

CHEMICAL MODIFICATION OF WATER HYACINTH FOR THE REMOVAL OF DYESTUFFS

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Abstract: Water Hyacinth (WH), an aquatic weed, is a good heavy metal adsorbent. Their adsorbing capacity and binding selectivity can be increased by converting the WH's hydroxyl functional group into the desired ones. In this report, the chemical modifications of WH by cyanoethylation (WH-CE), amidoximation (WH-AO) were carried out. The chemical testing and the FTIR spectrums of the WH, WH-CE and WH-AO indicated that higher nitrogen content of the modified WH than that of WH was found with the existing of nitrile and amine functional group on WH-CE and WH-AO, respectively. The adsorption of Acid Blue 25 and Basic Blue 9 by WH and WH-AO were studied. Based on Freundlich adsorption isotherm, WH-AO has a much higher dye-adsorption capacity than does WH. The adsorption capacity of WH for BB9 was higher than AB25. For WH-AO, the adsorption capacity of AB25 was higher than WH.

Keywords: dyestuffs; water hyacinth powder; chemical modification of water hyacinth; adsorption

INTRODUCTION

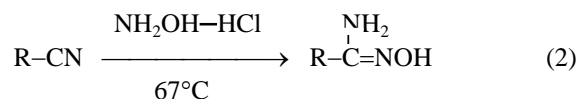
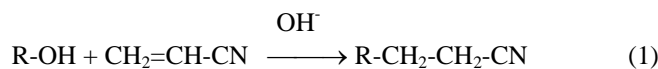
Water hyacinth (*Eichhornia crassipes*) is a perennial, freshwater, aquatic vascular plant with rounded, upright, shiny green leaves. The petioles of the plant are spongy with many air spaces which contribute to the buoyancy of the hyacinth plant. Water hyacinth (WH) is ranked eighth among the world's top 10 in growth rate and is found abundantly throughout Thailand. It is composed of 43-44% cellulose and 12-13% lignin (Strelpapatkul, 1989). Somboon et al. (1990) has reported that water hyacinth powder (WH) has a very high adsorption capacity for heavy metals (Cr, Cu, Ni, Pb and Zn). Like cotton, WH has the tendency to form a strong bond with direct dyes, reactive dyes, and basic dyes.

Color contamination from textile-dyeing effluents has been the target of great concern in the last few years, mainly due to its unsightliness but also due to its toxicity. The de-colorization of textile wastewater is a worldwide problem to which successful treatment technologies have been applied, including coagulation, adsorption, oxidation, and biological treatment. Coagulation can be used effectively to remove certain types of dyes. Generally, this process is most efficient when dealing with pigment-type materials or dispersed dyes. The process is least efficient when dealing with true water soluble dyes. The oxidation methods are effective only in wastewater having a very low concentration of organic color. The adsorption process by activated carbon and polymer resin is expensive, and it is difficult to regenerate the adsorbent (Bousher, Shen & Edyvean, 1997). These conventional methods are costly and require some skill to operate and to maintain. Consequently, the wastewater has been discharged untreated. There is a need for a more practical technology that is more effective and more selective to organic dyestuffs. In this report, the chemical modification of WH powder into two new products with different functional group was studied.

The main functional group of the natural cellulose (cotton) is the hydroxyl group (OH). The hydroxyl group could bond to the positive charges of the adsorbates such as heavy metal ions or cationic dyes. In case of silk, it is the amino group (negative charge) instead of the hydroxyl group. Thus, silk has the affinity for the anionic dyes. The conversion of the hydroxyl group of the cellulose to the amino group could be performed directly through the carbamoylation reaction. The conversion could be achieved by converting the hydroxyl group of WH to the nitrile group (CN) by cyanoethylation reaction with basic catalysts (Parker, 1993). A chemical reaction, to introduce the β -cyanoethyl group ($\text{CH}_2\text{CH}_2\text{CN}$), involves the addition of acrylonitrile ($\text{CH}_2=\text{CH}-\text{CN}$) to a compound carrying a reactive hydrogen (reaction 1).

Yields in cyanoethylation are generally high. The reaction is strongly exothermic and is usually carried out at moderate temperature in solvent such as dioxane or t-butanol. The cyanoethylated product can be subjected further to the usual nitrile

reactions such as hydration, hydrolysis and reduction. Morita, Higuchi & Sakata (1987) converted the cyanoethylated wood to the amidoximated wood by reacting with methanol saturated with hydroxylamine hydrochloride at 60°C. The reaction is shown in reaction (2).



MATERIALS

Water Hyacinth Powder

WH stalk was washed with tap water and cut into pieces of 0.20 cm or less in length. The cut WH pieces were dried overnight at room temperature before being ground and sieved to a size between 0.15 and 0.85 mm (20 - 100 mesh). The ground powder was oven-dried overnight at 103°C prior to use.

Dyestuffs

Dyestuffs selected for study and associated information are indicated in Table 1. The chemical structure of each dye is presented in Fig. 1. Dyestuffs are used as received without any purification. They are dried at 60°C for 3 hours prior to use.

Table 1. Dyestuffs selected for the studies.

Name of dyestuffs	Abbreviation	Type of Dye	CI No.
Acid blue 25	AB25	Acid	62055
Basic blue 9	BB9	Basic	52015

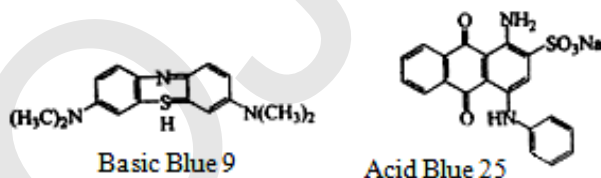


Figure 1. Chemical structure of dyes.

METHODS

Chemical Modification of WH

The hydroxyl functional group (OH) of WH is chemically converted into the amine group (NH₂) by indirect conversion to the nitrile group (CN) via the cyanoethylation reaction and then converting into the amino group via the amidoximation.

Cyanoethylation of WH: Place WH into 4.0% NaOH saturated with NaI for 30 min. The mixture is pressed to a wet pickup of 150% with a piece of cloth. The damped WH is quickly placed in a three-necked round-bottomed flask and equips the flask with a reflux condenser. Heat the mixture to a constant temperature of 60°C after adding acrylonitrile. After 12 hours, allow the flask to cool and neutralizes the mixture with 0.1 M acetic acid. Wash the product in the Buchner funnel, using DI water, until a constant pH of the rinsed water is observed. The product (WH-CE) is dried in a vacuum oven at 70°C.

Amidoximation of WH: Place WH-CE into methanol saturated with hydroxylamine hydrochloride in a round bottom flask and refluxed the mixture 67°C for 15 hours. The product was washed in the Buchner funnel with deionized water until a constant pH of the rinsed water is observed, then washed the product with methanol and dried in a vacuum oven at 70°C. This product is called WH-AO.

Determination of Wavelength at Maximum Adsorption

The dye adsorption spectrum of each dye is determined by dissolving dye in deionized water. The dye solutions were scanned with a UV-VIS Spectrophotometer. The wavelength at the maximum adsorption (λ_{\max}) was determined from the spectrum.

Adsorption Isotherm Study

The adsorption isotherms were determined by shaking fixed weights of WH or WH-AO with known volume of dye solutions having concentrations ranging from 50 to 550 mg-dye/l, at room temperature.

RESULTS AND DISCUSSION

Some Physical Properties of WH Powder

The surface area of WH powder (0.15 - 0.85 mm) is 1.01 m²/g, indicating a non-porous solid. The pH_{zpc} was determined by the method described by Huang & Ostovic (1987). The pH_{zpc} of WH is about 6.3, indicating that WH has a weakly acidic surface which is of the cationic type.

WH is a weak cationic ion exchanger, the total cation exchange capacity was found to be 1.0 meq/g. The total exchange capacities for a number of commercial resins ranged from 2.5 to 4.9 meq/g of resin on a dry basis. The total exchange capacity of WH is low because of its low surface area.

Chemical Properties of WH and the Modified WH

Solubility tests are performed on WH, WH-CE and WH-AO. The solubility test in acid or a basic solvents can reveal whether the compound in a base (amine), an acid, or a neutral substance. WH, WH-CE and WH-AO are all soluble in sulfuric acid (Table 2). The solubility of WH-CE, but not WH, in pyridine indicates that some of the OH groups of WH are converted into the nitrile groups, as revealed by the IR spectrum. Aromatic amine (amide) is soluble in pyridine. WH-CE and WH-AO are soluble in pyridine, while only WH-AO is soluble in benzaldehyde. The solubility tests and along with the IR-spectra of WH-AO show that it is quite possible that WH-AO contains the amine functional groups.

Table 2. Some chemical testing of WH and modified WH

Type of WH	Solubility Test			Amide Test		Amine Test		Nitrogen Content, %
	H ₂ SO ₄	Pyridine	Benzaldehyde	Ammonia smell	Color of Litmus paper	Nitrous acid test	Hinsberg's test	
WH	Y	N	N	N	Red	No bubble	N	0.28
WH-CE	Y	Y	N	Y	Blue	No bubble	N	7.81
WH-AO	Y	Y	Y	Y	Blue	Bubble at 4°C	N	7.73

Note: Y = positive test and N = negative test

The smell of ammonia resulting from the WH-CE and WH-AO tests confirms the presence of the CN group on WH-CE, and the presence of either the CN group or the amide group on WH-AO. If most of the CN functional groups on WH-CE are converted, then the smell of ammonia will indicate the presence of the amide groups on WH-AO. The positive nitrous acid test on WH-AO indicates the presence of the primary amine. The differing results from the nitrous acid test indicate that WH-AO contains the amino group. The ammonia smell from the nitrous acid test comes from the presence of the amide group, not the CN group. The Hinsberg's reagents do not dissolve the WH and all of the modified WH and thus no reaction occurred. The Hinsberg's test cannot differentiate the modified WH, and thus the presence of the amine group cannot be determined.

The nitrogen (N) content of WH and the modified WH was determined by the Total Kjeldahl Method (TKN). The fact that the N content of WH-CN (about 7.81%) is higher than that of WH (about 0.28%) confirms the conversion of the OH group of WH into the CN group of WH-CE. The N content of WH-AO is not twice as much as that of WH-CE could be because of the N content of C=N cannot be determined by the Kjeldahl method.

Thin layer chromatography can be performed on WH-CE and WH-AO only because of their ability to be dissolved in pyridine. The retardation factor (R_f) value of WH-CE and WH-AO are 0.88 and 0.63, respectively. It is clearly shown by the R_f values that the CN functional groups of WH-CN are consumed, and the new products (WH-AO) have different functional groups.

The Spectrum of WH and the Modified WH

WH is a natural fiber, which is primarily composed of cellulose, lignin, and wax. The IR-spectrum of WH would therefore contain many bands at the different absorption regions. The WH IR-spectrum cannot be accurately interpreted to identify its functional groups. It can, however, be used as one of the tools to differentiate the modified WH. In the infrared spectrum of WH (Fig. 2), the broad band between 2,800 and 3,000 cm^{-1} results from C-H stretching vibrations. The band at 665.59 cm^{-1} is from the rocking of the CH_3 and CH_2 groups.

The spectrum of WH-CN is shown in Fig. 3. The OH functional group of WH (or WH-OH) is converted into the nitrile group by cyanoethylation (reaction 2). The strong band at 2,252.51 cm^{-1} result from $\text{C}\equiv\text{N}$ stretching. The broad band of O-H stretching centered at 3,476.39 cm^{-1} is still apparent. The adsorption bands in the range of 2,850 to 2,950 cm^{-1} , and at 1,677.05 cm^{-1} and 1,104.38 cm^{-1} , indicate the stretching frequencies of C-H, C=C, and C-O-C, respectively.

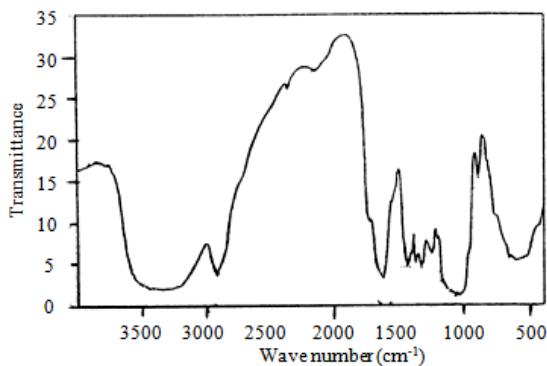


Figure 2. FTIR-Spectrum of WH

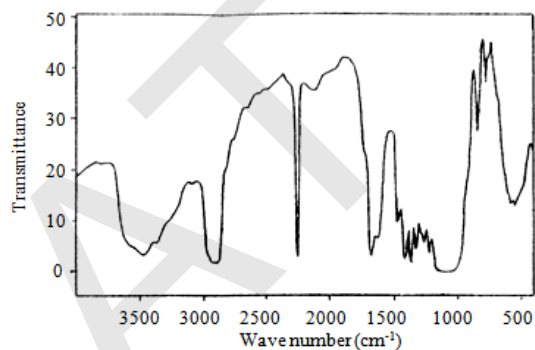


Figure 3. FTIR-Spectrum of WH-CE

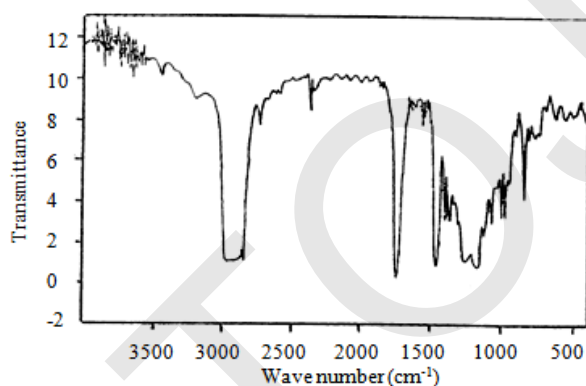


Figure 4. FTIR-Spectrum of WH-AO

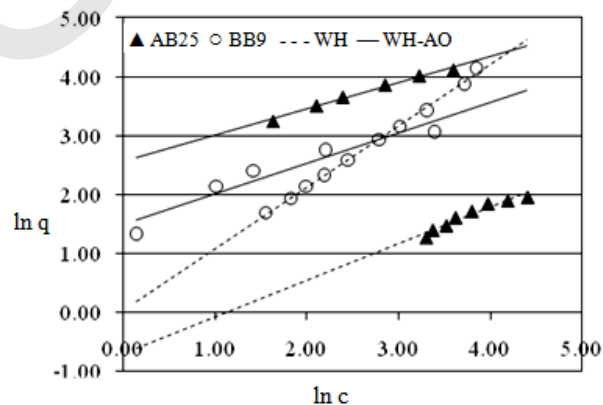


Figure 5. Freundlich adsorption isotherm.

The spectrum of WH-AO is shown in Fig. 4. The fact that there is no broad absorption band around 3,500 cm^{-1} indicates that most of the hydroxyl groups are largely consumed. The intensity of the $\text{C}=\text{N}$ vibration (1,630 - 1,680 cm^{-1}) lies between that of the $\text{C}=\text{O}$ vibration (1,600 - 1,950 cm^{-1}) and the $\text{C}=\text{C}$ vibration (1,560 - 1,680 cm^{-1}). In the spectrum of WH-CN there is, however, no band in the range of 1,680 to 1,950 cm^{-1} as indicated in Fig. 3. It is possible that the strong band at 1,742.68 cm^{-1} (Fig. 4) is the vibration of $\text{C}=\text{N}$ and not that of $\text{C}=\text{O}$ or $\text{C}=\text{C}$. There is a weak absorption at around 3,440 cm^{-1} which is most likely the stretching vibration of either the primary amines or the secondary amines. Most of the primary amines show two spikes in the N-H stretching. The secondary amines generally show one N-H spike in the absorption range of 3,400 to 3,530 cm^{-1} . If the band at 3,440 cm^{-1} is one of the stretching vibrations of the OH group, then it should be a broad band. There are two bands at 1,180 and 1,280 cm^{-1} that could be the stretching vibrations of the C-N (aromatic) group. The band at 1,280 cm^{-1} also could be, however, the C-O-C stretching vibration.

Adsorption Isotherm

Adsorption isotherm data were fitted to the linear form of the Freundlich model. The plots of $\ln q$ against $\ln C$, for the adsorption of dyes by WH and WH-AO gave a straight line indicates that the adsorption process conforms to Freundlich adsorption isotherms. The values of K , n and the corresponding correlation coefficients (r), are presented in Table 3.

Table 3. Freundlich adsorption constants.

Adsorbent	Dyestuffs	K	n	r
WH	AB25	0.5034	1.62	0.938
WH	BB9	1.0500	0.96	0.998
WH-AO	AB25	12.8726	2.22	0.988
WH-AO	BB9	4.4817	1.96	0.916

The adsorptions of AB25 and BB9 by WH and WH-AO are shown in Fig. 5. The OH functional group of WH is first converted to the CN group and then to the NH_2 group. The WH-AO should, however, contain some OH, CN, and NH_2 groups. The OH group is a negatively charged group, while both CN and NH_2 are positively charged groups. The adsorption of AB25, an anionic dye, by WH-AO is much higher than that by WH, indicating the net positive charge of WH-AO. The positive charges of both CN and NH_2 on WH-AO can form hydrogen bonding with $=\text{O}$ groups of AB25 molecules. At a high equilibrium dye concentration, the adsorption of BB9 by WH-AO is lower than that by WH, due to the repellency between the positive charge of dye and the positive charge of WH-AO.

CONCLUSION

The hydroxyl functional groups of WH are chemically converted to the nitrile group by cyanoethylation reaction. Some part of these nitrile groups are converted to the amine group by amidoximation reaction. AB25, an anionic dye, has a net negatively charge while that of BB9, a cationic dye, has a net positively charge. WH-AO has a higher positive charge comparing to WH and therefore can adsorption AB25 much more than BB9. The lower adsorption of BB9 by WH-AO is due to the higher repulsion force between the positive charge of BB9 and the positive charge of WH-AO.

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