

ADSORBENT EFFECTIVENESS OF α -CELLULOSE/HUMIC ACID WITH EPICHLOROHYDRIN CROSS-LINKING AGENT ON METHYL ORANGE DYE

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Abstract: Adsorption of methyl orange (MO) using epichlorohydrin cross-linked humic acid/cellulose composite has been carried out. This study aims to synthesize epichlorohydrin cross-linked humic acid/cellulose composites, determine the optimum pH, contact time, and initial concentration and study MO desorption. The adsorbent production begins with the isolation of cellulose from empty palm oil bunches (EFB) obtained from North Sumatra and the isolation of humic acid from peat soil obtained from Rawa Pening. Then humic acid was cross-linked to cellulose in an alkaline solution (NaOH), then epichlorohydrin was added as a cross-linking agent while heating at 60°C for 2 hours. Epichlorohydrin cross-linked humic acid/cellulose adsorbents (AH/Cell-ECH) were further characterized using FTIR, XRD and SEM spectroscopy. MO solutions before and after adsorption were analyzed using UV-Vis spectrophotometry. MO desorption studies used HCl pH 4, 0.1 and 1.0 M NaCl and 40% and 60% ethanol. FTIR characterization showed that the AH/Sel-ECH adsorbents had active groups, including –OH, –C=O, and –COOH. Characterization using XRD showed diffraction peaks in the 2 θ region around 11.41, 20.25, 22.55, and 42.66 $^\circ$, indicating the presence of galactose, xylose, glucose and polysaccharide phases. The SEM-EDX results showed that the surface of the adsorbent had non-uniform pore sizes, and the surface morphology tended to be clean and free of debris. It indicated the presence of C, O, and N elements in AH/ECH-cells and S, N elements after MO adsorption. The optimum interaction of AH/Sel-ECH with MO occurred at pH 2 with 150 mg/L MO, and a contact time of 120 minutes was obtained. MO adsorption by AH/ECH-cells followed a pseudo-second-order kinetics model and the Freundlich isotherm with an MO adsorption capacity of 9.84×10^{-5} mmol/g, respectively. Desorption studies showed that 60% ethanol was the most effective solution for desorption of MO.

Keywords: *Adsorption, Humic Acid, Cellulose, Epichlorohydrin, Crosslinking*

INTRODUCTION

Methyl orange dye is mainly produced in the textile industry. Pigments that aim to beautify textile materials have an impact on environmental sustainability. Dye waste is an organic compound that is difficult to decompose and is resistant and toxic [1]. If the waste is discharged into water, apart from causing the water to have a high level of color, it will also cause a significant increase in BOD; sunlight will be blocked by the dye, thereby inhibiting the photosynthesis process of aquatic plants. This disrupts the ecosystem within and causes environmental pollution. Of the many shades, methyl orange is a dye often found in textile industry waste. Methyl orange is an anionic dye with an azo group in the form of a dark orange powder with a molecular size of $1.58 \times 0.65 \times 0.26$ nm [2].

Several dye removal methods include filtration, chemical precipitation, ion exchange, adsorption and membrane systems [3]. Adsorption is a recovery method to prevent the increasingly widespread danger of heavy metal and dye pollution in the environment. This is because the adsorption method has several advantages, including relatively simple processing, relatively high efficiency, effectiveness, and not impacting the environment [4]. The adsorption process uses adsorbents from natural materials. Natural adsorbents are used because they are relatively safe, and the costs are pretty cheap. Raw

materials used as adsorbents include cellulose, alumina, silica, humic acid, etc.

Cellulose, a polysaccharide, contains –OH and –COOH groups for adsorbent use. Cellulose can be obtained from empty oil palm fruit bunches. Empty palm oil bunches are the main lignocellulosic waste that has not been utilized optimally, so many empty bunches are left without processing. If not handled properly, EFB (empty oil palm bunches) will become waste and cause environmental pollution [4]. TKKS constitutes 23% of fresh fruit bunches containing lignocellulosic material of 55-60% dry weight. Lignocellulose is the main component of EFB, which can adsorb heavy metals because they include active groups such as –OH and –COOH [5]. The presence of the –OH group can cause polar properties in the adsorbent, so it can adsorb substances that are polar rather than less polar substances. Cellulose has functional groups that can link with metal ions [6]. Cellulose is the most abundant natural biopolymer with a relatively strong mechanical strength of up to 10,000 Mpa, and cellulose has a chemical structure similar to chitosan, making it possible to produce a homogeneous mixture that combines the properties of chitosan and cellulose well [7].

Humic acid contains major functional groups such as carboxylate, -OH phenolate, and –

OH alcoholate. Humic acid also includes other small groups such as carbonyl, phosphate, sulfate, and amide. All of these groups can interact with metal ions in solution. Due to the presence of functional groups and the ability to interact with metal ions, humic acid can be used to adsorb dissolved metals in water. Apart from that, the carboxylic active group and phenol group of humic acid can also remove pollutants in water, namely the negative charge of dyes in acidic conditions.

Besides having many advantages as an adsorbent, humic acid has weaknesses, namely high solubility at high pH, which is unsuitable for use as a sole adsorbent [8]. The application of humic acid as a sole adsorbent has obstacles, namely high solubility \geq 95% at medium pH 6 (Santoso et al., 2007). On the other hand, cellulose has a lower adsorption ability than humic acid, which has a better ability to absorb metals and dyes through good ion exchange and chelating activity. Another alternative method needs to be used, and these two materials are modified by immobilizing humic acid on other polymer compounds or materials with cross-linking of the polymer chain, which is more recommended to form cellulose and cross-linked [9] to reduce the solubility of humic acid. Epichlorohydrin increases the stability of humic acid complexes due to the solubility of humic acid at high pH. The humic acid group is connected to another group via a covalent link connected by epichlorohydrin, and a stable product is obtained in the expected pH range. Immobilization through cross-linking aims to ensure that the compound does not dissolve easily in water, affecting its adsorption capacity. Another aim is to increase the selectivity of cross-linked cellulose towards specific heavy metal ions. This technique is first used to link metal ions to cellulose functional groups, then cross-link them with a cross-linking agent and remove them with a chelator [10].

Based on the background above, heavy metal pollution and dyes such as cadmium and methyl orange have dangerous effects on the environment and human health if they exceed the threshold and are seen from their non-biodegradable existence. Therefore, a method is needed to remove heavy metals and dyes by efficiently utilizing cellulose and humic acid from natural materials, which are abundant and have relatively large functional groups to adsorb cadmium metal and methyl orange paint. The immobilization of cellulose and humic acid with the cross-linking agent epichlorohydrin is intended to reduce the solubility of the humic acid adsorbent so that it can be applied in various pH ranges.

RESEARCH METHODS

Material

The materials used in this research were empty palm oil bunches from Medan as a source of cellulose and peat soil from Rawa Pening as a source of humic acid. The chemicals used are HNO₃ (Merck),

epichlorohydrin (Merck), cadmium sulfate octahydrate (3CdSO₄ .8H₂O), methyl orange (Merck), pro analysis quality (pa) sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium hypochlorite (NaOCl) 12% (Merck), glacial acetic acid (CH₃COOH) (Merck), distilled water (Bratachem), ammonium hypochlorite (NH₄OCl), potassium nitrate (KNO₃), Na₂EDTA, sodium chloride (NaCl) and absolute ethanol (C₂H₅OH).

Instrumentation

There are several instrumentations used in this research, including Fourier-Transform Infra Red (FTIR, Shimadzu prestige 21), atomic absorption spectrophotometer (SSA Perkin Elmer 3110), Uv-Vis spectrophotometer (Thermoscientific 20D), X-ray Diffraction (XRD, Bruker D2 Phaset 2nd Gen), Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS JEOL JSM-6510 LA series).

Procedure

1. Isolation of Humic Acid

Five hundred grams of peat soil were extracted with 2500 mL of 0.1 M NaOH for 24 hours, then filtered, and the filtrate was added with 1M HCl until pH 2. Then, it was stirred and left for 24 hours. Filtering is carried out, and the residue is taken. The same procedure was carried out three times to purify the humic acid and dried at 105oC for 2 hours. Humic acid was then characterized using FT-IR.

2. Cellulose Isolation

Fifty grams of empty palm oil bunches were put into a beaker and added with distilled water while heated for 2 hours at 60⁰C. Then filtered, 500 mL of 2% NaOH was added to the residue while heated for 2 hours at 80⁰C. Next, filter and wash until the filtrate is neutral. The residue was added with 500 mL of 5% NaOCl and eight drops of glacial CH₃COOH and heated at 60oC for 1 hour. Then filtered and washed until neutral, 500 mL of 0.05 N HNO₃ was added while heated for 1 hour at 70oC. The residue was purified and flown until tepid, and 500 mL of 17.5% NaOH was added while heated at 60oC for 1 hour. The residue was dried at 60oC for 2 hours and then characterized by FT-IR.

3. Immobilization of humic acid and cellulose

Each 600 mg of cellulose was added to 6 mL of 0.3 M NaOH and then dissolved. Then, 120 mg of humic acid was added to 6 mL of 0.06 M NaOH and dissolved. The results of mixing humic acid and cellulose were combined, and 15 mL of epichlorohydrin was added while heated at 60oC for 2 hours and then filtered and dried.

Adsorption of MO on AH/S

1. Determination of optimum pH

0.02 g of humic acid immobilized by cellulose (AH/S) was contacted with 50 ppm of 50 mL of MO ion solution with a pH variation of 2-8 with a contact time of 120 minutes at room temperature. The solution was centrifuged for 10 minutes at a speed of 1200 rpm, and then the supernatant solution was taken slowly and analyzed using UV-Vis for MO.

2. Determination of adsorption isotherms

Work methods are carried out at this stage, such as determining the optimum pH. Still, the pH used is the optimum pH, with variations in concentration between 20-150 ppm with a contact time of 120 minutes at room temperature at a speed of 1200 rpm. The solution was centrifuged for 10 minutes at a rate of 1200 rpm, and then the supernatant solution was taken slowly and analyzed using UV-Vis.

3. Determination of reaction kinetics

The work method is carried out at this stage, such as determining the adsorption isotherm with the optimum pH. Still, the concentration for each Cd(II) and Cr(III) ion adsorbate is 50 ppm, with the contact time varying between 0-240 minutes at room temperature. The solution was centrifuged for 10 minutes and then analyzed using UV-Vis for MO.

MO Desorption Study

1. MO desorption

A total of 0.1 g AH/S was contacted with 250 mL of 250 ppm MO solution at optimum pH for 120 minutes at room temperature. The solution was centrifuged for 10 minutes at a speed of 1200 rpm, and then the supernatant solution was taken slowly and analyzed using UV-Vis. The precipitate formed under the falcon tube was oven-treated for 60 minutes. A total of 0.02 g of AH/S after adsorption that had been in the oven was put into 50 mL HCl pH 4, then stirred for 180 minutes and centrifuged for 10 minutes at a speed of 1200 rpm and the supernatant solution was taken for analysis using UV-Vis, while the precipitate formed soaked again in 0.1 M and 1.0 M NaCl solution, 40% and 60% ethanol with the same treatment.

2. Material characterization

Samples of humic acid (AH), cellulose (S), humic acid cross-linked on cellulose (AH/S) and residues that had absorbed MO were characterized using IR and SEM. XRD analysis for characterization of AH, S, AH/S, and AH/S-MO samples.

RESULTS AND DISCUSSION

Synthesis of Cellulose Cross-Linked Humic Acid (AH/S-Epi)

The cross-linking of humic acid in cellulose aims to reduce the solubility of humic acid at high pH

by combining two molecules to chemically bond, where the linking agent is used as a bridge between the two molecules.[11].This research used the linking agent epichlorohydrin, which will then bind to the active groups of humic acid and cellulose. The choice of cellulose as a buffer for humic acid is because cellulose has non-toxic properties, is easily found in nature, has active hydroxyl groups, which can bind with metal ions and dyes and is stable at various pH conditions. The epichlorohydrin cross-linked humic acid/cellulose composite was synthesized by adding 0.3 M NaOH to cellulose and 0.06 M to humic acid and using several variations in epichlorohydrin dosage. The first method is mixing cellulose and humic acid, then 7.5 mL of epichlorohydrin is added; the second method is the same mixing of cellulose and humic acid, then 15 mL of epichlorohydrin is added, and for the third method, the same treatment is then added with 30 mL of epichlorohydrin. According to research [18], the hydroxyl group dominates among the functional groups of humic substances (HS). It is reactive enough to react with the epoxy group in the presence of a catalyst in alkaline media. This reaction immobilizes HS on a cellulose matrix via a cross-linker containing epoxy groups.

The cross-linking reaction between humic acid/cellulose and epichlorohydrin is through a covalent bond between the carbon atom of epichlorohydrin and the hydroxyl group of humic acid and cellulose by breaking the epoxide ring of epichlorohydrin and releasing a chlorine atom [12] because the reactive group of epichlorohydrin is present. On epoxide and chlorine rings [13]. According to [13], the absorption capacity of epichlorohydrin cross-linked chitosan on MO increases with increasing epichlorohydrin until the optimum epichlorohydrin composition. The absorption decreases slightly if the epichlorohydrin composition continues to be improved. The addition of epichlorohydrin to chitosan will result in a distance between the chitosan polymer chains so that between the chitosan polymer chains and other chitosan polymer chains.

Then, initial testing was carried out to obtain the optimum adsorbent by adsorbing MO on each variation of epichlorohydrin to produce optimum adsorption capacity.

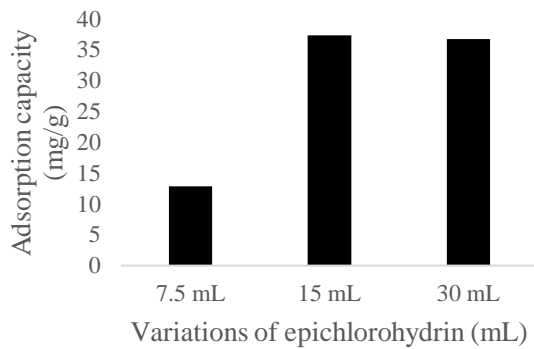


Figure 1. Variation of epichlorohydrin on adsorption capacity

Figure 1 shows that the adsorption capacity for MO ions is 12.9, 37.4 and 36.8 mg/g. This can differ due to competition for functional groups to bind to epichlorohydrin. The addition of more and more epichlorohydrin causes the epichlorohydrin groups to bind and interact with the groups of humic acid and cellulose, resulting in competition for groups, which causes the number of -COOH and -OH groups available to become less so that the interaction with humic acid and cellulose becomes increasingly reduced.

Characterization of AH/S-Epi Adsorbent FT-IR Characterization

Characterization using FTIR aims to identify functional groups contained in a material where the information obtained is valuable group absorption peaks at characteristic wave numbers.

The FTIR spectrum of cellulose is visible at various wavenumber peaks. At a wave number of 3448 cm^{-1} , it shows the stretching vibration of -OH, 2900 cm^{-1} indicates the stretching vibration of -CH trying on CH₂ from the CH₂-OH group of cellulose, 1635 cm^{-1} shows the presence of an aromatic C=C or C=O group. From the pyranose ring on cellulose [14].

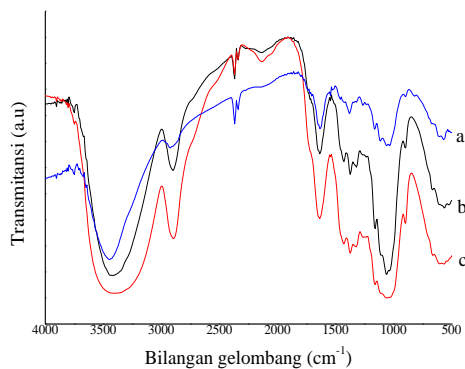


Figure 2. FTIR characterization results (a) AH/Epi-Cell + MO (b) AH/Epi-Cell

Meanwhile, humic acid has a characteristic absorption peak at a wave number of 3425 cm^{-1} , indicating the presence of -OH stretching vibrations, 2924 cm^{-1} indicating the presence of -CH trying vibrations, and 1627 cm^{-1} indicating the presence of -CO stretching vibrations: a sharp peak change and a new absorption peak for AH/S-Epi [15]. The wave number for bending vibration COC on cellulose in the absorption area of 1056 cm^{-1} with a small intensity after cross-linking with epichlorohydrin at the peak of 1056 cm^{-1} occurs a shift. It shows a sharp peak with high intensity. This shows the large number of COC bonds, which explains the presence of epichlorohydrin bound to cellulose and humic acid. A new absorption peak appears in the area around 1273 cm^{-1} , indicating the stretching vibration of -CO, which originates from humic acid but has a low intensity because the composition of humic acid is lower than that of cellulose. In this study, the presence of the -OH group in the AH/Sel-ECH adsorbent was estimated at a wave number of 3448 cm^{-1} , but after interacting with MO, there was a shift towards a wave number of 3449 cm^{-1} . Then, the -CO absorption band at wave number 1056 cm^{-1} changes to a frequency of 1033 cm^{-1} after interacting with MO. In addition, after AH/Sel-ECH adsorbed MO, it showed a new absorption area at wave number 1111 cm^{-1} , indicating CN vibrations originating from MO [16].

XRD Characterization

XRD analysis aims to compare the crystallinity of S, AH/S, AH/S-Cd and AH/S-Cr to predict the effect of adding humic acid, epichlorohydrin, and adsorbents on the crystal lattice.

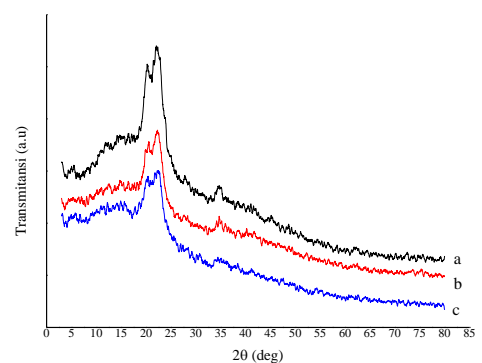


Figure 3. XRD diffractograms (a) AH/Epi-Cell, (b) AH/Epi-Sel + Cd, (c) AH/S-Epi + MO

Figure 3 shows general similarities in the diffractogram pattern between AH/Epi-Cells before and after interacting with MO. This is indicated by the shift in the 2θ angle after AH/Sel-ECH interacts with MO, as presented in Table 1. The AH/Sel-ECH adsorbent also showed the same

thing after interacting with MO. The loss of peaks at 2θ 11.417 $^\circ$ and 27.810 $^\circ$ and a decrease in the intensity of other characteristic peaks was due to the insertion of MO in the adsorbent. This shows that no damage to the AH/Sel-ECH structure occurred after interacting with MO [17].

Table 1. AH/Sel-ECH diffractogram data before and after interaction

Sample	2θ (degree)	I	d(Å)
AH/ECH-Cell	11.417	1023	7.744
	20.250	2821	4.381
	22.060	12931	4.026
	27.810	407	3.205
AH/Cell-ECH + MO	20.360	3092	4.358
	22.640	5804	3.924
	30.760	243	2.904
	33.890	216	2.642

SEM-EDX Characterization

SEM-EDX analysis aims to determine the surface morphology of the material and the elemental content contained in the material.

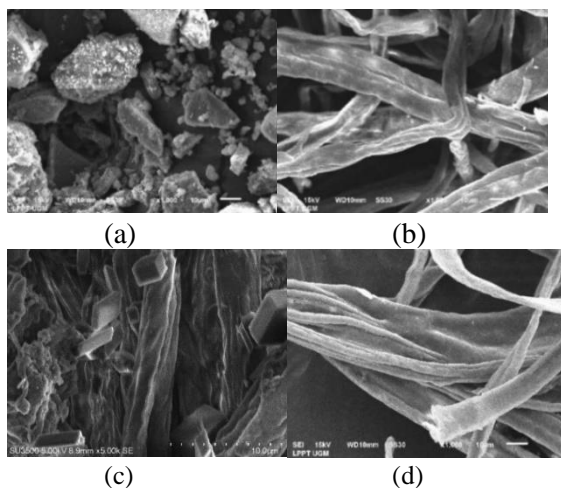


Figure 4. SEM image with 1000 times magnification (a) AH, (b) S, (c) AH/S-Epi, (d) AH/S-MO

The results of the cross-linking of humic acid on cellulose are shown in Figure 4. (c) it can be seen that the dominant material is cellulose in the form of fibres. This is also supported by FTIR data, where the AH/S spectrum is dominated by cellulose absorption. The composition of humic acid is much less than cellulose, namely in a ratio of 1:5, making the AH/S material dominated by cellulose [18]. Figure 5. (d) is an SEM image for AH/S-MO, which does not show a significant difference between AH-S and AH-S-MO where there are lumps covering the surface of the AH/S-Epi adsorbent pores, and they are filled full of MO molecules. These clumps indicate the presence of MO attached to the surface of the AH/S-Epi adsorbent. Further analysis was carried out using EDX

to confirm whether or not there was adsorbate adsorbed on the adsorbent [19].

Table 2. EDX results

Element	AH/ECH-Cell		AH/Cell-ECH + MO	
	Mass (%)	Atoms (%)	Mass (%)	Atoms (%)
C	33.33	38.30	43.6	50.4
N	33.33	32.89	14.3	14.2
O	33.33	28.81	39.4	34.2
CD	-	-	-	-
S	-	-	2.54	1.13
Cl	-	-	0.16	0.07

Note: the (-) sign means not detected

The EDX data in Table 2 shows that the AH/Sel-ECH adsorbent has successfully adsorbed MO. Then, on the AH/Sel-ECH adsorbent, which had adsorbed MO, the elements S, N, and Cl, which came from the MO molecule, were detected. In the AH/Sel-ECH adsorbent, which has adsorbed MO, there is an increase in the mass percentage of the N element to 14.3% (% atom \approx 14.2%), which comes from MO molecules from the previous 33.33% (% atom \approx 32, 89%) in AH/Cell-ECH. The S and Cl elements detected after the adsorbent interacted with MO had a mass percentage of 2.7% and 1.13%, respectively. This SEM-EDX data can strengthen the evidence that the AH/Sel-ECH adsorbent has successfully adsorbed MO [20].

MO Desorption Study

Desorption studies were carried out on the AH/Sel-ECH adsorbent to determine the interactions that play a role in MO adsorption. Desorption is carried out after the adsorbent absorbs MO under optimum conditions. MO desorption is done using HCl pH 4, 0.1 M and 1.0 M NaCl solutions and 40% and 60% ethanol solutions.

In MO desorption, a pH 4 HCl solution is used as a desorbent to protonate the active group on the adsorbent because of its acidic strength so that the previously bound MO will be released. NaCl solution is used to determine the existence of electrostatic interactions between the adsorbent and MO [21]. The strength of the Na⁺ ion from NaCl can release the bound MO cation charge so that the MO will be removed from the adsorbent. A mixed solution of ethanol and water was used to determine the interactions between the adsorbent and MO through hydrophobic interactions and hydrogen bonds.

CONCLUSION

Based on the results of the research conducted, the following conclusions were

obtained Synthesis of humic acid/cellulose adsorbent with epichlorohydrin cross-linker (AH/Sel-ECH) to adsorb Cd(II) and MO ions has been carried out. The adsorption capacity for MO dye is 9.84×10^{-5} mmol/g. The optimum pH conditions for AH/Sel-ECH adsorption of MO dye was 120 minutes, respectively, with kinetics following the Ho Pseudo Second Order Kinetic model with respective adsorption capacities for MO are 3.03×10^{-1} mmol/g. The adsorption of MO on AH/Sel-ECH both follow the Freundlich isotherm pattern. Hydrogen bonds and hydrophobic interactions dominate the interactions that play a role in the adsorption mechanism of MO.

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