WATER HYACINTH (*EICHHORNIA CRASSIPES*) MODIFIED CITRIC ACID AS A METAL ADSORBENT IN LABORATORY LIQUID WASTE

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ABSTRACT

The cellulose content in water hyacinth (*Eichhornia crassipes*) shows potential as an adsorbent medium in the management of heavy metal waste generated from laboratory activities. Water hyacinth (*Eichhornia crassipes*) contains 60% cellulose which is rich in hydroxyl groups so that it can interact with metal ion adsorbate components. Water hyacinth adsorbent was modified using citric acid and its functional groups (carboxyl, hydroxyl, and lactone) were analyzed using Boehm titration. The modified adsorbent was applied to laboratory waste and the levels of copper (Cu), Chromium (Cr) and Cadmium (Cd) were analyzed using Atomic Absorption Spectrophotometry. Water hyacinth adsorbent was characterized using a Fourier Transform Infrared spectrometer to determine the active groups in the adsorbent. The FTIR results of the modified adsorbent showed that there was an absorption peak of the C=O ester group at wave numbers 1733-1734 cm^{-1} indicating an esterification reaction between cellulose and citric acid. Adsorption of chromium and cadmium metals had the highest percentage reduction at a dose of 2 grams of 98% and 37.40%, while for copper metal at a dose of 1.5 grams of adsorbent was 63.34%.

Keywords: Water hyacinth; adsorption; citric acid; heavy metals

Introduction

Practicum and research activities carried out at the chemical laboratory of Maulana Malik Ibrahim State Islamic University Malang involve the use of hazardous chemicals which produce by-products in the form of liquid waste containing heavy metals. Disposal of metal waste into waters without processing the waste can cause environmental pollution. There are several modern methods for managing heavy-containing wastewater such as precipitation,[1] electrochemistry using metal ions,[2] and microorganisms[3] have been developed to remove heavy metal content in the wastewater. This method has shown satisfactory results but requires quite expensive and time-consuming operations. The adsorption method is a choice for removing heavy metals because it is easy and effective in its application. The adsorption method is the most effective in metal adsorption because it has a different surface area, microporous structure, high absorption, and low cost.[4] Absorbents from agricultural solid wastes in both natural and modified forms have been used successfully to remove metal ions from the aqueous phase and have been recognized as a sustainable solution for low-cost wastewater treatment.[5]

Water hyacinth (*Eichhornia crassipes*) is a weed plant whose population is growing rapidly in waters. In recent years, water hyacinth has been researched as a good candidate for pollutant removal or even as a bioindicator of heavy metals in aquatic ecosystems. Water hyacinth has high removal rates for heavy metals such as iron (Fe), zinc (Zn), copper (Cu), chromium (Cr), cadmium (Cd), manganese (Mn), mercury (Hg) and arsenic (As) from aqueous solutions.[6] The results of the study stated that water hyacinth

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contains 25% cellulose, 33% hemicellulose, and 10% lignin.[7] Cellulose is the most abundant natural biopolymer in the world and presents a higher chemical composition variability for the presence of several hydroxyl groups.[8] The cellulose content provides great potential to make water hyacinth as an adsorbent medium. The more hydroxyl groups in cellulose will bind more metal ions. In this case the electronegative oxygen atom easily releases H as H^+ (proton) and quickly captures the metal cation to replace the position of the released proton.[9,10] The parts of water hyacinth that can be utilized are the stems and leaves in powder form so that direct use is an economical metal ion adsorbent. Adsorption on water hyacinth occurs in active groups, such as carboxyl and hydroxyl.[11] Demineralization of water hyacinth is carried out to reduce mineral levels using low concentrations of acid so that the active groups that bind to minerals become unbonded.[12,13] The results of Yulianti et al.,[14] showed that the amount of metal adsorbed on corn stalks after demineralization with hydrogen chloride was higher, namely 2.61 mg/g compared to 1.45 mg/g which did not undergo demineralization .

The adsorption capacity can be increased by modifying the functional groups in the adsorbent. The high cellulose content in water hyacinth adsorbents causes this adsorbent to be rich in hydroxyl groups so that it has the potential to be modified through chemical reactions.[15] Modification of cellulose using citric acid is due to the fact that some of the hydroxyl groups experience acylation to form carboxylic groups which have higher adsorption strength as metal ion chelating agents.[16] Heated citric acid dehydrates and forms anhydrous which is reactive and reacts with the hydroxyl in cellulose form esters. The adsorption capacity of cellulose modified with 1 M citric acid was 42.9 mg/g with a total acid group of 4.83 meq/g while the adsorption capacity without modification was 1.62 mg/g with a total acid group of 2.11 meq/g. Modification with citric acid can increase the number of acid groups in the adsorbent.[17,18] The addition of carbonyl and hydroxyl groups from the addition of citric acid causes the adsorbent after modification to have a higher chemical reactivity than cellulose. The method that can be used to determine the total active groups present in the adsorbent is the Boehm titration to determine the active groups of acids, including carboxyl, hydroxyl, and lactone groups. The more active groups in the adsorbent, the potential for adsorbing metal ions will increase.[19,14] In this study, the preparation and demineralization of water hyacinth adsorbents were carried out, then modified using citric acid and tested for their adsorption ability on heavy metals in laboratory waste.

Methods

The material used in this research were water hyacinth from the Blitar Regency, liquid waste from the Chemistry Laboratory of Maulana Malik Ibrahim State Islamic University Malang in the category of metal waste, distilled water, 98% NaOH (Merck), 99.5% citric acid (Merck), 37% HCl (Merck), 65% HNO_3 (Merck), $AgNO_3$ (Merck), Na_2CO_3 (Merck), $NaHCO_3$ (Merck), phenolphtalein indicator, KBr powder.

a. Water hyacinth adsorbent preparation

Water hyacinth plants without roots were washed and cut into small pieces. The drying process was done in the sun for ± 7 days and followed by heating using an oven for 24 hours at 60°C then blended and sieved using 100-200 mesh to get the adsorbent. 100 g of the adsorbent was added to 0.1 M hydrochloric acid 300 mL, stirred, and incubated for 24 hours at room temperature. The solution was filtered and the residue obtained was rinsed using distilled water until the filtrate water approached pH 7 (The filtrate was tested with $AgNO_3$ solution). Then the residue was dried in an oven at 60°C for 4 hours and cooled.

Water hyacinth adsorbent was modified using various citric acid concentrations of 0.5; 1.0; 1.5; 2.0; and 2.5 M. The ratio between water hyacinth and citric acid adsorbents was 1:5. Then was stirred using a stirrer at 250 rpm for 30 minutes at room temperature and then

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heated at 50 °C for 24 hours. Then the temperature was raised to 120°C for 90 minutes. Then the adsorbent was washed with distilled water until pH 7 and dried at 50°C to a constant weight

b. Analysis of water hyacinth adsorbent using the Boehm titration method

0.25 grams of modified water hyacinth was added in 25 mL of reagents, then incubated for 24 hours while occasionally stirring, and then filtered through filter paper. 10 mL of the filtrate was taken and put into Erlenmeyer, then 20 mL of 0.05 N HCl and 2-3 drops of phenolphthalein indicator were added and then titrated using 0.05 N NaOH.

c. Identification of water hyacinth adsorbents with Fourier-transform Infrared Spectroscopy

Modified water hyacinth and without water hyacinth adsorbent were homogenized with Potassium Bromide using a mortar and then pressed into pellets. Pellets that have been formed are placed in a sample holder and exposed to infrared light at a wave of 500-4000 cm^{-1}

d. Adsorption of copper, chromium, cadmium metals in laboratory waste with variations in adsorbent doses

The laboratory liquid waste was homogenized and the pH is adjusted to 7 and left for 24 hours until a precipitate formed. The filtrate was separated from the precipitate and mixed with water hyacinth and modified water hyacinth adsorbent then incubated for 120 minutes. Then the solution was filtered, and the filtrate was used for further analysis.

e. Analysis of metals with Atomic Absorption Spectrophotometer

Chemical laboratory liquid waste before and after the adsorption process was taken as much as 50 mL, added 10 mL of 65% nitric acid, and heated at 100 °C until soluble then cooled. The sample was analyzed using an Atomic Absorption Spectrophotometer.

Result and Discussion

a. Identification of water hyacinth adsorbents

The results obtained in the adsorbent preparation process are green powder and do not clot. Then demineralization using 0.1 M HCl produced a brownish green powder and was paler than the adsorbent without demineralization. The sample weight was also reduced to 29.3% of the original weight. This is because some minerals have reduced in number so that the weight of the biomass has decreased. Demineralization is carried out to reduce interfering minerals in water hyacinth which can potentially compete with metal ions to be absorbed and increase the concentration of H^+ ions.[12] The conditioning of the water hyacinth adsorbent at pH 7 was due to the acidity of the adsorbent affecting the adsorption process. When the adsorbent is under acidic conditions it causes the availability of H^+ ions to increase. [20]

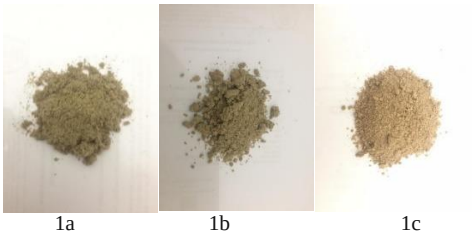

Figure 1. Water hyacinth powder before demineralization (1a), after demineralization (1b), and after modification with citric acid (1c)

During the heating process citric acid will dehydrate and turn into anhydrous (COO^-) which is reactive. The citric acid will react with the hydroxyl groups of cellulose and lignin to form esters.[16] Figure 2 shows that the esterification reaction between citric acid and water hyacinth cellulose is characterized by the presence of acid groups such as carboxyl (-COOH) and hydroxyl (-OH). The reaction that occurs in the nucleophilic oxygen atom on C-6 cellulose attacks the carbonyl group of anhydrous citric acid which is electrophilic. The OH group in citric acid with the OH group in cellulose occurs substitution so that the

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resulting carbon chain becomes longer and cellulose citrate is formed.

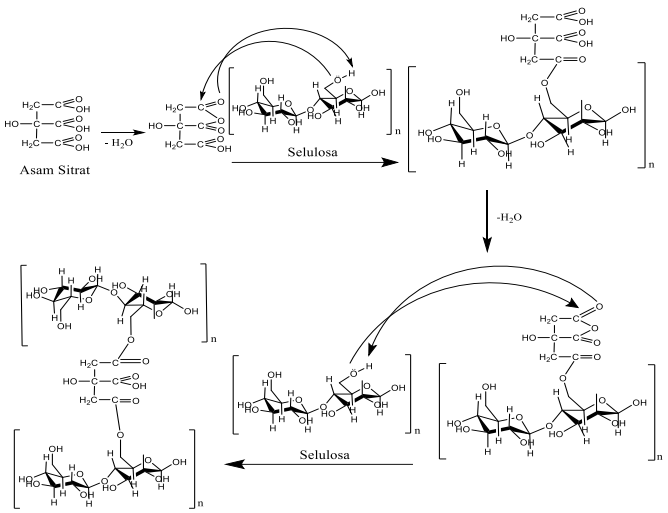

Figure 2. Esterification reaction in the modification process[16]

The results of the esterification reaction can also be shown by the Fourier-transform Infrared Spectroscopy spectra presented in Figure 3. The wave number 1733-1734 cm^{-1} shows the absorption peak of the C=O ester group present in the citric acid modified water hyacinth adsorbent, while in the pure water hyacinth adsorbent there is no absorption peak at the wave number 1733-1734 cm^{-1}. This shows that the presence of a C=O ester group indicates the success of the modification.

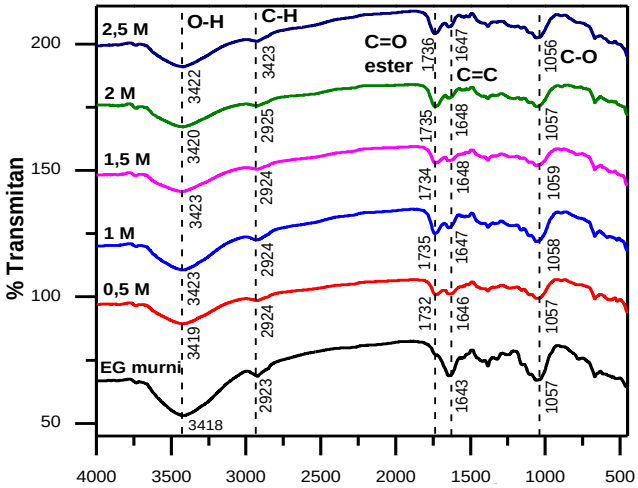

Figure 3. FTIR spectra of water hyacinth and citric acid-modified water hyacinth adsorbents with various concentrations of citric acid

b. Determination of the active group of water hyacinth with the Boehm titration method

Based on Table 1, it is known that differences in citric acid concentrations can affect the total acid groups present in the water hyacinth adsorbent, which consists of carbonyl, hydroxyl, and lactone groups. The highest total acid groups were found in citric acid-modified water hyacinth with a concentration of 2.5 M, which was 7.20 meq/gram. While the lowest total acid groups were at a concentration of 0.5 M, namely 5.8 2 meq/gram. This shows that the water

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hyacinth that has the potential to adsorb metals optimally is citric acid modified water hyacinth with a concentration of 2.5 M. The calculation of the lactone groups shows that there are no lactone groups in the adsorbent. An analysis using the One Way ANOVA method to find out the significant difference between citric acid concentrations in the adsorbent showed that the calculated F is smaller than the F table equal to H_0 accepted and H_1 rejected, which means that there is no effect or significant difference between citric acid concentrations.

c. Adsorption of metal using variations in dosages of water hyacinth adsorbents

The waste to be adsorbed is first prepared using sodium hydroxide to neutralize the pH of the waste and form metal hydroxides so that precipitate forms in the waste.

Sodium hydroxide is well known strong base and reacts with metals and metal ions aggressively so that the metal concentration value in the waste also decreases as shown in Table 2.

Table 1. Concentration of acid group based on Boehm titration

Citric Acid Variations (M)	Total Acid Groups (meq/g)	Carboxyl (meq/g)	Hydroxyl (meq/g)	Lactone (meq/g)
0.5	5.82	1.15	4.67	0
1.0	6.17	1.74	4.43	0
1.5	6.51	1.84	4.67	0
2.0	6.88	2.49	4.39	0
2.5	7.20	2.44	4.76	0

Table 2. Metal content in waste before and after sodium hydroxide treatment

Metal Type	Waste Concentration (ppm)		% Decrease
	Laboratory Waste	Waste+ sodium hydroxide	
Chromium	211	75	64.00
Cadmium	0.199	0.155	22.11
Copper	811	269	66.79

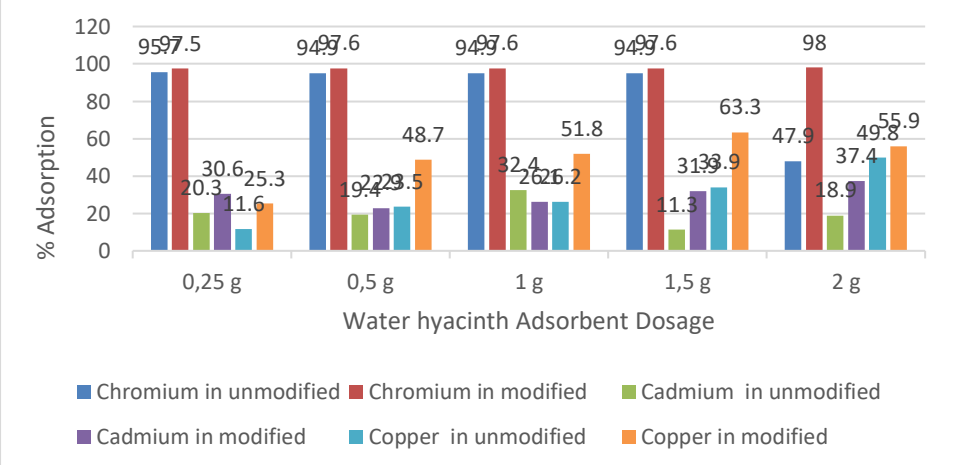

Figure 3. Percentage of metal concentration decrease before and after adsorption with various doses of water hyacinth adsorben

The results obtained after reacting with sodium hydroxide are clearer colored waste and has a pH of 7. The hydroxide precipitate is formed due to the separation of metal ions present in the waste and forms the compound $M(OH)_n$. The hydroxyl group in sodium hydroxide will cause the formation of bonds between the metal and the OH group to increase.[16]

Overall, the percentage of metal reduction in the waste adsorbed on modified water hyacinth was higher than pure water hyacinth. This shows that the modified water hyacinth can absorb more metals than unmodified water hyacinth. The large number of metals adsorbed by modified water hyacinth is due to the large number of functional groups that actively adsorb metals such as carboxyl and hydroxyl groups.[17] The percentage reduction of copper metal adsorbed by modified water hyacinth increased with increasing dose of adsorbent used and decreased at a dose of 2 grams. This is because if the mass of the biosorbent has exceeded its optimum conditions it will cause unsaturation on the active site of the biosorbent resulting in a decrease in the adsorption efficiency at high adsorbent doses. In addition, there is clumping and a decrease in the surface area of the adsorbent so that there are no more sites that can absorb metal ions as a result the effectiveness of the adsorbent decreases.[21] At a dose of 2 grams of water hyacinth adsorbent, the adsorbent after modification had a greater percentage of decreased adsorption than the adsorbent before modification, namely 98% for chromium metal, 37.40 % for cadmium metal and 55.9 for copper metal. This is because the adsorbent before modification has fewer active groups than after modification. The addition of carbonyl and hydroxyl groups from the addition of citric acid to the adsorbent causes the adsorbent after modification to have a higher chemical reactivity than cellulose.[14] Statistical analysis on SPSS with Two Ways ANOVA (Randomized Block Design) using a significant level of 5% showed that there was an effect of the dose of water hyacinth adsorbent on the ability to reduce metals before and after modification with citric acid.

Conclusion

The results indicated that an esterification reaction had occurred between citric acid and water hyacinth adsorbent with the emergence of an absorption peak of the C = O ester group at wave number 1735 cm^{-1}. Modification of the water hyacinth adsorbent with variations in citric acid concentration had an effect on the total active groups produced, namely the highest was 3.94 meq/g at 2.5 M citric acid concentration. Metal adsorption in laboratory waste showed the best results at a dose of 1.5 grams with a reduction percentage of copper metal of 63.34% and a 2 gram dose with an adsorption percentage of 98% for chromium metal and 37.40% for cadmium metal.

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