# Synthesis Of Charcoal-Chitosan Composite and Its Application As A Naphthol Blue Black Dye Adsorbent

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**Abstract.** The charcoal-chitosan composites have been synthesized, followed by adsorption tests on naphthol blue black (NBB) dye. This study aimed to investigate the properties and effect of chitosan dosage in producing charcoal-chitosan composite, specifically focusing on its ability to adsorb NBB. Charcoal-chitosan composites with different ratio variations were analyzed for their ability to adsorb NBB at variable contact time, pH, and initial concentration. The FTIR characterization results demonstrated the interaction between chitosan and activated charcoal in the charcoal-chitosan composite. This was confirmed by the overlapping absorption of −NH and −OH functional groups at a wave number 3354.18 cm-1 and absorption of C=O functional group at a wave number of 1647.52 cm-1. Increasing the dosage of chitosan leads to a higher water content percentage in the composite, while simultaneously reducing the stability of the composite in acidic pH. The experimental findings indicated that the adsorption process of NBB reached equilibrium after 60 minutes of contact time, with the most favorable conditions observed at a pH of 3.40. The charcoal-chitosan composites with ratios of 8:2, 8:4, 8:6, and 8:8 exhibited adsorption capacities of 42.16 mg/g, 39.60 mg/g, 34.68 mg/g, and 31.5 mg/g, respectively, towards NBB.

**Keywords:** adsorption, charcoal-chitosan composite, naphthol blue black (NBB)

## INTRODUCTION

Synthetic dyes are extensively utilized in diverse sectors, especially in the textile industry. In addition, synthetic dyes are also used in the food and beverage industry [1]. These dyes are widely used by home industries that discharge waste into the environment without prior waste treatment. The detrimental effects of synthetic dyes on both human health and the environment are significant [2]. Waste-containing dyes are usually in a liquid state. As an illustration, the liquid waste generated during batik production is typically alkaline and contains significant organic matter [3]. Batik production produces waste with a concentrated color and emits a pungent odor [4]. Before being discharged into the environment, it is necessary to treat the waste first. Adsorption is the most often employed technique for liquid waste treatment due to its user-friendly nature and cost-effectiveness. Adsorption is the process of a substance being absorbed onto the surface of an adsorbent material [5][6].

Adsorbents used in adsorption are usually made from inorganic minerals [7][8], synthetic organic materials [9], and natural organic materials[10] [11]. Chitosan and charcoal are commonly employed as natural adsorbents [12]. Charcoal is utilized as an adsorbent due to its extensive surface area resulting from an abundance of micropores, enabling it to exhibit significant adsorption capacity and leading to capillary symptoms [13]. Utomo et al. found that the absorption of activated carbon from sugarcane bagasse on naphthol yellow dye in liquid waste had a relatively high adsorption capacity of 93.55% [14]. Despite its potential as an effective adsorbent, the adsorption ability of charcoal has the disadvantage that the adsorption properties of dyes occur physisorption by relying on Van der Waals interactions and π⎯π stacking, so it is easily released again[15][16]. Therefore, charcoal needs to be modified to increase its adsorption capacity. One of the modifications that can be done is by utilizing chitosan. The selection of chitosan as a material for modifying charcoal was based on its abundance of active functional groups, specifically amine groups and hydroxyl groups [17]. The addition of chitosan to the charcoal is expected to enrich the active functional groups in the resulting composite, to maintain the adsorbed dye through chemisorption. Based on these reasons, it is necessary to conduct research on the modification of charcoal with the addition of chitosan with various variations in the ratio of chitosan addition, and also study its ability to adsorb naphthol blue black dye.

## EXPERIMENTAL

## Materials and Instrumentation

The materials were chitosan powder from shrimp shells (GMP) (medium molecular weight, DD 85%), activated charcoal (p.a Merck) (with particle size <100 mesh), 100% acetic acid (E. Merck), NaOH crystals, concentrated HCl, naphthol blue black (NBB) (Aldrich), distilled water, and Whatman Filter paper No. 42. The tools used were analytical balance (Ohaus), oven (Thermologic), glassware (pyrex), shaker (Wise Shake), and pH meter (DrGray). The instruments used for analysis were a UV-Vis spectrophotometer (Genesys 10v) and an FTIR spectrophotometer (Platinum Atr Bruker).



### Preparation of Charcoal-Chitosan Composite

Charcoal-chitosan composites were synthesized by combining 8 grams of charcoal with 200 mL of chitosan solution at different concentrations (1%, 2%, 3%, and 4%). The dosage variations were obtained with a weight ratio of charcoal:chitosan of 8:2, 8:4, 8:6, and 8:8 . The charcoal in the chitosan solution was stirred until homogeneous, after which 200 mL of 0.5 M NaOH solution was slowly added while stirring quickly. The charcoal-chitosan gel was left for 24 hours, filtered using Whatman paper No. 42, and washed until neutral. The charcoal-chitosan gel was then dried using an oven at 60ºC until constant weight. The resulting charcoal-chitosan composite was then analyzed for functional group characteristics using an FTIR spectrophotometer, moisture content analysis using the gravimetric method, and stability analysis at acidic pH.



### Effect Of Contact Time On The Ability Of Charcoal-Chitosan Composite to Adsorb Naphthol Blue Black Dye

A 0.5 gram of charcoal-chitosan composite was contacted with 100 mL of 50 ppm NBB solution. The mixture was stirred using a shaker with varying contact times of 5, 10, 30, 60, and 120 minutes at 120 rpm. The charcoal-chitosan composite and filtrate were separated using Whatman filter paper No. 42. The concentration of the remaining dye in the filtrate was measured for absorbance using a UV-Vis spectrophotometer.

### Effect Of pH on the Ability of Charcoal-Chitosan Composite to Adsorb Naphthol Blue Black Dye

A total of 0.5 grams of the charcoal-chitosan composite was contacted with 100 mL of NBB solution at various concentrations of 50, 100, 150, 200, and 250 ppm, whose pH had been adjusted to acidic, neutral, and basic. The mixture was shaken using a shaker for the optimum contact time at 120 rpm. The charcoal-chitosan composite and filtrate were separated using Whatman filter paper No. 42. The concentration of the remaining dye in the filtrate was measured for absorbance using a UV-Vis spectrophotometer.

### Effect Of Initial Concentration on The Ability of The Charcoal-Chitosan Composite to Adsorb Naphthol Blue Black Dye

A total of 0.5 grams of the charcoal-chitosan composite was contacted with 100 mL of NBB solution at various initial concentrations of 50, 100, 150, 200, and 250 ppm, whose pH had been adjusted to the optimum pH. The mixture was shaken using a shaker for the optimum contact time at 120 rpm. The charcoal-chitosan composite and filtrate were separated using Whatman filter paper No. 42. The concentration of the remaining dye in the filtrate was measured for absorbance using a UV-Vis spectrophotometer.

**RESULTS AND DISCUSSION**

**Preparation and Characterization of Charcoal-Chitosan Composite**

Charcoal-chitosan composites were made with several variations in the weight ratio of charcoal-chitosan, namely 8:2, 8:4, 8:6, and 8:8. The addition of a higher dose of chitosan results in the formation of larger and more agglomerated charcoal-chitosan composite particles with a more uneven surface, as observed through their visible physical properties. Fig. 1 illustrates this.

|  |  |  |  |
| --- | --- | --- | --- |
| WhatsApp Image 2024-01-09 at 11  (a) | WhatsApp Image 2024-01-09 at 11  (b) | WhatsApp Image 2024-01-09 at 11  (c) | WhatsApp Image 2024-01-09 at 11  (d) |

FIGURE 1. Charcoal-chitosan composite with ratios of (a) 8:2, (b) 8:4, (c) 8:6, and (d) 8:8.

**Characterization Of Functional Groups Of Charcoal-Chitosan Composite Using FTIR Spectroscopy**

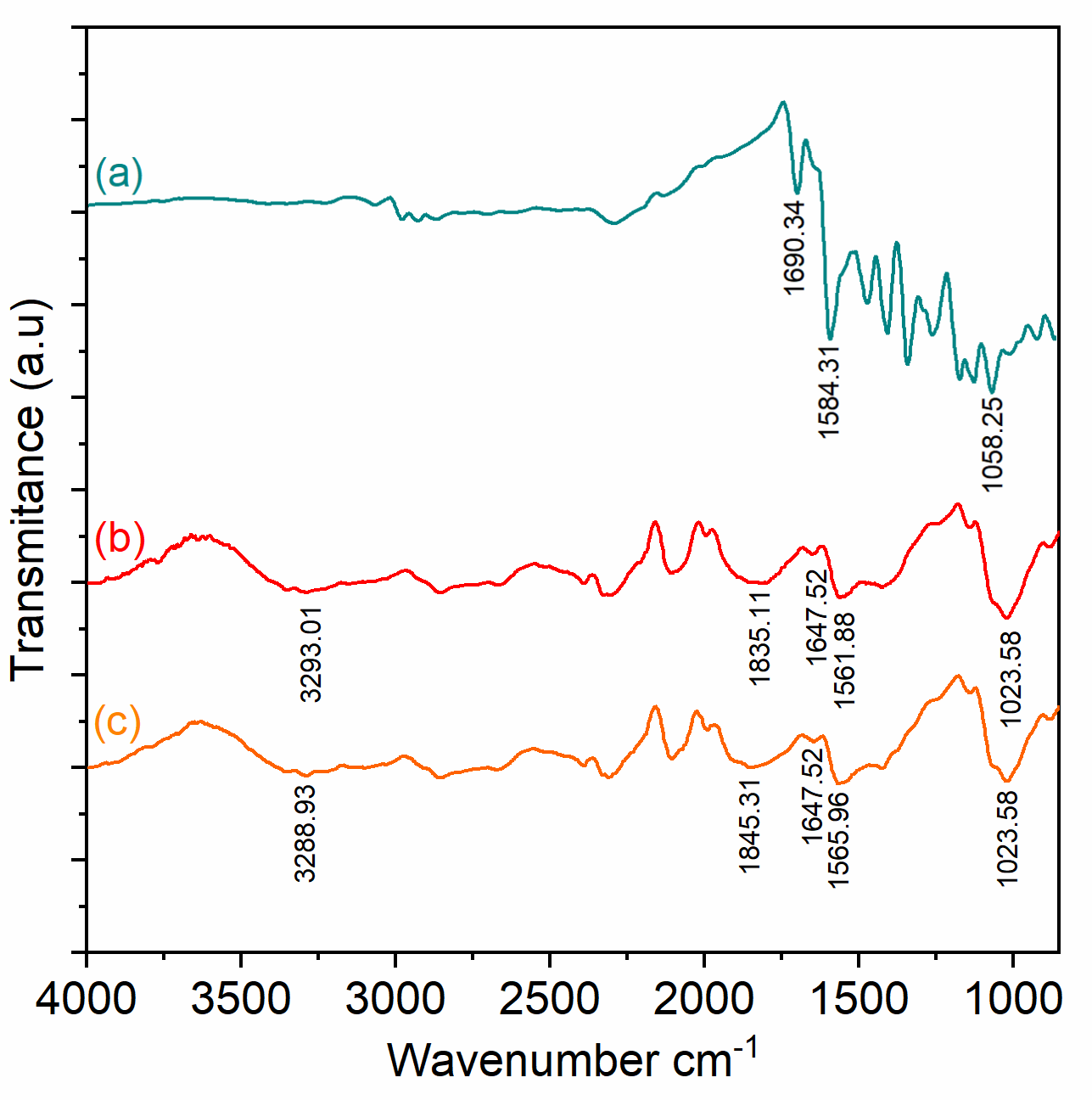




FIGURE 2. IR spectrum of: (a) activated carbon, (b) chitosan, (c) charcoal-chitosan composite.

Absorption at a wave number of 1690.34 cm-1 appears in activated charcoal and charcoal-chitosan composites but does not appear in chitosan because chitosan does not have a C=O group. According to Mentari & Maulina [18], the presence of the C=O group in charcoal creates polarity, making it a suitable adsorbent. C=O group absorption also appeared in the charcoal-chitosan composite but experienced a shift with a smaller intensity, namely at a wave number of 1647.52 cm-1. In the chitosan spectrum, the −NH group absorption appears, which overlaps with –OH at a wave number 3293.01 cm-1. This absorption also appears in the charcoal-chitosan composite a wave number 3288.93 cm-1, but the intensity decreases. This absorption does not appear in the FTIR spectrum of charcoal. The appearance of C=O (carbonyl), −NH (amine), and −OH (hydroxyl) groups on the composite shows the integration of charcoal and chitosan. This integration can increase the surface activity of the composite and allow various mechanisms of binding dye molecules including physical adsorption and chemical interactions.

**Moisture Content**

FIGURE 3. Moisture content at various ratios of charcoal-chitosan composite

Fig. 3 demonstrates a positive correlation between the dosage of chitosan and the water content in the composite. This indicates that increasing the dosage of chitosan in the composite leads to higher moisture content. This is due to the presence of amine (-NH2) and hydroxyl (-OH) functional groups in chitosan which have a strong ability to bind water molecules. According to Ariyani et al., chitosan easily absorbs water vapor in the surrounding air because it has amine, N-acetyl, and polar hydroxyl groups [19]. All the ratios of the charcoal-chitosan composite satisfy the criteria specified in SNI 06-3730-1995 regarding the quality of moisture content. High-quality activated charcoal typically contains a moisture level below 15%.

**Stability Of Charcoal-Chitosan Composite At Acidic pH**

Stability analysis of composites under acidic conditions is important because protonation and deprotonation processes can affect their structure. Instability can cause parts of the composite to dissolve or undergo structural degradation, especially due to the protonation of chitosan. If the composite becomes unstable, its structural integrity may be lost, which will reduce the adsorption efficiency. Therefore, it is important to optimize the chitosan content to achieve a balance between maintaining stability and maximizing adsorption efficiency.

FIGURE 4. Stability of charcoal-chitosan composite in acid solution

Fig. 4 demonstrates a negative correlation between the concentration of chitosan added and the stability of the charcoal-chitosan composite. The decreased stability of the charcoal-chitosan composite may result from the protonation of certain chitosan -NH2 groups under acidic conditions, leading to the dissolution of certain portions of the chitosan. According to a study by Aranaz et al, chitosan tends to become protonated and break down in acidic conditions [20]. This study shows that increasing the dosage of chitosan can reduce the stability of the composite under acidic conditions, which may limit its use in real applications to treat acidic wastewater.

### Effect Of Contact Time On The Ability Of Charcoal-Chitosan Composite To Adsorb Naphthol Blue Black Dye

To achieve optimal adsorption performance, it is important to adjust the charcoal-chitosan ratio such that the contact time is not too long and the adsorption capacity remains high. A ratio that is too high or low can affect this balance. Fig. 5 shows a positive correlation between the contact time and the NBB adsorption percentage until the equilibrium time is reached. In the charcoal-chitosan 8:2 and charcoal-chitosan 8:6 composites, adsorption equilibrium was reached at a contact time of 30 minutes. In contrast, in the charcoal-chitosan 8:4 and charcoal-chitosan 8:8, adsorption equilibrium was reached at 60 minutes.

FIGURE 5. Relationship curve between contact time and adsorption percentage of NBB dye on charcoal-chitosan composite

Once adsorption equilibrium is achieved, the curve becomes linear. This result indicates that the interaction of the composite and NBB dye occurs chemically, such as interaction through hydrogen bonding and electrostatic interaction, so that it is not easily detached due to the collision between the adsorbent and water during stirring. After the equilibrium time is achieved, there is no significant increase in the adsorption process. This is because the surface of the adsorbent becomes saturated with the dye, forming a layer that covers the adsorbent layer [21]. The addition of chitosan dosage causes the composite to take longer to reach adsorption equilibrium and reduce the adsorption capacity. This can be caused by changes in the composite structure such as reduced porosity and decreased availability of active sites due to increased interactions between chitosan molecules and water or other molecules.

**Effect Of pH On The Ability Of The Charcoal-Chitosan Composite To Adsorb Naphthol Blue Black Dye**

Based on Fig. 6, the highest dye adsorption ability occurs at acidic pH, and the lowest occurs at alkaline pH. NBB dye is an anion dye that interacts with the amine groups in chitosan, which are polycations at acidic pH. In addition, chitosan undergoes expansion at acidic pH, which exposes the active side and enhances its adsorption capacity [22].

FIGURE 6. Effect of pH on the adsorption ability of NBB on charcoal-chitosan composites.

**Effect Of Initial Concentration On The Ability Of The Charcoal-Chitosan Composite To Adsorb Naphthol Blue Black Dye**

FIGURE 7. Relationship between initial concentration and adsorption ability at equilibrium (mg/g).

Fig. 7 demonstrates a positive correlation between the starting concentration and the amount of NBB adsorbed at equilibrium. In this study, maximum adsorption occurred at an initial concentration of 200 ppm—the composite ratio of charcoal-chitosan 8:2 yields a 42.16 mg/g value. Similarly, the composite ratio of charcoal-chitosan 8:4 yields a 39.60 mg/g value. The composite ratio of charcoal-chitosan 8:6 yields a value of 34.68 mg/g, while the composite ratio of charcoal-chitosan 8:8 yields a value of 31.57 mg/g. A higher initial concentration causes a decrease in the amount of NBB adsorbed. This phenomenon is believed to occur due to the excessive initial concentration, resulting in a high frequency of collisions among particles. These collisions lead to the adsorbate being densely packed and, hence, easily released. Based on Fig. 7, increasing the dosage of chitosan in the composite reduces the adsorption capacity towards NBB dye. Although chitosan increases the number of active groups, an excessive amount seems to limit the adsorption efficiency, this could be due to the closure of the charcoal pores by the chitosan layer. The decrease in adsorption capacity could also be due to the fact that increasing the dosage led to an increase in moisture content. High moisture content causes water molecules to occupy the adsorption active sites on the composite surface which can inhibit the interaction between the dye molecules and the composite, thus reducing the adsorption capacity.

**CONCLUSION**

The appearance of a peak at wave number 3288 cm-1 and 1647.52 cm-1 in the FTIR spectra of the composite indicates the formation of a charcoal-chitosan composite. The higher the dose of chitosan added, the higher the water content and the lower the stability of the composite in acidic pH. In the adsorption ability test of charcoal-chitosan composite on NBB dye, adsorption equilibrium was reached at a contact time of 30 minutes, and the optimum occurred at acidic pH. The maximum adsorption ability of charcoal-chitosan composites with ratios of 8:2, 8:4, 8:6, and 8:8 were 42.16 mg/g, 39.60 mg/g, 34.68 mg/g, and 31.5 mg/g, respectively.

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