

Synthesis and Performance Evaluation of Magnetized Modified Coal Fly Ash as Adsorbent for Naphthol Blue Black Dye Removal from Synthetic Dye Wastewater

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Abstract

Due to its harmful environmental impact, dye removal from wastewater has become a major concern in the textile industry. This research focuses on the adsorption of naphthol blue black (NBB) dye by synthesizing coal fly ash with alkali (sodium hydroxide solution) and Fe_3O_4 (magnetite) to accelerate the separation of dyes from aqueous solutions. Magnetized modified coal fly ash (MMCFA) was characterized by XRF, SEM, and FTIR analysis. Batch experiments were carried out to study the effect of pH, initial concentration, and contact time on dye removal efficiency. The results showed that the adsorption of NBB dye reached the optimum condition at the initial concentration of 100 mg/L with 6 pH and 120 minutes and contact time. The ability of MMCFA to adsorb NBB dye was higher than that of sieved coal fly ash (SCFA) and modified coal fly ash (MCFA). Adding alkali and Fe_3O_4 was proven to increase the adsorption ability of SCFA. The percentage of NBB dye that was adsorbed by MMCFA, MCFA, and SCFA at optimum conditions were 96.39%, 89.83%, and 89.33%, respectively.

Keywords: adsorption; alkali; coal fly ash; magnetite; naphthol blue black

1. Introduction

In the textile industry, synthetic dyes are used in most dyeing processes. Unlike natural dyes, synthetic dyes are cheap and easy to get (Agustina et al., 2011). Most textile industries use azo compounds, the largest group of stable synthetic dyes, in the dyeing process (Ferkous, Hamdaoui, & Merouani, 2015). Naphthol blue black (NBB) is one of the synthetic dyes in the azo group. This substance has frequently been used in the textile industry to color fabrics made of wool, nylon, silk, and batik. If NBB dye exceeds the specified limit concentrations, it cannot naturally decompose. Furthermore, it is carcinogenic, and its mutagenic properties badly impact the environment. (Ferkous, Hamdaoui, & Merouani, 2015). Therefore, NBB dye wastewater should be treated before being discharged into water bodies.

Adsorption is one of the wastewater treatment methods that has proven to be the most effective because the process is relatively simple and cheap (Lubis, Sheilatina, Nika, & Putra, 2016). Materials that can be used as adsorbents include activated carbon, polymeric materials, and composites. Activated carbon is widely used as an adsorbent. This is presumably because the presence of functional groups and the surface area of the material

can affect the adsorption capacity. However, the material is considered relatively expensive, although it can be regenerated (Astuti, Chafidz, Al-Fateesh, & Fakeeha, 2021).

Coal fly ash is a by-product of coal combustion and the form of powder particles in the flue gas used as an energy source in power plants. The abundant availability of CFA impacts the cheap price of the material (Jain, Dwivedi, & Waskle, 2016). Around 40% of CFA is processed into building materials such as bricks and paving; the rest is only piled up in landfills. Disposal of large amounts of CFA can cause air pollution and soil degradation because they contain toxic elements. The toxic chemical elements of CFA include Pb, Hg, Cd, Ba, Ge, Ce, and U (Missengue-Na-Moutoula, 2016). CFA's characteristics are good adsorption capacity, non-toxicity, hydrophilicity, and susceptibility to biodegradation (Dash, Chaudhuri, Gupta, & Nair, 2018). CFA is composed of the main components of silica oxide (SiO_2) and aluminum trioxide (Al_2O_3), which has an active site and is an unburned carbon mesoporous material so that it has the potential as an adsorbent (Astuti, Chafidz, Al-Fateesh, & Fakeeha, 2021). CFA synthesis was carried out with sodium hydroxide modifications to increase the pore size and adsorption capacity (Astuti, Chafidz, Al-Fateesh, & Fakeeha, 2021) (Purbasari, Ariyanti, Sumardiono, Shofa & Manullang, 2022). The use of CFA as an adsorbent has

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problems in the water separation process because the particle size is too small. If the separation process is carried out by centrifugation, it will require high cost and energy consumption. An alternative is needed to overcome this problem. One of which is the addition of a magnetic adsorbent (Harja, et al., 2021).

Fe_3O_4 (magnetite) nanoparticles are used to adsorb synthesis because of their beneficial properties. Those are surface functional groups, magnetic responsiveness, biodegradability, and biocompatibility (Harja et al., 2021). Synthesis of Fe_3O_4 in CFA as an adsorbent in wastewater treatment is chosen because it has several advantages, such as the maximal number of active sites, high porosity, and high surface area (Harja et al., 2021). This method is economical as the Fe compound attached to the surface of the adsorbent is rapidly separated from the solution without requiring additional steps such as filtration or centrifugation. In this study, CFA as an adsorbent for NBB dyes from aqueous solutions was modified with sodium hydroxide and Fe_3O_4 to increase the adsorption capacity and accelerate the adsorbent separation. We investigated the effects of pH, contact time, and initial concentration on NBB removal.

2. Materials and Method

Materials used Naphthol Blue Black Dye Solution. Laboratory grade naphthol blue black (NBB) is a diazo anionic aromatic organic compound with the molecular formula $\text{C}_{22}\text{H}_{14}\text{N}_6\text{Na}_2\text{O}_9\text{S}_2$; supplied in powder form by Rajawali. NBB was used without further purification to prepare a synthetic aqueous solution used as adsorbate. A stock solution was prepared by dissolving 0.5 g of NBB in 1000 ml of distilled water.

Coal fly ash (CFA) was obtained from a power plant in East Java, Indonesia. The CFA was sieved with a standard sieve of 100 mesh. The CFA was washed using

distilled water to remove contaminants in the material and then dried using an oven at 110 °C for 4 hours, obtaining sieved-CFA (SCFA). For modified-CFA (MCFA), 50 g of SCFA was refluxed with 300 ml of 2 M NaOH (Pro Analysis, Merck) solution at 60 °C for 2 hours and stirred occasionally. The solution is then filtered using Whatman filter paper No 5. Furthermore, the filtrate was washed using distilled water to pH value of ± 7 , and dried using an oven at 110 °C for 3 hours. One gram of Fe_3O_4 (Technical, purity of 99,9%) was mixed with 9 g of MCFA in a planetary ball mill for 4 hours at a stirring rate of 300 rpm and then washed with distilled water until the pH is neutral and dried at 60 °C for 24 hours. The dried MCFA were sieved using a standard 100 mesh sieve to obtain magnetic modified CFA (MMCFA).

Three samples of SCFA, MCFA, and MMCFA were used as dye adsorbents and characterized. The chemical composition contained in the samples was analyzed using X-Ray Fluorescence (XRF) with equipment of ZSX Primus II Rigaku. A scanning electron microscope (SEM) using JED-2300 JEOL instrument was used to determine the morphological characteristics of the pore surface due to the influence of the addition of alkali and magnetite compounds. Functional group analysis was performed using Fourier Transform Infrared Spectroscopy (FTIR) (Nicolet iS10 Thermo Scientific) at a wavelength of $4000\text{--}400\text{ cm}^{-1}$ using the KBr method.

Adsorption experiments were performed using 0.6 g of SCFA, MCFA, and MMCFA, respectively, to 50 ml of NBB dye solution in 100 ml Erlenmeyer stirring rate of 120 rpm with variations of pH, contact time, and initial concentration. The pH variation was carried out by adding 0.1 N HCl or NaOH solution to the NBB dye solution with an initial concentration of 100 mg/L. After 4 hours, the solution was filtered and analyzed using a UV-VIS spectrophotometer (Shimadzu UV 1601). Variation of

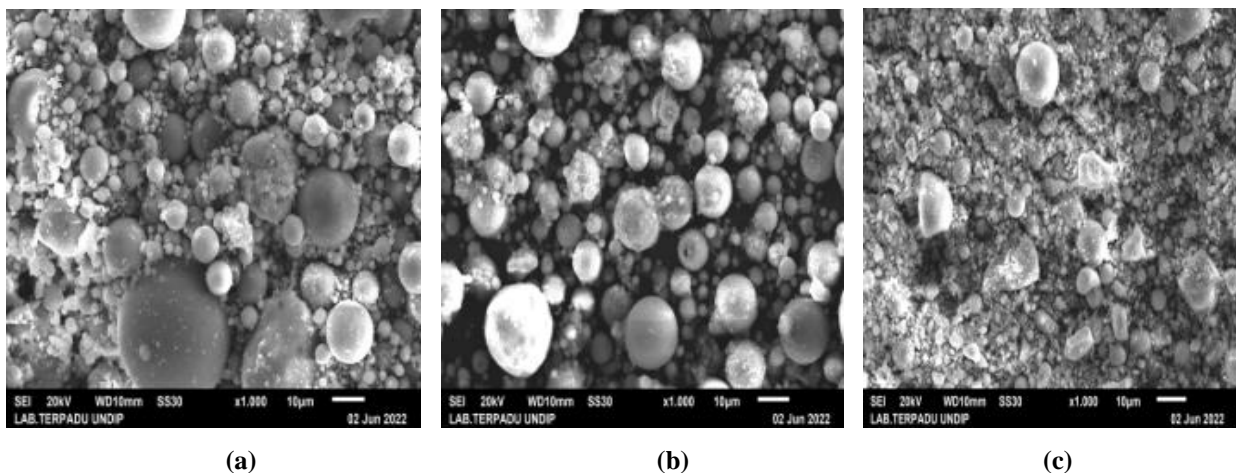


Figure 1. SEM micrographs of (a) SCFA: (b) MCFA: and (c) MMCFA

Table 1. XRF analysis results

| Component | SCFA | MCFA | MMCFA |
|--------------------------------|------------|-------|-------|
| | Weight (%) | | |
| MgO | 1.56 | 1.93 | 1.32 |
| Al ₂ O ₃ | 10.00 | 11.90 | 10.50 |
| SiO ₂ | 18.80 | 22.80 | 22.20 |
| CaO | 9.48 | 9.94 | 9.51 |
| Fe ₂ O ₃ | 9.06 | 10.60 | 18.20 |
| K ₂ O | 0.93 | 1.04 | 1.01 |
| TiO ₂ | 0.76 | 0.91 | 0.83 |
| SO ₃ | 0.38 | 0.12 | 0.18 |
| P ₂ O ₅ | 0.15 | 0.15 | 0.13 |
| MnO | 0.12 | 0.13 | 0.13 |

contact time was conducted at the initial concentration of 100 mg/L and pH of 6. Meanwhile, a variation of the initial concentration was held at pH of 6 for 4 hours. The total removal efficiency of NBB dye solution was calculated by Equation 1.

$$\text{NBB adsorbed (\%)} = \frac{(c_0 - c_t)}{c_0} \times 100 \quad (1)$$

C_0 is the initial concentration of NBB dye (mg/L), and C_t is the concentration of NBB dye at equilibrium time (mg/L).

3. Results and Discussion

3.1 Characterization of Adsorbents.

The chemical composition of coal fly ash was determined by XRF characterization (Table 1). The major component of coal fly ash was Si, Al, and Fe. Coal fly ash was composed of minerals containing several oxides in the crystalline phase, i.e., mullite and quartz (SiO₂) (3Al₂O₃.2SiO₂(Astuti et al., 2020). The result of XRF characterization on SCFA contained 18.8 % SiO₂, 10.0 % Al₂O₃, and 9.06 % Fe₂O₃. Meanwhile, the percentage of SiO₂, Al₂O₃, and Fe₂O₃ in the MMCFA increased to 10.5%, 22.2 %, and 18.2 %, respectively. The significant increase of Fe in MMCFA may be due to the modification of the addition of Fe₃O₄, which caused Fe to attach to the adsorbent pores.

Surface morphology analysis of SCFA, MCFA, and MMCFA was performed using a scanning electron microscope (SEM). The operating conditions were set at 20 kV voltage with 1000x magnification, as shown in Figure 1. SCFA (Figure 1a) had a spherical shape with a smooth surface. After adding NaOH solution, MCFA (Figure 1b) had a rough and porous surface. This indicates that adding NaOH solution as an activator can open the

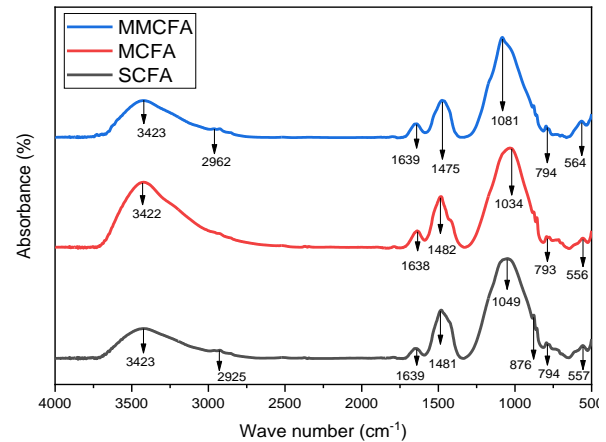


Figure 2. FTIR spectra of (a) SCFA; (b) MCFA; and (c) MMCFA

structure and enlarge the pore volume (Astuti & Mahatmanti, 2010).

Meanwhile, MMCFA (Figure 1c) had a surface that looked more solid or denser due to the presence of Fe₃O₄. This was in accordance with the XRF results that showed the increase in iron oxide content in MMCFA.

FTIR analysis was carried out to identify the chemical structure on the surface of SCFA, MCFA, and MMCFA, which functioned as active sites for NBB dye adsorption. Figure 2 shows the similarity of the spectra for all samples with a wavelength of 4000-400 cm⁻¹. Absorption band 3570-3200 cm⁻¹ with a peak of 3423 cm⁻¹ contains -OH the hydroxyl group of adsorbed water molecules on the surface (Coates, 2006). In addition, there is a silica SiO-H stretching group in the absorption band of 3700-3200 cm⁻¹ (Smidh, Bohm, & Schwanninger, 2011). The frequency wavelength of 2970-2950 cm⁻¹ with a peak of 2962 cm⁻¹ interprets the existence of an asymmetric C-H methyl group (-CH₃). The absorption band 2935-2915 cm⁻¹ with a peak of 2926 cm⁻¹ indicates the presence of a methylene C-H functional group asymmetric stretching vibration (Coates, 2006). The wavelength frequency of 1685-1630 cm⁻¹ with an absorption peak of 1639 cm⁻¹ has a C=O from the amide group (Smidh, Bohm, & Schwanninger, 2011). The peak observed at 1410-1490 cm⁻¹ are likely due to the C-O of the carbonate group (Coates, 2006). The Si(Al)-O-Si group is shown at an absorption peak around 1150-800 cm⁻¹(Karanac et al., 2018). The band at 794 cm⁻¹ indicates the presence of quartz minerals with symmetric Si-O functional groups (Jeyageetha & Kumar, 2013). While the peaks around 800-500 cm⁻¹ are represented on Si-O-Si and Al-O-Si symmetric stretching (Fauzi, Nuruddin, Malkawi, & Bakri, 2016). The absorption peak around 400-600 cm⁻¹

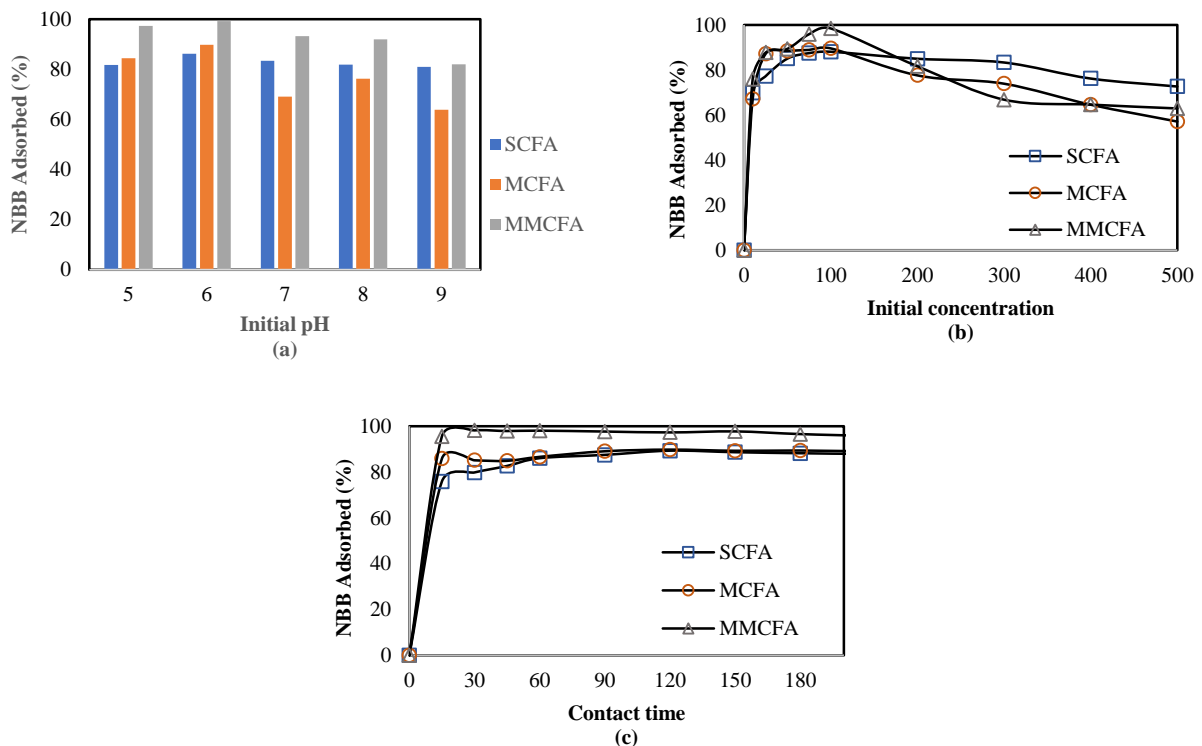


Figure 3. Effect of (a) pH; (b) contact time; and (c) initial concentration on the NBB dye removal by SCFA, MCFA, and MMCFA

represented Si-O/Al-O amorphous silica (Karanac et al., 2018). Furthermore, the peak at around 565 cm^{-1} represented Fe-O groups (Karanac et al., 2018). The highest intensity of this peak found in MMCFA came from the highest iron oxide content compared to SCFA and MCFA.

3.2 Performance Evaluation of Adsorbents.

SCFA, MCFA, and MMCFA were applied as NBB dye adsorbents from synthetic dye wastewater. The effects of pH, contact time, and initial concentration were investigated in this adsorption process. Solution pH affects surface charge and ionization of adsorbents (Astuti, Chafidz, Al-Fateesh, & Fakeeha, 2021).

The optimum adsorption efficiency was obtained at pH 6 with the ability to adsorb NBB dye by SCFA, MCFA, and MMCFA of 86.22%, 89.78%, and 99.17%, respectively, as shown in Figure 3a.

On the surface of metal oxides, hydroxides, such as Fe-OH have a charge when dispersed in the aqueous medium. This charge appears due to the amphoteric nature of the hydroxyl surface. It can be controlled using pH and ionic strength in the aqueous medium. Reaction on the surface of the Fe-OH sites with H^+ and OH^- ions can form positive (Fe-OH_2^+) and negative (Fe-O^-) surface charges. The Fe-OH surface is neutral at pH_{pzc} . When the pH is

lower than pH_{pzc} Fe_3O_4 ($\text{pH}_{\text{pzc}} \text{Fe}_3\text{O}_4 = 6.4$), the surface of Fe_3O_4 is positively charged because it is protonated, so it can react with anions (Maylani, Sulistyarningsih, & Kusumastuti, 2016). In an acidic solution, the hydroxyl group in the adsorbent would be protonated, so there is an electrostatic bond between the hydroxyl group and the NBB anion, which increases the adsorbed NBB anion (Astuti, Hidayah, Fitriana, Mahardhika, & Irchamsyah, 2020). Therefore, experiments in this study were performed at pH 6.

In addition to the pH value, the contact time significantly influences the adsorption equilibrium. Generally, the adsorption increases rapidly at the beginning of the process, as in Figure 3b. Adsorption increased in the first ten minutes due to rapid external mass transfer to the adsorbent surface. This is followed by slowing diffusion processes within the particles, reaching equilibrium, and stopping adsorption processes (Astuti, Hidayah, Fitriana, Mahardhika, & Irchamsyah, 2020). In this study, with 6 pH value and 100 mg/L initial concentration, the adsorption equilibrium began to be reached after 120 minutes. It was shown that the curve began to lead in a linear direction. The total removal efficiency of NBB dye at 120 minutes by

SCFA, MCFA, and MMCFA was 89.33 %, 89.83 %, and 96.39 %, respectively.

The effect of the initial concentration of NBB dye solution on adsorption efficiency using SCFA, MCFA, and MMCFA as adsorbents is shown in Figure 3c. Maximum adsorption efficiency of NBB dye by SCFA, MCFA, and MMCFA was observed at an initial concentration of 100 mg/l was established, i.e., 88.17%, 89.72%, and 98.50%, respectively. The greater the initial concentration, the more the adsorbed NBB dye until it reached equilibrium. The initial adsorbate concentration provides a significant driving force. The force causes an increase in adsorption capacity or efficiency, where the rate of mass transfer of the adsorbate to the adsorbent is also faster (Astuti, Fitriana, Mahardhika, & Irchamsyah, 2020). The adsorption ability decrease after reaching equilibrium because the number of active sites that adsorb the NBB dye solution decreases, and the surface of the adsorbent becomes saturated. After an initial concentration of 300 mg/L, Figure 3c shows that MMCFA had the lowest adsorption efficiency compared to SCFA and MCFA. The addition of magnetite compounds was thought to reduce the average pore size in MMCFA so that the surface is saturated faster than SCFA and MCFA.

4. Conclusion

Magnetized Modified Coal Fly Ash (MMFCA) was successfully synthesized with NaOH solution and Fe₃O₄ (magnetite). MMCFA application as NBB dye adsorbent showed optimum efficiency obtained at pH of 6, initial concentration of 100 mg/L, and contact time of 120 minutes. In this study, the adsorption efficiency of NBB dye by MMCFA was higher than that of SCFA and MCFA, with the total removal efficiency of NBB dye was 96.39 %. This may be due to the increased number of active sites due to alkali and magnetite modifications.

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