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Adsorption of Copper Metal from Electroplating Wastewater Using Activated Charcoal of *Gracilaria sp.*

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Abstract

Gracilaria sp. is a red algae group seaweed (*Rhodophyceae*) that is commonly used in wastewater treatment because of its ability to adsorb metals and is economical. Utilization of *Gracilaria sp.* as an adsorbent for copper (Cu) metal has been carried out but has a low efficiency. In this study, activation was carried out with sodium chloride (NaCl) at various concentrations of 0%, 5%, and 10%, accompanied by variations in pH in acidic (pH 6), neutral (pH 7), and alkaline (pH 8) conditions, as well as variations in mass. Activated charcoal of *Gracilaria sp.* is characterized by testing water content, ash content, and iodine adsorption. After characterization, activated charcoal of Glacilaria sp. was applied to electroplating industrial wastewater containing heavy metal Cu for 1 hour. The results showed that the use of 1 g of activated charcoal of *Glacilaria sp.* using 5% NaCl at pH 8 has the best efficiency of 96.70% for Cu adsorption. Based on the data, it can be concluded that the use of activated charcoal of *Gracilaria sp.* potential to be used in the electroplating wastewater treatment process.

Keywords: Activated carbon; Electroplating wastewater; *Glacilaria sp.*; Copper; Adsorption

1. Introduction

Sources of heavy metal pollutants come from industrial, domestic, mining, and agricultural wastes. Based on their function, heavy metals are divided into two, namely essential metals and nonessential metals. Essential metals needed by the human body in certain doses include molybdenum (Mo), cobalt (Co), sodium (Na), manganese (Mn), magnesium (Mg), iron (Fe), calcium (Ca), potassium (K), zinc (Zn), and cuprum (Cu) (Zoroddu *et al.,* 2019). This metal is dangerous because it tends to accumulate in human body tissues and causes poisoning (Malik *et al.,* 2019). One of the industries that is growing in this modern era is the electroplating industry, which is used in the automotive, jewelry, construction and building industries, electrical equipment, electronic equipment and connectors, sanitation, and packaging. In addition to providing benefits to industry, electroplating activities can generate waste. The entry of industrial waste into the water without going through an appropriate wastewater treatment process results in an increase in the concentration of heavy metals in the water. Some of the heavy metals found in electroplating wastewater include iron, chromium, zinc, nickel, manganese, and copper (Soemantojo and Wulan, 2002; Sajjanar and Kumar, 2018).

The technology for treating wastewater containing heavy metals can be done biologically, physically, or chemically through bioremediation, electrocoagulation, electrodialysis, precipitation, adsorption, flocculation, coagulation, and reserve osmosis (Mardiyono *et al.,* 2019). The choice of adsorption technique in waste treatment is considered quite effective compared to membrane technology, electrochemical conversion, ion exchange, and coagulation because it is simpler, cheaper, has a lower risk of toxic sludge, and has a fast regeneration process (Asere *et al.,* 2019).

The use of bio adsorbents in waste treatment technology is promised because of their abundance and low cost (Pathak *et al.,* 2015). Several studies have been conducted using seaweed such as *Gracilaria sp.* as a bio adsorbent to adsorb lead (Pb) and copper (Cu) in pond water (Ridwan Harahap *et al.,* 2019). *Gracilaria sp.* is a red seaweed or rhodophyta which is widely distributed in Indonesian waters and is cultivated (Farid *et al.,* 2013). The content of polysaccharides in the cell wall of *Gracilaria sp.* able to bind heavy metals and form complex compounds with organic substances contained in the thallus (Qumain, 2016). The results showed that *Gracilaria sp.* able to adsorb lead (Pb) and copper (Cu) along with the increase in bio adsorbent concentration and contact time.

Modifying *Gracilaria sp.* as a precursor for activated carbon synthesis can increase its adsorption capacity (Suhas *et al.,* 2016). Activated carbon has been utilized as an adsorbent for wastewater and food coloring (Saleem *et al.,* 2019; Laksaci *et al.,* 2019). Activated carbon from *Garcilaria sp.* and *Sargassum sp.* can remove chromium from waste up to 91.53% and 91.98%, respectively (Esmaeili *et al.,* 2010). In addition to being a metal adsorbent, activated charcoal can adsorb ammonia in waste. *Glacilaria sp.* can adsorb ammonia with an efficiency of 16.2% and an adsorption capacity of 0.233 mg/g in a polyurethane membrane (Nurman and Ginting, 2022). This certainly greatly supports the effectiveness of *Glacilaria sp.* when used in wastewater treatment. The use of activated charcoal *Glacilaria sp.* as bio adsorbent of heavy metals such as Pb (Wang *et al.,* 2020), Cu (Lavania-Baloo *et al.,* 2017), Ni (El-Naggar and Rabei, 2020), and Cr (GracePavithra *et al.,* 2019) has been widely used in water treatment, but its use in electroplating industrial waste treatment is still limited. Therefore, the aim of this study was to see how effectively *Gracilaria sp.* can be used as an activated charcoal precursor in adsorbing copper metal from electroplating industry wastewater using the NaCl activator. The NaCl activator was used in this research because it is cheap, easy to find, and safer than other chemicals. Activation was carried out with NaCl concentrations of 0%, 5%, and 10% for 2 hours.

2. Methodology

2.1 Materials

The materials used consisted of: red seaweed (*Gracilaria sp.*) obtained from the Murareja beach in Tegal, Central Java, NaCl, HCl, $AgNO_3$, HNO_3, I2, $Na_2S_2O_3$, $CuSO_4.5H_2O$, $C_{13}H_{14}N_4O$, H_2SO_4, NaOH, whatman no.42, and aquadest. All reagents used were obtained from Merck. The equipment used consisted of: oven (LabTech), test sieve shaker type haver ELM 200 Premium, Atomic Absorption Spectrometry (AAS) (Shimadzu), thermo scientific muffle furnice, analytical balance type ATX224, vortex portable mixer (Amtast), nephelometer (LabTech), magnetic stirrer, pH meter ATC-pen type PH-009, multi-parameter analyzer 3200 M, desiccator, porcelain cup, and glassware (pyrex).

2.2 Preparation and characterization of activated charcoal of Gracilaria sp.

Experiments were carried out in several batches, namely: production of *Gracilaria sp.* algae bio adsorbent; characterization of *Gracilaria sp.* algae bio adsorbents; activation of *Gracilaria sp.* algae bio adsorbent with NaCl; measure the levels of copper (Cu) waste and the pH of the electroplating liquid waste; determine the optimum pH with a variation of pH 4, 5, 6, 7, and 8; determining the optimum dose of *Gracilaria sp.* algae bio adsorbent by using the jar test after using the algae bio adsorbent *Gracilaria sp.* with doses of 1 ppm, 2 ppm, 3 ppm, 4 ppm, and 5 ppm at a speed of 80 rpm with a temperature of 25 oC and a contact time of 2 hours; measuring the levels of copper (Cu) from electroplating liquid waste after being treated with the bio-adsorption process; and calculating the removal efficiency of copper (Cu) from electroplating wastewater using the *Gracilaria sp.* bio-adsorption method.

Gracilaria sp. was cleaned, dried, and heated at a temperature of 60 ºC for 7 hours, mashed, and then filtered to 100 meshes. *Gracilaria sp.* was activated by stirring at speed of 700 rpm in NaCl with various

concentrations of 0 %, 5 %, and 10 % with a ration of 1: 4 (g/mL) for 5 hours at 45 °C. The results obtained were filtered and dried at a temperature of 105 °C. *Gracilaria sp.* which has been activated and then carbonized at a temperature of 500 °C for 1 hour, washed, and dried. After that activated charcoal of *Gracilaria sp.* was followed by soaked in 1 M HCl (1: 2 v/v ratio) for 24 hours, filtered, washed until neutral and free of chloride. The resulting filtrate was measured for its pH using a pH meter until it was neutral (pH 6 - 7). The activated carbon was sieved with a size of 100 mesh, characterized, and applied as an adsorbent for Cu metal from electroplating spare part wastewater.

2.3 Characterization of activated charcoal

2.3.1 Determination of water content

Determination of water content in activated charcoal of *Gracilaria sp.* refers to SNI-01-1682-1996.

$$Water\ (\%) = \frac{w_1}{w_2} \times 100\ \%$$

The mass loss of activated charcoal is denoted by w_1 and the mass of activated charcoal is denoted by w_2.

2.3.2 Determination of ash content

Determination of ash content in activated charcoal of *Gracilaria sp.* refers to SNI-01-1682-1996 ([SNI]-01-1682-1996, 1996).

$$Ash\ (\%) = \frac{w_1 - w_2}{w} \times 100\ \%$$

The weight of the activated charcoal and porcelain cup after igniting is denoted by w_1, the weight of the porcelain cup is denoted by w_2, and the weight of the sample before igniting is denoted by w.

2.3.3 Determination of iodine adsorption

Determination of iodine adsorption in activated charcoal of *Gracilaria sp.* refers to SNI-01-3730-1995 ([SNI]-01-3730-1995., 1995).

$$Iodine\ adsorption = \frac{(V_1 - V_2)\ x\ N\ x\ 126{,}9\ x\ 5}{W}\ mg/g$$

The initial volume of $Na_2S_2O_3$ 0.1 N is denoted by V_1, the final volume of $Na_2S_2O_3$ 0.1 N is denoted by V_2, the normality of $Na_2S_2O_3$ is denoted by N, the weight of the charcoal is denoted by W, 126.9 is the atomic weight of iodine, and 5 is the dilution factor.

2.4 Wastewater sample test

Utilization of carbon precursors from *Gracilaria sp.* as activated charcoal in wastewater treatment was tested by measuring the metal content of Cu using AAS at a wavelength of 324.8 nm. Cu processing efficiency is calculated using the following formula:

$$Efficiency\ (\%) = \frac{C_0 - C_t}{C_0} \times 100\ \%$$

Cu (II) concentration before processing is denoted by C_0 and Cu (II) concentration after processing is denoted by C_t.

3. Results and discussion

Electroplating waste was obtained from a spare part industry located in the Bogor area of West Java Province, Indonesia. The spare part is coated with Ni, Cu, and Cr metals by immersion in a metal bath to produce waste water. Prior to the absorption of Cu metal from electroplating industrial waste using *Glacilaria sp.* activated charcoal, Cu metal content was determined in wastewater samples prior to processing. The metal test parameters include testing for pH levels and Cu levels. The results of the initial measurement of the waste obtained a pH of 6.2 and a concentration of Cu of 20.88 ppm. This value exceeds the threshold value set by the Minister of Environment in Regulation No. 5 of 2014 concerning Wastewater Quality Standards, which determines the limit for Cu content in electroplating waste, namely a maximum of 3 ppm (Kementerian Lingkungan Hidup Republik Indonesia, 2014). This research is focused on the absorption of Cu metal because previous research has been done on the analysis of Cr metal content in electroplating waste.

The adsorbent capacity is influenced by several factors, such as distribution and pore volume, specific surface area, and the presence of functional groups on the surface (Gautam *et al.,* 2014). Therefore, in this study, a carbonization process was carried out to produce a high-purity carbon framework, followed by an activation process to increase the pore volume and create new pores so that it could increase its adsorption power. Activation can be done physically or using chemicals. The advantage of chemical activation lies in the use of time and a lower temperature in the process of activating the material (Suhas *et al.,* 2016).

One of the chemicals that can be used as an activator is NaCl. NaCl functions as a dehydrator in the carbonization process, which can limit the formation of tar. The tar that is formed in the carbonization process can cover the pores of the activated charcoal so that the resulting surface area will be smaller and the adsorption power will weaken (Mu'jizah, 2020). Research by Indah *et al.* (2021) showed that activated carbon from the red algae *Glacilaria sp.*, which was activated using NaCl, had an adsorption power of magnesium metal of 98.24%. Research on the use of variations in NaCl concentrations has been carried out by Mu'jizah (Mu'jizah, 2020), which shows that the best characterization of activated carbon is at a 30% NaCl concentration with an absorption power of 575 mg/g. Mirwan (Mirwan, 2005) showed that the best activated carbon was produced at a concentration of 15% NaCl with a soaking time of 10 hours. In this study, variations in contact pH and concentration of NaCl were used. The results of the characterization of activated charcoal (*Gracilaria sp.*) using variations in NaCl concentration can be seen in Table 1.

Based on Table 1, it is known that the increase in ash content is proportional to the increase in NaCl concentration, which causes an increase in metal oxides contained in activated charcoal during the carbonization process (Hendrawan *et al.,* 2017). Meanwhile, the increase in NaCl concentration resulted in a decrease in water content and iodine adsorption due to the formation of tar in the carbonization process, which was able to cover the pores of the activated carbon so that the surface area was reduced and was able to reduce the adsorption power (Mu'jizah, 2020).

The adsorption capacity can be determined by the iodine number, which is a quantity that indicates the ability of the adsorbent to adsorb iodine. The addition of iodine solution functions as an adsorbate, which will be absorbed by activated charcoal. The absorption of iodine solution is indicated by a reduction in the concentration of iodine solution. The greater the value of the iodine number, the greater the adsorption power of an adsorbent. Iodine absorption testing was carried out to determine the ability of activated charcoal to absorb colored solutions so that it can be used as an indicator of good activated charcoal adsorption capacity (Qian *et al.,* 2018). The absorption capacity of activated charcoal for iodine correlates with the number of micropores formed on the activated charcoal. The higher the absorption of iodine, the more micropores are formed on the activated charcoal. Based on the results of the characterization, the activated charcoal that has the highest iodine absorption is the activated charcoal of *Glacilaria sp.* activated with 5 % NaCl.

Apart from increasing the adsorbent capacity, one of the developments in metal adsorption techniques from waste can be carried out through coagulation and precipitation (Zheng *et al.,* 2020). The degree of acidity of the contact solution affects the rate of formation of the formed metal hydroxides. Because of this, in this work, contact pH variations were also investigated by measuring pH following contact with changes in the mass of *Glacilaria sp.* activated charcoal found in Table 2.

Table 1. Characterization of activated charcoal from *Gracilaria sp.*

| NaCl concentration (%)	Water content (%)	Ash content (%)	Iodine adsorption (mg/g)
0	13.54	20.79	74.55002
5	3.83	56.58	560.9672
10	3.15	61.87	254.6881

Based on Table 2 it is known that there is no significant difference in pH after contact with activated charcoal when the pH is raised. At acidic pH, the solubility of Cu metal is greater, resulting in an increase in pH after contact that is more dominant than neutral pH or alkaline pH due to the formation of metal hydroxides (Çelebi *et al.,* 2020). In terms of mass variation, there was a significant decrease in pH with the use of 4 g of activated charcoal *Glacilaria sp.* from alkaline pH to acidic pH. The increased mass of activated charcoal causes a layer to form on the surface, which reduces the adsorption capacity (Indah *et al.,* 2021). Meanwhile, the addition of 6 g of activated charcoal mass causes an increase in pH due to the abundant mineral content in *Gracilaria sp*. can increase the pH. The results of measuring the Cu metal content of waste before and after contact with activated charcoal *Gracilaria sp.* using AAS at

a wavelength of 324.8 nm yield a regression equation $y = 0.1086x + 0.0015$ with variations in standard solution concentrations ranging from 1 to 5 ppm. Figure 1 shows the results of using the regression equation to determine Cu levels and activated charcoal efficiency.

Based on Figure 1, it is known that the adsorption of Cu metal will increase with increasing the pH of the solution because at an alkaline pH, the number of protons is lower and the hydroxide ion is able to bind the metal more optimally. Meanwhile, an increase in the mass of activated charcoal decreases the adsorption efficiency of Cu metal due to the formation of tar on the surface of the activated charcoal, thereby reducing the adsorption capacity of Cu metal (Dewi and Dewi, 2019). This is in line with the research of Anggraini et al. (Anggraini *et al.,* 2022), which stated that the addition of an adsorbent causes aggregate to form, which results in a decrease in the

Table 2. Changes in the pH conditions of electroplating wastewater after application of activated charcoal from *Gracilaria sp.*

NaCl concentration (%)	Activated charcoal mass (g)	pH variation	pH after contact
5	1	6	7.29
		7	7.52
		8	8.27
	2	6	7.30
	4	7	6.29
	5	8	6.82
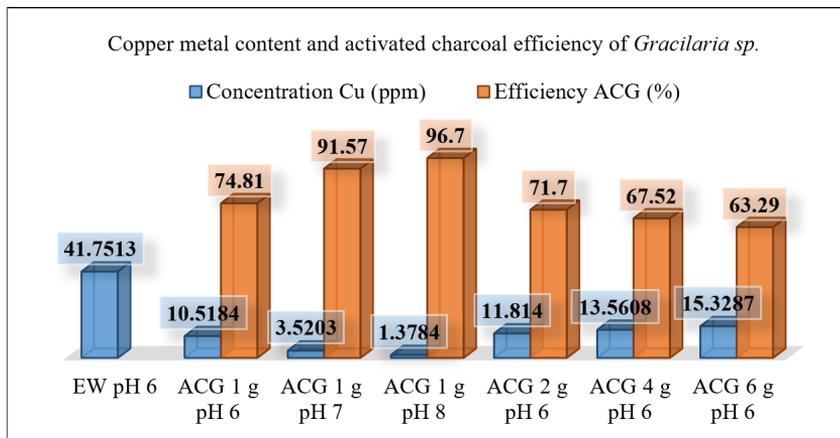
*ACG: Activated charcoal of *Graclaria sp.* with NaCl 5%;
EW: Electroplating waste
■ Described as the adsorption concentration after added by adsorben

Figure 1. Cu metal content and activated charcoal efficiency before and after adsorption

surface area and efficiency of the adsorbent. In contrast to several previous studies that stated that at pH 4 - 6, the adsorption effectiveness of Cu metal was more effective because the solubility of metal ions was greater in a weakly acidic environment, the adsorbent could absorb more maximally (Isam *et al.,* 2019; Lavania-Baloo *et al.,* 2017; Bashir *et al.,* 2020). The most effective adsorption of Cu metal occurred on charcoal activated by 5% NaCl with a mass of 1 g at pH 8 for Cu metal adsorption of 1.3784 ppm with an efficiency of 96.70%. This is in accordance with the results of Lavania-Baloo *et al.* (2017), which state that the utilization of activated charcoal from *Glacilaria sp.* is very effective for removing Cu metal.

4. Conclusion

The results showed the ability of activated charcoal from *Gracilaria sp.* to adsorb Cu metal from electroplating wastewater. It is effectively carried out with a mass of 1 g of *Gracilaria sp.*, which was activated by 5% NaCl at pH 8.

Acknowledgment

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