Characterization of Prigi South Coast Coral and Its Development as Adsorbent of Nickel Ions

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Abstract. The abundance of dead coral reefs or coral skeleton around the coast of Prigi Beach has the potential to be abundant and used as an adsorbent to reduce nickel content. Nickel in high concentrations can cause water pollution problems. It is urgently needed for the development of adsorbents at this time. This study aims to determine the characterization of coral adsorbents using XRF, SEM, and FT-IR and to then determine the optimization of the size and contact time of corals in the nickel ion adsorption process. The stages of this research consisted of taking coral samples at Prigi beach, production coral adsorbents using the pyrolysis method, coral activation process, characterization of corals with XRF, FT-IR and SEM and application of coral adsorbents for nickel metal ion adsorption. The FT-IR results show the O-H vibration of the carboxylate group at a wave number of 3232.70 cm^{-1}, aliphatic C-H bending vibration at a wave number of 2916.37 cm^{-1}. Strain vibrations at wave number 1788.01 cm^{-1} are associated with C=O ketones and in the range 1247.94 cm^{-1}indicate C-O strain vibrations. SEM analysis found that corals had a rough morphology and the presence of micropores. The adsorption efficiency showed that the adsorbent at 200 mesh size was able to absorb the highest nickel ion of 84.52% with a contact time of 168 hours.

1 Introduction

Most of the metal industrial waste contains heavy metals, including nickel (Ni). Sources of heavy metal pollution come from various human activities such as industrial waste, mining waste and fly ash [1–2]. The treated waste management can reduce the negative impact on the surrounding ecosystem. Atici et al (2008) stated that heavy metals in waters containing pollutants can threaten the lives of fish, invertebrates, and humans, causing adverse impacts on environmental ecology and diversity of aquatic organisms[3].One way to remove heavy metals from water is using the adsorption method. Adsorption is a physical phenomenon that occurs at the surface of a solid (adsorbent) phenomenon with a pollutant (adsorbate) in the form of a gas phase or a liquid phase [4–5]. Adsorption on the surface of solids has selective properties, meaning that only one component is adsorbed from various mixtures of substances. The amount of adsorbed substance increase until it reaches a state of equilibrium with adsorbent[6].Various kinds of adsorbents that can be used in the process of removing

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heavy metals, one of which is biochar bioadsorbent which is activated charcoal. Biochar is a porous wood charcoal substance or commonly referred to as charcoal produced from carbon-containing materials with special treatment, revealing high adsorption power is obtained. Biochar is made from various wastes such as cocoa husk, mangrove stalk, candlenut shell, and coconut shell. Biochar was chosen because of its large surface area, high adsorption capacity, and ease of use.

The Prigi Sea is a southern coastal sea located on the edge of the Indonesian Ocean, Trenggalek Regency. Many coral skeletons were found on the shore. Coral skeletons are strong, durable, and rich in carbon, tannins, and humid acids, etc. The abundance of coral skeletons scattered on the southern coast of Prigi can be used as an adsorbent in the form of biochar. This is because tannins contain phenolic compounds that have an OH group. In addition, there are carboxyl and hydroxyl functional groups in cellulose, these groups act as heavy metal binders [7].

Production of biochar from coral skeleton is one of the newest innovations in environmental chemistry, which can later be used as a comparison of its adsorption power with biochar derived from other materials. Coral skeletons can be used as bioindicators to detect heavy metal pollution in the surrounding ecosystem [8]. Biochar is rich in carbon products in it, which is obtained from the heating process of biomass in a closed container without air [9].Characterization of biochar on adsorption power containing the chemical functional groups as biochar are formed during activation. This is due to the interaction of free radicals on the carbon surface with other atoms such as nitrogen and oxygen produced by the treatment. Researcher have studied the analysis of heavy metal distribution and determination methods in seawater [10–11].

Correge et al., (2004) investigated the metal/Ca and oxygen isotopes in coral skeleton have been used to reconstruct sea surface temperatures rainfall, upwelling and river discharge events[12]. Coral skeletons also describe the anthropogenic and/or terrestrial influences on marine environments CO_2 increase. Here in the natural sources, the coral skeleton can be used as a biochar model to absorb Ni ions.

2 Materials and Method

2.1 Preparation and characterization sample

Coral Skeleton sampling was carried out on the south coast of Prigi then put in a plastic bag. Production biochar from coral skeleton was cleaned and dried at 60 °C for 48 hours. The sample was pounded and wrapped with chiffon cloth for the bulk sample size. The bulk was dried in an oven at 60 °C for 48 hours, then sieved using 2 sizes, 200 and 400 mesh. The sample was then transferred to a porcelain dish, and heated in a furnace (Thermolyne Furnace F6000) at 600 °C (10 °C/minute heating rate) for 2 hours.

During the chemical activation process, the sample was then activated using a 2% NaOH solution. The carbon was soaked for 4 hours and ensured that the entire surface was completely submerged in the activator solution. The carbon was then rinsed until it reaches a neutral pH. The carbon was filtered and reheated at 60 °C for 2 hours. The 2 grams sample biochar was finally characterised and analyzed using FT-IR (Shimadzu IR Prestige 21), XRF (PANalytical, Type: Minipal 4) and SEM (Inspect-S50).

The artificial waste solution containing Ni(II) metal on a laboratory scale was prepared. For the preparation of a standard solution of Ni^{2+}, 4.045 grams of solid $Ni(NO_3)_2.6H_2O$ was weighed, put into a 1000 ml volumetric flask, added with distilled water up to the mark, and a standard Ni^{2+} solution of 800 ppm was obtained.

The application of coral skeleton biochar adsorbent was applied to heavy metal adsorption based on variations in contact time. 0.3 gram in the size of bulk, 200 and 400 mesh was weighed and put into an Erlenmeyer, respectively. The 5 mL of Ni^{2+} solution was added with a concentration of 800 ppm. The sample was then stirred using a shaker for 24 hours at a speed of 150 rpm. The filtrate and precipitate were separated using a centrifuge at 350 rpm for 10 minutes. The resulting filtrate was taken using a pipette as much as 0.5 ml, then put into a 50 ml volumetric flask, HNO_3 was added to the mark. The remaining sample was stirred using a shaker again for 24 hours, the same steps were repeated with variations in contact time during day 1 to day 7. The samples were then analyzed by AAS (Thermo Scientific ICE 3000 Series).

2.2 Data Analysis Techniques

Initial and final concentration sample data was obtained through the calibration curve method of standard solution of $Ni(NO_3)_2.6H_2O$. The biochar characterization of coral skeleton was used SEM for calculating and determining the size of the diameter and radius. The character for the functional group of biochar was analyzed by FTIR with the Origin Software application.

3 Results and Discussion

3.1 Coral skeleton biochar characterization

The finished powder material is then characterized using XRF which aims to determine the content of oxide compounds, especially the content of heavy metals in the material. The result of coral identification before pyrolysis is listed in Table 1.

This XRF analysis was applied to determine the initial content of metals and metal oxides present in biochar coral. As listed in Table 1, it is shown that coral biochar contains the highest Ca content (90.43%). Ca plays a role in the adsorption process of heavy metals, regarding the characteristics and effect its adsorption of bichromate ions. The results showed that the presence of Ca^{2+} cations was able to adsorb more Ni^{2+} concentrations.

Table 1. Coral composition data

Coral			
Element	**Rate (%)**	**Oxide**	**Rate (%)**
Si	1.60	SiO_2 _	2.90
S	0.10	CaO	89.88
Ca	90.43	TiO_2	0.26
Ti	0.24	MnO	0.03
Mn	0.05	Fe_2O_3	1.70
Fe	1.82	SrO	3.83
Sr	5.00	MoO_3	1.10
Zr	0.20	Eu_2O_3	0.20
Mo	0.30	Lu_2O_3	0.12
Eu Li	0.10 0.15		

3.2 The results of the FT-IR spectrum of the $CaCO_3$ biochar

The result of the FT-IR spectrum of $CaCO_3$ biochar before and after activation is shown in Fig. 1.

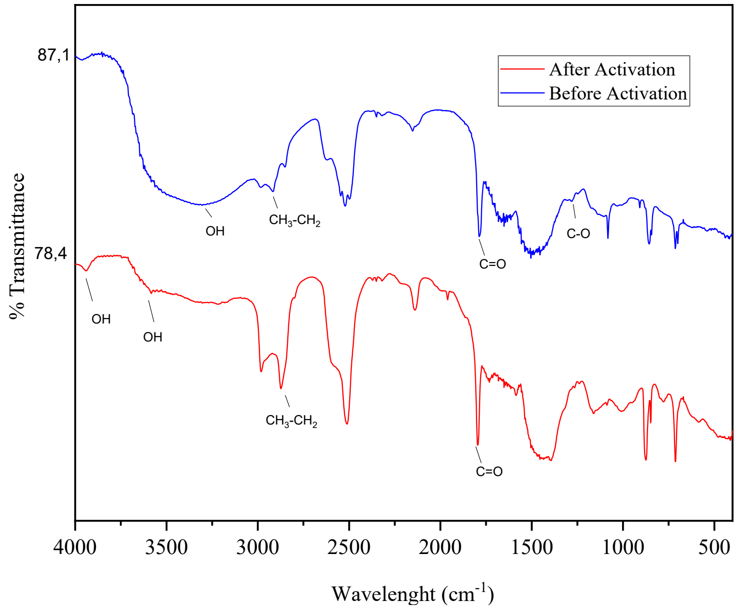


Fig. 1. Coral FTIR results before and after activation

FT-IR spectrum analysis on biochar before activation showed the presence of -OH stretching vibrations in the main absorption band of 3232 cm^{-1} which was associated with O-H vibrations of the carboxylate or phenolic groups. This is in line with Zhang et al (2017) discussion of biochar characterization from husks, rice, and bamboo [13]. Aliphatic CH_3 and CH_2 stretching vibrations is recorded at wave number 2916 cm^{-1}. The strain vibration at wavenumber 1788 cm^{-1} is related to the C=O vibration of ketones, carboxylate esters and esters. The peaks found in the range of 1099-1247 cm^{-1} indicate the presence of C-O stretching vibrations. Whereas in biochar after activation, the spectrum of the FT-IR results changes due to the pyrolysis process, which has an impact on its absorption capacity. As shown in Fig. 1, there is a change in the peak intensity of the biochar before activation, the peak intensity of the hydrogen-OH bond stretches at 3232 cm^{-1}, while for mangrove biochar after activation, the peak of the -OH bond almost disappears at wave numbers 3589 and 3940 cm^{-1}. The band at the peak of 1788cm^{-1} which corresponds to the C=O strain vibration shows changes during pyrolysis. An increase in peak intensity of 1729 cm^{-1} indicates the formation of more oxygen functions on the biochar surface [13]. Strain vibrations CH_3 and CH_2 aliphatic was detected at wave number 2983 cm^{-1}. The existence of a shift in the wave number of the -OH group indicates that the energy is greater, effected by the wave number in accordance with Planck's equation ($E = h/\lambda$). The carboxyl, carbonyl, -OH groups present in biochar show their involvement in the absorption of heavy metal Ni(II). Reaction equation is written, as follows in Fig. 2.

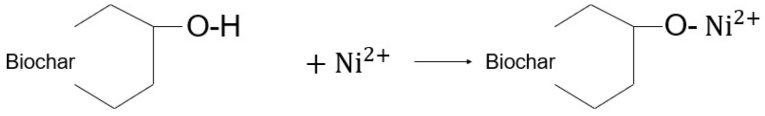
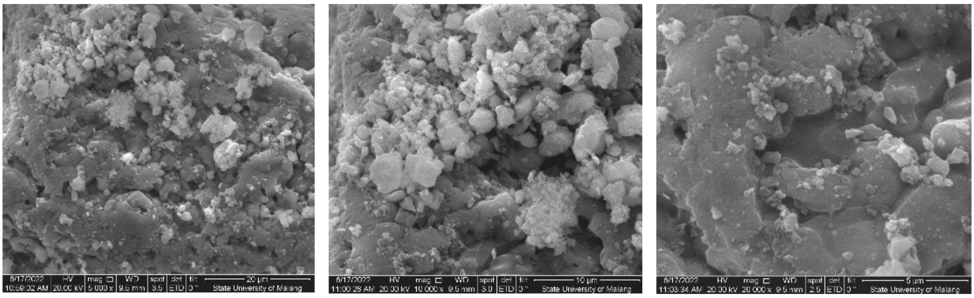


Fig. 2. Reaction mechanism of biochar absorption heavy metal Ni^{2+}

3.3 The results of the SEM biochar



(a) (b) (c)

Fig. 3. Coral electron microscope at magnification (a) 5000x, (b) 10000x, (c) 20000

Characterization using SEM was carried out to determine the morphology of corals. The analysis was carried out at 5000x, 10000x, and 20000x magnifications. As shown in Fig. 3, The 10000x Coral SEM shows a relatively coarse and porous morphology. With the presence of pores on the surface of the coral, the coral can be used as an adsorbent. Therefore, in the adsorption process, there is an intra-particle mass transfer process that occurs in the pores and along the pore walls. The presence of pores in the coral can be used as an adsorbent in the adsorption process with intra-particle displacement along the pore walls.

3.4 Coral Skeleton Biochar Adsorption Test

Application of the adsorption power of biochar to an artificial waste solution containing Ni^{2+} with variations in contact time on days 1-7, obtained the percent adsorption value (% recovery). The results of the percent adsorption of biochar on heavy metal Ni(II) is listed in Table 2.

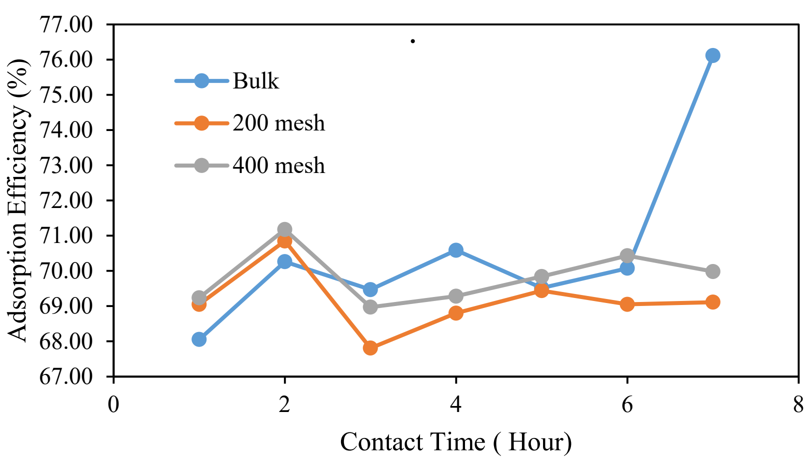


Fig. 4. Graph of coral adsorption efficiency in sizes bulk, 200 mesh, and 400 mesh

As shown in Fig. 4, it is found that the optimum time for coral in bulk to the waste solution containing Ni^{2+} ions was on day 1. The contact time is directly proportional to the adsorption process. The longer adsorption process is depended on the more substances, which are adsorbed, revealing the diffusion process. It is also proven in research that contact time affects the adsorption process has reached the equilibrium point. Fig.4 shows the bulk size coral adsorption test in waste solution containing Ni^{2+} ions in the optimum time (7^{th} day).

Coral adsorption test with a size of 200 mesh against a waste solution containing Ni^{2+} ions was found in the optimum adsorption time on the 6th day. This proves the adsorption process has reached the equilibrium point indicating the greatest adsorption ability.

Table 2. Results of the Ni^{2+} ion adsorption analysis based on variations in contact time

Contact Time (Days)		Concentration		Adsorption Presentation (%) bulk	*net* [Ni $^{2+]}$ (mg/kg)
	[Ni $^{2+]}$ Initial conc. (mg/L)	[Ni $^{2+]}$ Final conc. (mg/L)	[Ni $^{2+]}$ Adsorbed (mg/L)		
1	800	255.56	544.44	68.06	9074.01
2	800	237.92	562.08	70.26	9368.04
3	800	244.25	555.75	69.47	9262.43
4	800	235.31	564.69	70.59	9411.52
5	800	243.88	556.12	69.51	9268.65
6	800	239.41	560.59	70.07	9343.19
7	800	191.08	608.92	76.12	10148.67
Contact Time (Days)		**Concentration**		**Adsorption Presentation (%) 200 mesh**	***net* [Ni $^{2+]}$ (mg/kg)**
	[Ni $^{2+]}$ Initial conc. (mg/L)	**[Ni $^{2+]}$ Final conc. (mg/L)**	**[Ni $^{2+]}$ adsorbed (mg/L)**		
1	800	247.61	552.39	69.05	9206.53
2	800	233.20	566.80	70.85	9446.72
3	800	257.55	542.45	67.81	9040.87
4	800	249.60	550.40	68.80	9173.40
5	800	244.50	555.50	69.44	9258.29
6	800	247.61	552.39	69.05	9206.53
7	800	247.11	552.89	69.11	9214.81
Contact Time (Days)		**Concentration**		**Adsorption Presentation (%) 400 mesh**	***net* [Ni $^{2+]}$ (mg/kg)**
	[Ni $^{2+]}$ Initial conc. (mg/L)	**[Ni $^{2+]}$ Final conc. (mg/L)**	**[Ni $^{2+]}$ adsorbed (mg/L)**		
1	800	246.12	553.88	69.24	9231.37
2	800	230.59	569.41	71.18	9490.21
3	800	248.23	551.77	68.97	9196.17
4	800	245.74	554.26	69.28	9237.59
5	800	241.27	558.73	69.84	9312.13
6	800	236.55	563.45	70.43	9390.81
7	800	240.15	559.85	69.98	9330.77

Conc. means concentration

4 CONCLUSION

Coral adsorbents were synthesized using the pyrolysis method. The synthesized adsorbents used to reduce coral metal levels were proven by XRF, SEM, FT-IR and AAS. XRF results on coral samples showed calcium levels of 90.43%, SEM results showed a relatively rough and porous morphology. With the presence of pores on the coral surface, intra-particle mass transfer processes can occur inside the pores and along the pore walls. FTIR analysis shows the presence of -OH, C=O, C-O, and C-H groups which play a role in the heavy metal binding process. Coral adsorbents produced the highest adsorption percentage of 76.12% on the bulk size with the optimum time on the 7th day.

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