

PREPARATION OF HUMIC-CHITOSAN COMPOSITE AND ITS APPLICATION IN REMOVAL OF SULPHUR BLACK DYES FROM AQUEOUS SOLUTION

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Abstract

Humic acid(HA) is a complex molecule that exists naturally in soils, peats, oceans and fresh waters. It is an excellent natural and organic compound to provide plants and soil with a concentrated dose of essential nutrients, vitamins and trace elements. In this research, HA was extracted from the peat collected from Moeswe Village, Oattara Thiri Township, Naypyitaw, Myanmar by alkali extraction method. The yield percents of HA was found to be (6.869)%. The extracted HA was characterized by Fourier Transform Infrared Spectroscopy (FT IR). The spectroscopic analysis shows that HA contains carboxylic, phenolic and alcoholic functional groups. According to SEM image, HA possesses the voids and aggregate nature. The crystallographic information of extracted HA was investigated by XRD analysis. The nature of thermal stability of extracted HA as well as decomposition such as dehydration, liberation of volatile materials and combustion of HA were studied by Thermal Analysis. The extracted HA was composited with commercially available chitosan in three different weight ratios (1:1, 2:1 and 1:2). The composites were characterized by FT IR, XRD, SEM and TG-DTA spectroscopic methods. HA, commercially available chitosan and their composites were studied. The removal of sulphur black from aqueous solution by using humic-chitosan composite was examined. This research demonstrates that HA can be utilized as a solvent in the solving of environmental problems to some extents.

Keywords : humic acid, chitosan, composites, removal, dyes

Introduction

Humic acid is the major component of natural organic matter in soil, water and sediments, it can be obtained from any source of organic matter, among them peat and coal at different maturation degree (Skhonde, 2006; Novak, 2001). Researches involving coal for HA extraction basically aim to use this macromolecule as a soil fertilizer. However, HA has interesting surface properties, such as the presence of oxygenated functional groups, and an ability to interact with metals and metal oxides under different conditions (Skhonde, 2006). Humic molecules have great potential to be used as a dispersant in ceramic suspensions, acting similarly to the polyacrylic acids commonly used with alumina (Stevensen, 1994; Skhonde, 2006). The HA structure requires a complete characterization in order to properly evaluate its reactivity from a specific raw material, although the average properties of HA from different sources are comparable (Novak, 2001).

Peat is a light brown to black organic material, which is formed under water logged conditions from the partial decomposition of mosses and other bryophytes, sedges,

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grasses, shrubs, or trees (Cocozza *et al.*, 2003). Significant amounts of organic carbon are stored in the form of peat.

In this research, HA was extracted from peat in Moeswe Village, Oattara Thiri Township, Naypyitaw, Myanmar by alkali extraction method. The extracted HA was used in the removal of sulphur black dye which has been widely used in textile industry, Myitnge Town, Amarapura Township, Mandalay, Myanmar.

Materials and Methods

Hydrochloric acid (HCl), sodium hydroxide (NaOH), acetic acid (CH₃COOH), chitosan and sulphur black dyes were purchased from Able chemical company. The crude HA was extracted from the peat by alkali extraction method. All of the chemicals used were analytical reagent grade. Distilled water was used in the preparation of all experimental solution.

Extraction of Humic Acid from Peat Sample

Alkali Extraction Method

Humic acid was extracted from coal sample by using alkali extraction method (MARIA ORTIZ DE SERRA and M.SCHNITZER, 1972) extracted humic acid from dark chestnut soil by alkali extraction method. Similarly, (Saito and Seckler, 2013) extracted humic acid from an organic-mineral fertilizer. According to above alkali extraction method, humic acid was extracted from peat sample collected from the area of Moeswe Village, Oattara Thiri Township, Naypyitaw, Myanmar.

The peat sample was grounded by using mortar and pestle, and sieved to pass a 2.0 mm sieve. The sample was adjusted with 0.1 M HCl to provide a final concentration that has a ratio of 200 mL liquid /20 g dry sample. The suspension was shaken for 2 h and then supernatant was separated from the residue by decantation after allowing the solution to settle for 24 h or by low speed centrifugation. Then 0.1 M NaOH was added to give a final extractant to peat ratio of 10 : 1. The solution was shaken for 4 h. The alkaline suspension was allowed to settle overnight and the supernatant was collected by means of decantation and centrifugation. The supernatant was acidified with 6 M HCl with constant stirring to pH 1.0 for 4 h and the suspension was allowed to stand for 15 h. Humic acid was separated centrifugation as precipitate.

Characterization of the Extracted Humic Acids

FT IR analysis of the extracted humic acids

The extracted HA (0.035g) from peat was mixed with 0.346 g of potassium bromide (KBr) to give a concentration of 1% by weight. The KBr-humic acid samples were then pressed into solid disc. After the background was corrected, the pellet was measured using Perkin Elmer 1600, Fourier Transform Infrared Spectrometer (FT IR) with a scan speed of 16 scans / sec from 600-4000 cm⁻¹.

XRD analysis of the extracted humic acids

The extracted HA from peat was examined by using XRD-Diffractometer (D8 Advance, BRUKER, Germany).

SEM analysis of the extracted humic acids

The sample was examined by scanning electron microscope for a visual inspection of surface morphology at the Department of Research and Innovation (DRI), Ministry of Education, Yangon, Myanmar.

Thermal gravimetric analysis of the extracted humic acids

The extracted HA from peat was analysed by Hi-TGA 12950 Thermo Gravimetric Analyzer.

Preparation of Humic-Chitosan Composites

Chitosan (0.25 g) was dissolved in 15 mL of 10 % acetic acid solution and stirred at 80 °C. After dissolution of chitosan in the acetic solution, the extracted HA (0.25 g) was also added into the chitosan solution and stirred at 80 °C. Finally, the heterogeneous composite solution was dried at room temperature to get 1:1 humic-chitosan composite. Similarly, humic-chitosan composite (1:2) and (2:1) were prepared.

Characterization of Humic-Chitosan Composites

FT IR analysis of humic-chitosan composites

Humic-chitosan composite (0.035g) was mixed with 0.346 g of potassium bromide (KBr) to give a concentration of 1% by weight. The KBr and humic-chitosan composite samples were then pressed into solid disc. After the background was corrected, the pellet was measured using Perkin Elmer 1600, Fourier Transform Infrared Spectrometer (FT IR) with a scan speed of 16 scans/sec from 600-4000 cm^{-1} .

XRD analysis of humic-chitosan composites

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Thermal gravimetric analysis of humic-chitosan composites

Humic-chitosan composite was analysed by Hi-TGA 12950 Thermo Gravimetric Analyzer.

Construction of Calibration of the Dye Solution

To select the maximum absorption wavelength λ_{max} , for a particular sulphur black dye (0.5625 M), a curve was plotted by determining the colour index (absorbance) of the dye solution as a function of wavelength (530 to 740 nm). The absorbance of the dye solution at different wavelengths were determined by UV spectrophotometric method. The concentration chosen was 6.2500 M. Half dilution of the stock dye solution was made by using distilled water as a diluent. In this process, the calibration curve was used to evaluate the residual colour index (absorbance).

Determination of the Removal of Dyes by Using Humic Acid and Humi-Chitosan Composites

Into a 50 mL of dye solution in 100 mL conical flask, each of the sample: humic acid (0.1 g) and humic-chitosan composite (0.1 g) was carefully added at ambient temperature ($30 \pm 2^\circ \text{C}$) and shaken for 15 min. Each dye solution was filtered and the clear filtrate was determined spectrophotometrically at the interval of every 15 min.

Results and Discussion

Extraction of Humic Acid from Peat

The peat sample, peat powder, the extracted HA are shown in Figures 1 (i), (ii) and (iii), respectively.



Figure 1 Peat sample, peat powder and humic acid

Characterization of the Extracted Humic Acids (HA)

The extracted HA was characterized by modern techniques such as FT IR, XRD, SEM and TG-DTA spectroscopic methods.

FT IR spectrum of HA from peat is shown in Figure 2. In this spectrum, the highest absorption band of the sample was at 3364 cm^{-1} due to the O-H stretching of carboxylic acids, phenols and alcohols. This broad band can also be attributed to N-H stretching of amide group. The band at 1627 cm^{-1} was due to C=O stretching of COO^- , ketonic C=O, aromatic C=C conjugated with COO^- . The peak at 1001 cm^{-1} (C-O stretching vibration of alcohols, ethers, carboxylic acids or C-N stretching vibration of amines) and 910 cm^{-1} (Out of plane bending of O-H of carboxylic acids) respectively.

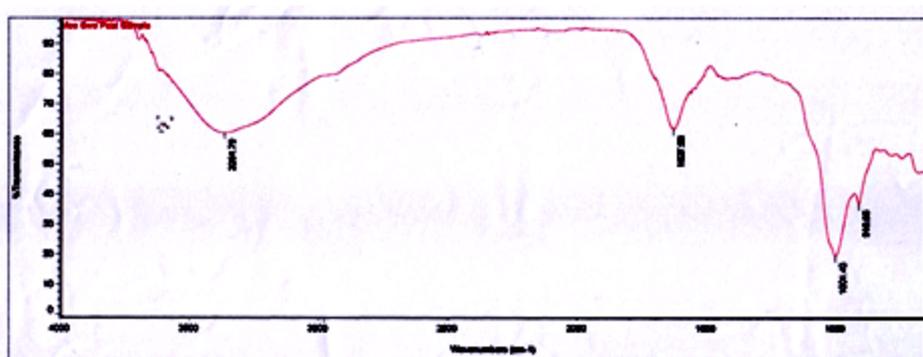


Figure 2 FT IR spectrum of the extracted humic acid from peat

The XRD diffractogram of the extracted HA was shown in Figure 3. The amorphous like nature of humic acid was found by XRD analysis.

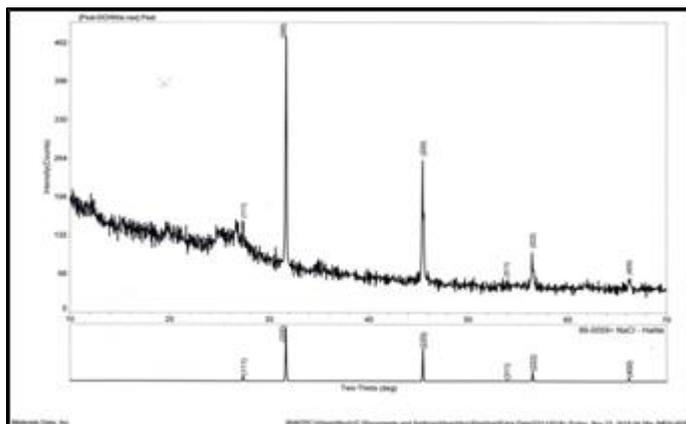


Figure 3 XRD diffractogram of the extracted humic acid from peat

The SEM micrograph of the extracted HA is shown in Figure 4. Some individual aggregates of HA particles were observed in the extracted HA. The dark shadow in SEM images was caused by thickness of HA particles.

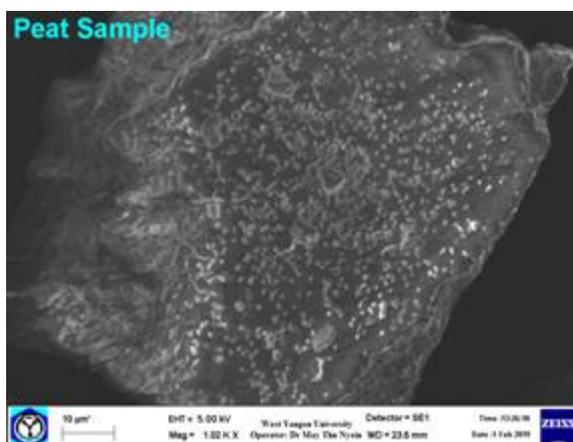


Figure 4 SEM micrograph of the extracted humic acid from peat

Thermal gravimetric analysis of the

The TG-DTA thermogram of extracted HA is shown in Figure 5. This figure depicts the onset temperature and decomposition temperature of humic acid. According to the TG-DTA analysis, the nature of decomposition such as the release of free water as well as the liberation of volatile materials and combustion were found between 40 °C and 600 °C. The exothermic peak was clearly observed in the TG-DTA thermogram, which may be due to decomposition of specimen.

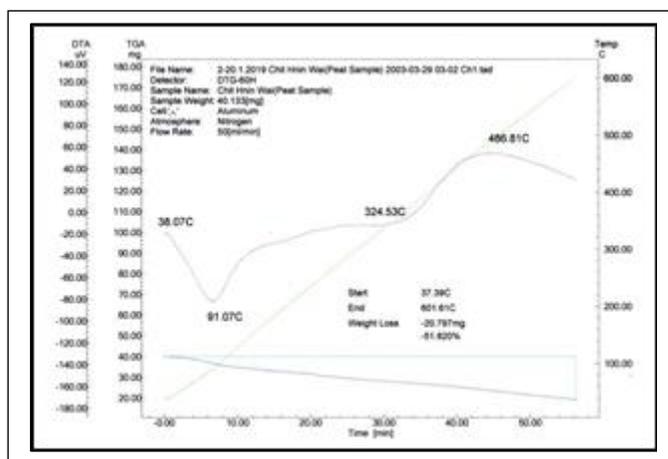


Figure 5 TG-DTA thermogram of the extracted humic acid from peat

Characterization of Humic-Chitosan Composites

Humic-chitosan composites in three different weight ratios: 1:1, 1:2 and 2:1 were characterized by modern techniques such as FT IR, XRD, SEM and TG-DTA analysis.

Comparison between FT IR spectra of three different weight ratios of humic-chitosan composite is shown in Figure 6. In this spectra, all of the humic-chitosan composite consist of broad absorption band in the range of 3000 to 3500 cm^{-1} which is attributed to O-H stretching vibrations and around 3200 cm^{-1} to vibration of N-H. The stretching vibrations of methylene C-H occur at around 2800 cm^{-1} and the absorption peak at 1550 cm^{-1} corresponds to the N-H bending vibrations. The amide II band is used as the characteristic band of N-acetylation.

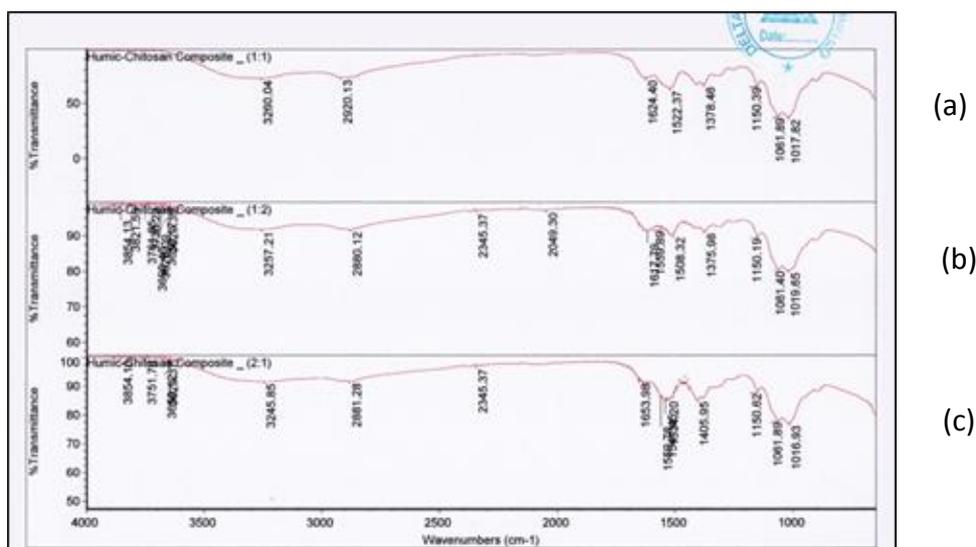


Figure 6 Comparison between FT IR spectra of three different weight ratios of humic-chitosan composites

(a) Humic-chitosan composite (1:1)

(b) Humic-chitosan composite (1:2)

(c) Humic-chitosan composite (2:1)

The XRD diffractograms of three different weight ratios of humic-chitosan composite [(1:1), (1:2) and (2:1)] are shown in Figure 7. The amorphous like nature of humic-chitosan composites were found by XRD analysis.

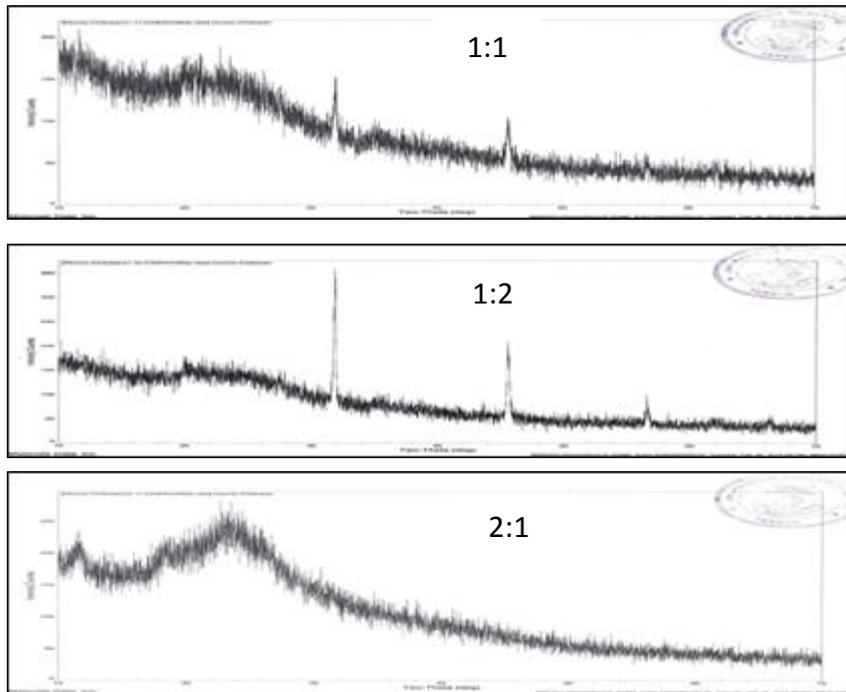


Figure 7 Comparison of XRD diffractograms of three different weight ratios of humic-chitosan composite [(1:1), (1:2) and (2:1)]

According to Figures 8, 9 and 10, the surface morphology of three different weight ratios of humic-chitosan composite can be seen. Among them, the morphology of humic-chitosan composite (1:1) has smoother surface than the other two composites. This means that the composition of HA to chitosan (1:1) is a better composition than the other ratios.

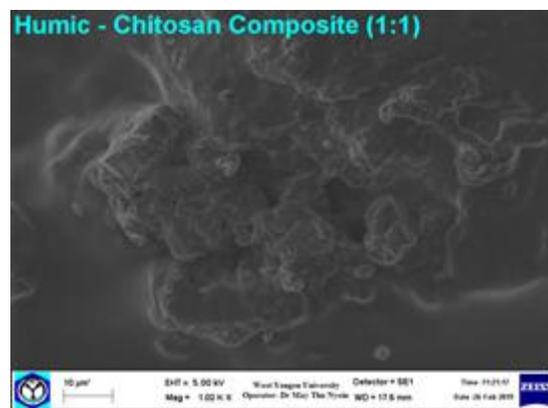


Figure 8 SEM micrograph of humic-chitosan composite (1:1)

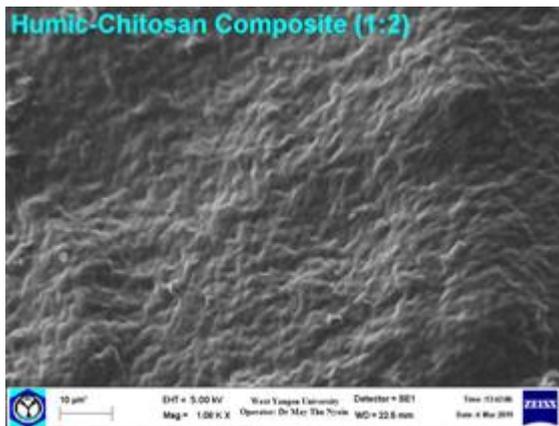


Figure 9 SEM micrograph of humic-chitosan composite (1:2)

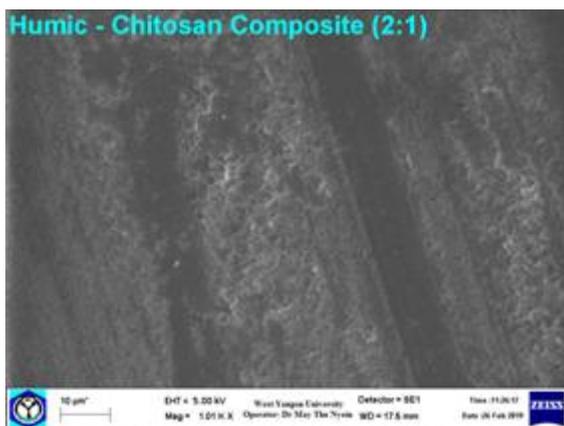


Figure 10 SEM micrograph of humic-chitosan composite (2:1)

Studying on the Figures 11, 12 and 13, the percent weight loss of three different ratios of humic-chitosan composite can be investigated. However, the percent weight loss of humic-chitosan composite (1:1) is more stable than the other composites.

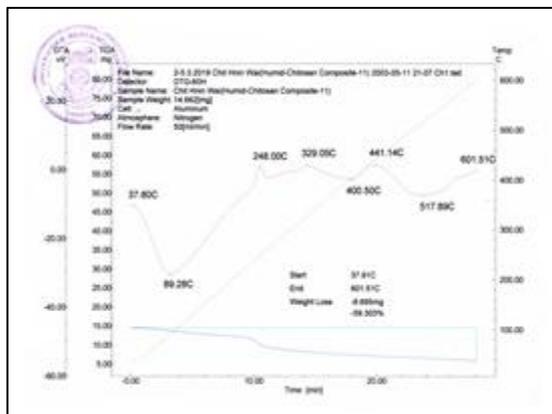


Figure 11 TG-DTA thermogram of humic-chitosan composite(1:1)

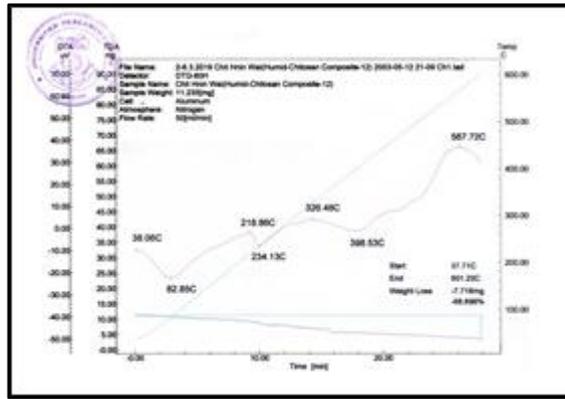


Figure 12 TG-DTA thermogram of humic-chitosan composite(1:2)

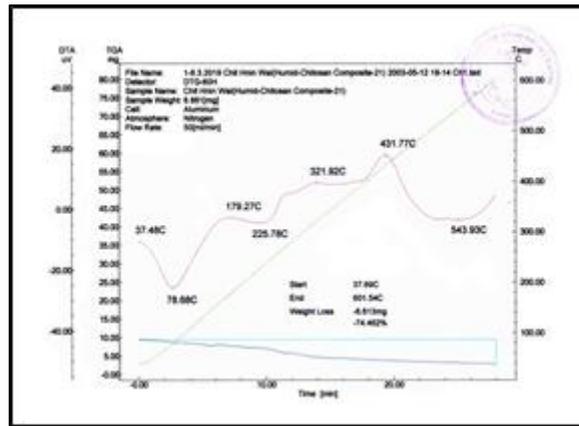


Figure 13 TG-DTA thermogram of humic-chitosan composite(2:1)

Calibration of the Dye Solution

According to Figure 14, the maximum wavelength of the dye solution is 620 nm. Figure 15 shows the standard curve of the dye solution by using maximum wavelength of 620 nm.

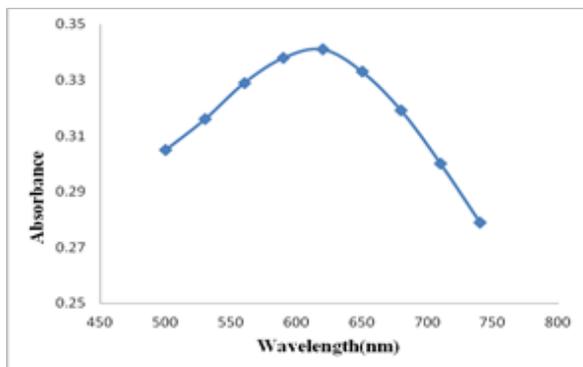


Figure 14 Maximum wavelength of the dye solution

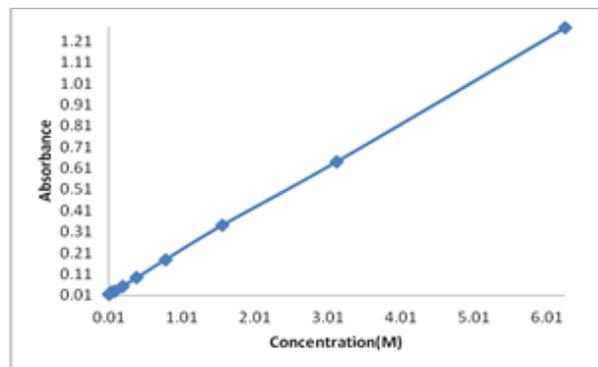


Figure 15 Calibration curve of the dye solution

Application of Humic Acid and Humic-Chitosan Composite in Removal Rates of Sulphur Black Dyes from Aqueous Solution

Before the comparison of the removal rates of sulphur black dye from aqueous solution between HA only and humic-chitosan composite, the composition ratios of three different weights of humic-chitosan composite were compared. Among them, the smoothest morphology and the highest thermal stability of humic-chitosan composite (1:1) was selected.

Figures 16 and 17 mention about the concentration vs time factor of HA only and humic-chitosan composite for the removal rate of dye solution. From these figures, the removal rate of HA only is better than the humic-chitosan composite (1:1).

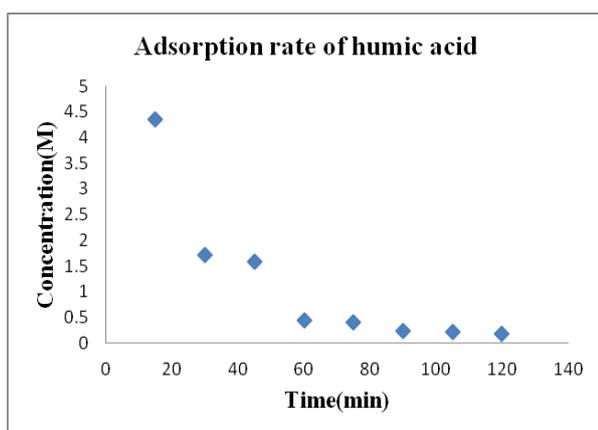


Figure 16 Adsorption rate of humic acid

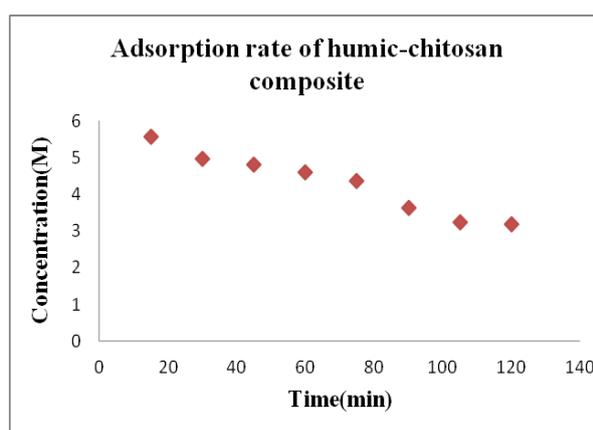


Figure 17 Adsorption rate of humic-chitosan composite

According to Table 1 and Figure 18, the sorption capacity for colour removal of sulphur black dye solution by HA is better than humic-chitosan composite (1:1).

Table 1 Sorption Capacities for Colour Removal of Sulphur Black Dye Solution by HA and Humic-Chitosan Composite

Time(min)	Humic acid(HA) %	Humic-Chitosan Composite %
15	30.40	10.72
30	72.48	20.64
45	74.72	23.04
60	92.96	26.4
75	93.44	30.24
90	96.16	41.76
105	96.64	48.00
120	97.12	49.12

Conditions

Initial concentration of dye solution = $6.2500 \times 10^{-4} \text{M}$

Dosage = 2 gL^{-1}

Temperature = ambient temperature

Stirring rate = 100 rpm

Contact time = 15 min

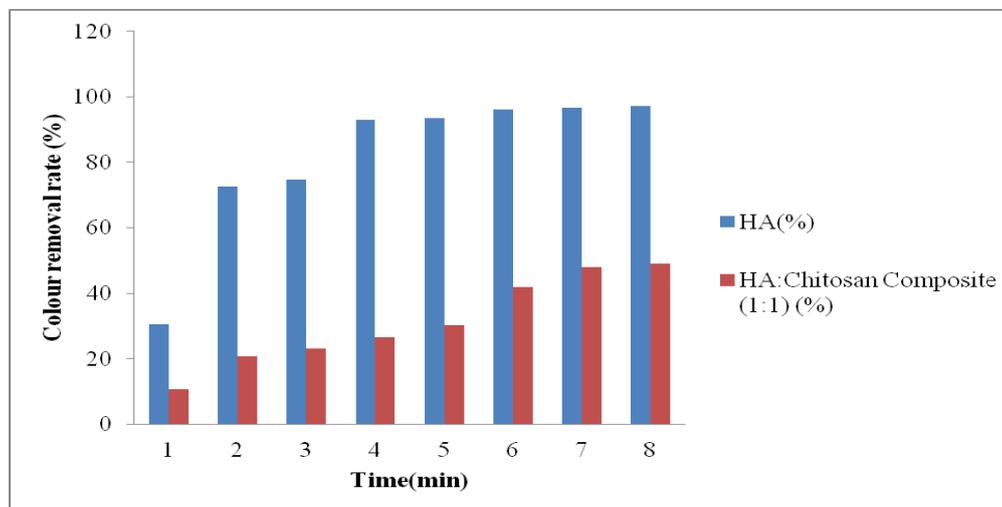


Figure 18 Sorption capacities for colour removal of sulphur black dye solution by HA and humic-chitosan composite

Conclusion

In this research work, HA was extracted from peat collected from Moeswe Village, Oattara Thiri Township, Naypyitaw, Myanmar by alkali extraction method. From the spectroscopic analysis, it was found that HA is composed of aliphatic and hydrophobic hydrocarbons. Observations from TG-DTA analysis indicated that the presence of fossilized organic carbon, HA compound was decomposed about 51.8% up to 600°C . According to SEM analysis, the morphology of extracted HA possesses the voids and aggregate nature. The extracted HA can be effectively used in the removal of sulphur black dye which has been widely used in the aqueous solution of textile industry in Myitnge Town, Amarapura Township, Mandalay, Myanmar. Moreover, the three different weight ratios of HA-chitosan composite [(1:1), (1:2) and (2:1)] were also prepared. According to SEM and TG-DTA analysis, HA:chitosan composite (1:1) is suitable one for the application of the removal of sulphur black dye from aqueous solution. Furthermore, the comparison of dyes removal rate percent of HA only and HA:chitosan composites, HA can influence the more effective removal rate than the other composites.

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