternative solution for removal metals ion. Fe and Mn are metals ion that produced in mining industrial activities. In this study, biochar has derived from coconut shell and wood. Biochars were produced in modified rector for 4 hours. The sorption abilities of biochars were measured in fixed column at laboratory in room temperature. Biochar derived from coconut shell has high sorption ability for removal metals ion than wood. Isotherm models of metals ion sorption fitting in Freundlich model. Isotherm model of metals ion sorption were evaluated with ARE and chi-square. Thus, biochars are potential carbon material to solve the wastewater problems.

Keywords: acid mine drainage, heavy metals, biochar, clamshell

Introduction

In recent decades, industrial activity has been generating wastewater and need to be treated using several steps due to the high heavy metals content and low pH. Ferro (Fe) and Mangan (Mn) are the heavy metals that produced on coal mining activity and are also emitted into wastewater [(Naswir et al., 2019a)'(Wibowo and M, 2019)]. Heavy metals on wastewater could give some negative impacts for human health and environment [(Mao et al., 2019)]. Several studies inform that heavy metals content on wastewater has been generated cancer, poisoning, skin disease and die [(Kim et al., 2007; Sun et al., 2018; Tolvanen et al., 2019)]. Although Fe and Mn has less toxicity than Chromium, the concentration of Fe and Mn still higher in several wastewater especially acid mine drainage and this heavy metals still limited by effluent standard [(Lee et al., 2002)]. Recent study inform that the methods of heavy metals removal from wastewater including precipitation, adsorption, ion exchange, electrodialysis and coagulation[(Zhang et al., 2019)]. Adsorption is the best and economic treatment for heavy metals removal from wastewater, moreover, adsorption efficiency is high removing heavy metals from aqueous solution.

Biochar, activated carbon, porous carbon and silica, bentonite, bio-adsorbents, sewage sludge are used as adsorbents to remove metals ion on wastewater [(Wibowo et al., 2019)-11]. Biochar is a low-cost adsorbent and carbon rich materials are produced from biomass in limited-oxygen conduction in the thermal process(Borchard et al., 2012) . In Indonesia, coal mining process has been generating wastewater called acid mine drainage, this condition generated problems about environment, biota life and human health. Acid mine drainage need some treatments to make the environment safe. Biochar as a potential sorbent are biomaterial with high surface area, good pores, porosity, neutral alkaline pH and functional groups [(Deem and Crow, 2017; Dong et al., 2011; McNamara et al., 2018)]. Recent studies informs that biochar has been using to remove metals ion from wastewater(Lv et al., 2018) including original biochar, biochar composites or modified biochar[(Khan et al., 2019; Tareq et al., 2018; Zhang et al., 2020)].

Although researchers were developing of biochar as a low-cost sorbent, the problem of biochar production has been finding especially on developing countries and rural areas. Biochar sorption on wastewater application has been limiting, it caused by competitive study has been complicated. Recent studies informs that biochar has produced using furnace and high-technology reactor[(Deng et al., 2018; Li et al., 2019, 2015)]. This condition made wastewater treatment using biochar still a problem. Also competitive study make this process too complicated, biochar production not yet developing use all of carbon materials, several studies inform that biochar has been producing by limited feedstock[(Hao et al., 2018; Paranavithana et al., 2016; Schneider et al., 2018)].

In this study, two biochars were prepared from wood and coconut shell. The biochars sorption capacity were investigated by batch experiment in laboratory. In previous study, the best biochar has derived from coconut shell[(Windeatt et al., 2014)], this study

compared the biochar derived from coconut shell and wood. The adsorption of Fe and Mn were evaluated using competitive sorption. This paper will describe the sorption abilities of biochars from coconut shell and wood including isotherm model.

Method and Materials

Prepaaration of Biochars

Coconut shell and wood were collected from Jambi, Indonesia. Pyrolysis of coconut shell and wood were used low-cost-modified pyrolysis reactor (Fig. 1) under limited-oxygen conduction for 4 hour, respectively. Biochars were crushed by Jaw Crusher, the size of biochars particle between 100-150 nm, respectively.
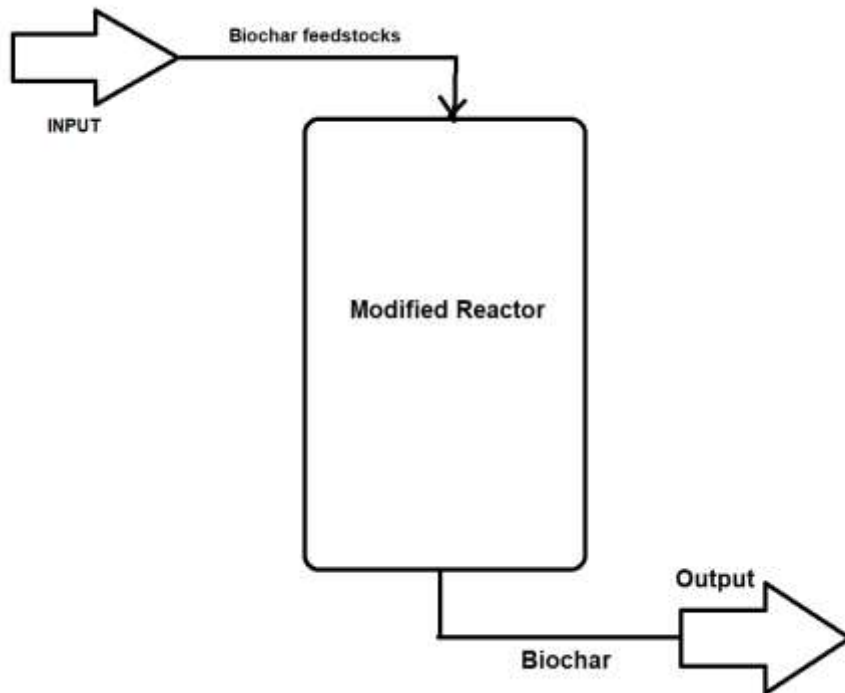
Figure 1. Low-cost-modified pyrolysis

Sorption Studies

500 ppm of Fe and Mn solutions were added onto 10 mg biochar in fixed column and the results were measured by atomic absorption spectrophotometer. Isotherm study fitting by Langmuir and Freundlich models. The concentration of solutions are 20, 40, 60, 80, 100, 200, 300, 400 and 500 ppm of Fe and Mn onto 10 mg biochar. Kinetic study calculated by zero, one and two-order, study of kinetic sorption Fe and Mn were measured in contact times from 0, 1, 5, 10, 15, 20, 25 and 30 minutes. Isotherm and kinetic study were evaluated by ARE and Chi-square to find the best models of sorption.

Percent Removal

Percent removals of metals ion were calculated using Eq. 1. Where, the Co is first metals ion in acid mine drainage and Ce is metals condition after sorption process.

$$Removal \ (\%) = \frac{Co - Ce}{Co} \ x \ 100 \qquad\qquad\qquad \text{Eq. 1}$$

Isotherm study

The different concentration of metals ion added into a solutions from 20, 30, 40, 50, 150, 200, 300, 400 and 500 ppm in the room tempetarure. The mass of adsorbents are 1 gr for 200 mL solution in a batch experimental. The models are evaluated using average relative error (ARE) (Eq. 2) and chi-square (Eq. 3).

$$ARE = \frac{100}{n} \sum \frac{|q_e - q_{e'm}|}{q_e} \qquad \text{Eq. 2}$$

$$\chi^2 = \sum \frac{(q_e - q_{e'm})^2}{q_{e'm}} \qquad \text{Eq. 3}$$

Result and Discussion

Metals ion Sorption

Sorption of Fe and Mn effect on time contacts in fixed column can see in Fig. 2. In this study coconut shell has sorbed metals ion better than wood biochar. Several study inform that the best pores and surface area of adsorbent is coconut shell (Tonucci et al., 2015). In the competitive study, another metal ion will give an impact on sorption process, it caused by the pores of biochar has filled by another metal ion. Also biochar from coconut shell has better sorption but the wood biochar also have good sorption of Fe and Mn in a solution. According Fig. 2, metals ion does not decreased after 30 minutes contact times, it caused by the pores of biochar has full of metals ion. In competitive study sorption abilities of biochars does not better than non-competitive, it caused by the metals ion in solution will fill the pores randomized, so it will be affected another one.
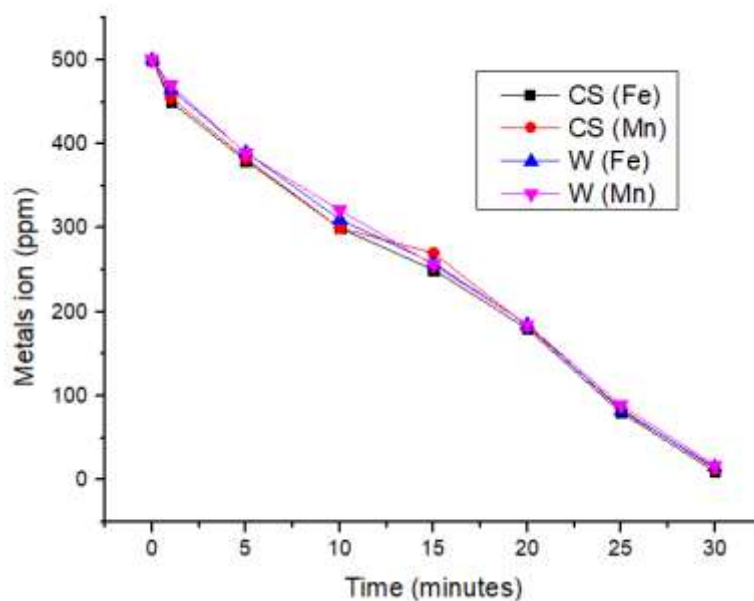
*) CS : Coconut shell
   W : Wood
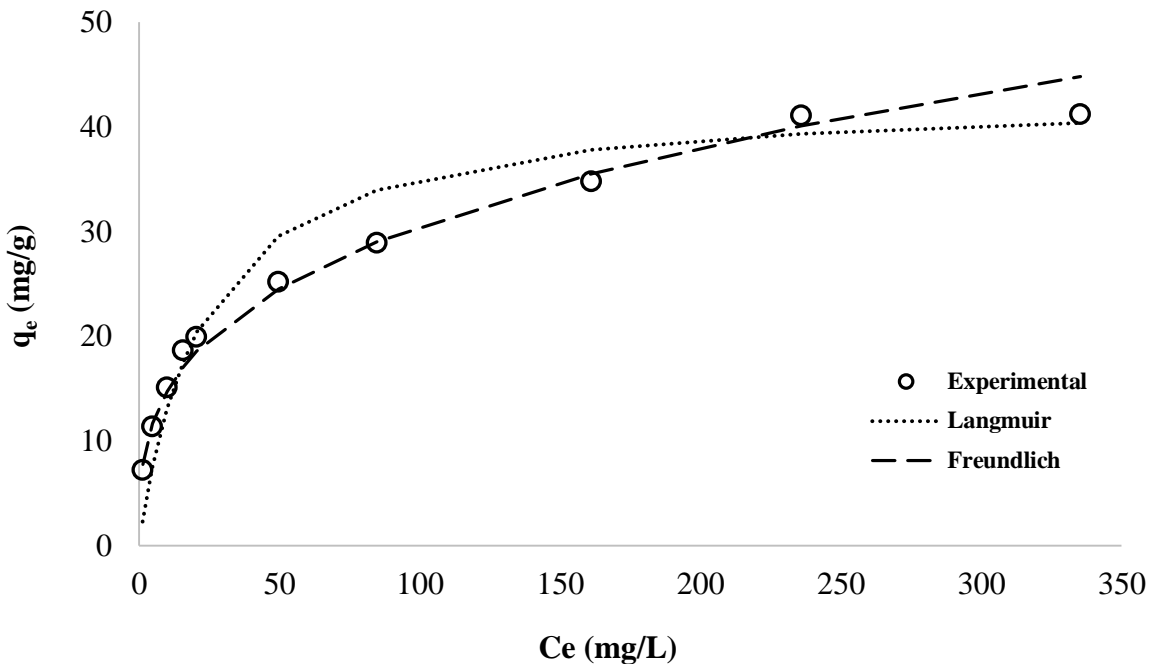
Figure 2. Metals ion sorption

Percent Removal

Removal percent of metals ion sorption into biochar can see in Table 1. According Table 1, biochar successfully remove Fe until 97% from aqueous solution after adding for 30 minutes at 500 rpm. The different results of removal percent of metals ion sorption caused by different feedstock of biochar. The different feedstocks will generated different characterization of materials such as pores, surface area, characteristic of crystal and else. Recent study inform that biochar has amorphous crystal(McNamara et al., 2018; Wang et al., 2020; Zhu et al., 2019). Although the system crystal of biochar is amorphous, the sorption ability of biochar is high.

Table 1. Percent removal of biochar sorption

Time (minutes)	Coconut Shell		Wood	
	Fe	**Mn**	**Fe**	**Mn**
0	0%	0%	0%	0%
1	10%	4%	7%	6%
5	24%	20%	22%	22%
10	40%	38%	38%	36%
15	50%	50%	48%	49%
20	64%	64%	63%	63%
25	84%	81%	83%	82%
30	98%	97%	97%	97%

Isotherm Models

The sorption of metals ion into biochars fitting with Freundlich model. Freundlich isotherm model assumes that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solutions is not constant at different solution concentrations(Li et al., 2011). The sorption of metals ion are presented in Fig. 3. The Freundlich model getting closer in experimental, these models were evaluated with ARE and chi-square (Table 1). According table 2, ARE has less than chi-square in every treatments, this condition inform that the models of sorption study are corrected.

Figure 3. Isotherm models of metals ion sorption

Table 2. Evaluated of isotherms model

Biochars Type	R^2	ARE	Chi-square
Coconut shell (Fe)	0.9904	12.509	4.301

Coconut shell (Mn)	0.9906	12.709	4.597
Wood (Fe)	0.9904	19.059	6.876
Wood (Mn)	0.9904	20.118	7.509

Conclusion

Biochar from different feedstocks were successful reduce metals ion in a solution untul 97%. The sorption process fitting with Freundlich model and the coefficient correlation has evaluated using ARE and chi-square (ARE > chi-suqare). This condition inform that biochar is a potential materials to as an alternative solution for wastewater treatment. The time contact and mass of biochar give some impact for sorption abilities, the best sorption abilities is biochar derived from coconut shell in 30 minutes contact time in batch experimental. The competitive study effected about biochar abilities, it caused by the pores of biochar has filling with other metal ion.

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