MOLEKUL
eISSN: 2503-0310
Articles
https://doi.org/10.20884/1.jm.2022.17.2.6358

Co-Precipitation Synthesis of Clay-Magnetite Nanocomposite for Adsorptive Removal of Synthetic Dye in Wastewater of *Benang Bintik* Batik

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Received August 30, 2021; **Accepted** June 09, 2022; **Available online** July 20, 2022

ABSTRACT. Clay is a natural material that has been widely applied as a low-cost adsorbent for removing various contaminants from wastewater. To improve its characteristics and activity, natural clay from Central Kalimantan was activated by acid and calcination treatments, then synthesized with magnetite (Fe_3O_4) in nanocomposite by co-precipitation method. The obtained nanocomposite was further characterized by Fourier transform infrared spectroscopy, X-ray diffraction, nitrogen adsorption, vibrating sample magnetometry, and transmission electron microscopy methods. The results showed that co-precipitation method has been successfully produced clay-magnetite nanocomposite from activated clay with specific surface area, saturation magnetization, and particle size were 37.458 m^2/g, 24.910 emu/g, and 50 nm, respectively. The obtained natural clay, activated clay, and clay-magnetite nanocomposite were then evaluated for adsorptive removal of naphthol blue black (NBB) synthetic dye from wastewater generated by an industry of *Benang Bintik* batik in Central Kalimantan using a batch system. The results showed that optimum pH for adsorptive removal process from these adsorbents were 2, while the optimum contact times of natural clay, activated clay, and clay-magnetite nanocomposite were 90, 60, and 60 minutes, respectively. The clay-magnetite nanocomposite also showed a much better removal efficiency (99.58%) than activated clay (86.28%) and natural clay (68.27%). The utilization of clay-magnetite nanocomposite as adsorbent not only can increase its removal efficiency against NBB dye, but also can facilitate the separation of the adsorbent solid phase from wastewater using an external magnetic field after the adsorptive removal process.

Keywords: Adsorption, clay, co-precipitationsynthetic dye, magnetite,.

INTRODUCTION

Batik is a traditional fabric of Indonesia cultural heritage that has a high artistic value (Azhar et al., 2015; Hasaniyah & Basri, 2019). It is a patterned fabric which is made by using a wax-resist dyeing technique (Sutari et al., 2015). Every pattern and motive applied to the whole batik fabric has its own meaning and philosophy related to culture of each region in Indonesia (Hasaniyah & Basri, 2019). The batik of *Benang Bintik* ("Spotted Thread") is a typical batik from the Central Kalimantan region (Usop & Usop, 2021). In the local language, "*Benang*" means a piece of the white cloth, while "*Bintik*" means a design applied on the top of the "*Benang*". The patterns and motifs applied in this batik fabric commonly reflects the culture of the *Dayak Ngaju* tribe, the indigenous tribe of Central Kalimantan. Those patterns and motifs are usually taken from paintings or carvings used by the *Dayak Ngaju* community to perform rituals or traditional ceremonies, such as *batang garing*, *mandau*, *burung tingang*, *huma betang*, *Balanga*, dan *kelakai*. In general, the motifs and patterns applied to the batik fabric use synthetic dyes because the colors produced are strong, stable and easily obtained. But unfortunately, synthetic dyes are toxic, carcinogenic and nondegradable (Kant, 2012; Rahayuningsih et al., 2020). Consequently, long-term use of these dyes can cause problems in health and the environment. In the dyeing process, about 80% of dyes stay on the fabric, while the rest will be discharged in water as a waste (Kant, 2012). Therefore, the generated wastewater must be treated before being discharged into the environment. But in reality, this wastewater is directly discharged into canals or waterbodies without prior treatment by the batik industry players in Central Kalimantan to reduce the operational costs.

Various methods have been developed by researchers to remove synthetic dyes from wastewater, such as activated sludge, coagulation/ flocculation, anaerobic and aerobic degradations, reverse osmosis, oxidation, ion exchange, electrochemistry, photocatalysis, and adsorption (Kant, 2012; Kumar et al., 2019). Among them, adsorption is a method that can be chosen because it is considered effective, easily prepared and relatively inexpensive operational costs (Kant, 2012; Kumar et al., 2019). It refers to a process in which a dissolved substance (adsorbate) is concentrated over the surface of solid substance (adsorbent) from the liquid or gaseous surroundings, where there are the physical/ chemical bonds between adsorbate and absorbent (Atkins, 1999; Kant, 2012; Kumar et al., 2019).

Clay is a material that can be used as an adsorbent (Kausar et al., 2018). It is a group of hydrous aluminosilicate minerals with the fine particle size. The clay is a natural material that has several advantages, such as high cation exchange capacity, large surface area, as well as chemically and mechanically stables. These advantages make this material widely used as an efficient dye adsorbent (Adeyemo et al., 2017; Kausar et al., 2018). Central Kalimantan is one of the provinces in Indonesia that has a huge clay reserve of about 8.9 million m^3 (Amarullah et al., 2002). The clay from this province has also been proven to be able to adsorb rhodamine B and methylene blue dyes with sufficiently large adsorption capacities of 34.29 and 30.29 mg/g, respectively (Sadiana et al., 2018). Therefore, natural clay from Central Kalimantan can be recommended as a low-cost and effective adsorbent for removing synthetic dyes from wastewater of *Benang Bintik* batik. However, the use of clay as adsorbent turns out to have drawback i.e., difficult to separate the adsorbent from aqueous solution after adsorptive removal process. To solve this problem, combination of the clay with magnetic material (magnetite; Fe_3O_4) as the clay-magnetite nanocomposite could be opted. The synthesis of this nanocomposite is conducted by co-precipitation method. The magnetic property produced in the clay can be used to facilitate the separation process between the clay and liquid phase using an external magnetic field (Cottet et al., 2004; Chen et al., 2016; Sadiana et al., 2018). Based on the background, the purposes of this study are to synthesize the clay-magnetite nanocomposite and to evaluate its use as an adsorbent for removing the synthetic dye in wastewater of *Benang Bintik* batik on a laboratory scale with operational parameters, namely pH and contact time.

EXPERIMENTAL SECTION

Materials

The natural clay was obtained from Central Kalimantan, while the wastewater was collected from an industry of *Benang Bintik* batik in Central Kalimantan, Indonesia. The wastewater sample was put in a dark plastic bottle, and it was placed into a cold box at the sampling site. Then, wastewater sample was placed in a refrigerator before beginning the experiment in the laboratory. Analytical grades of $FeSO_4{\cdot}7H_2O$, $FeCl_3{\cdot}6H_2O$, NH_4OH, $AgNO_3$, HCl, HNO_3, and NaOH were obtained from Merck, Tbk. All solutions were prepared using distilled water.

Preparation and Activation of Natural Clay

The natural clay obtained from Central Kalimantan was cleaned from rough impurities and heated using an oven at 70 °C for 3 hours. The cleaned clay was crushed and filtered with a 60 µm nylon mesh. Furthermore, 50 grams of natural clay after preparation were refluxed with 250 mL of HCl 3 M for 3 hours at 100 °C for chemical activation. The refluxed clay was filtered and washed with distilled water, and then chlorine tested using $AgNO_3$. The solid of clay was dried at 100 °C for 3 hours. Thereafter, the clay was crushed and filtered with a 60 µm nylon mesh. The clay was then calcined using furnace at 500 °C for 3 hours for physical activation. The natural and activated clays were characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and nitrogen adsorption methods.

Synthesis of Clay-magnetite Nanocomposite

The clay-magnetite nanocomposite was synthesized by co-precipitation method. The solutions of $FeSO_4{\cdot}7H_2O$ and $FeCl_3{\cdot}6H_2O$ were prepared at concentration of 0.025 M and 0.050 M in 100 mL , respectively. The 100 mL of 0.025 M $FeSO_4{\cdot}7H_2O$ solution was mixed with 100 mL of 0.050 M $FeCl_3{\cdot}6H_2O$ solution. The mixed solution were then added with two grams of activated clay, and stirred at 85 °C. Thereafter, NH_4OH solution was also added to achieve stable pH at 10. The obtained suspension was air-dried for 3 hours. Finally, the synthesized clay-magnetite nanocomposite could be separated using an external magnetic field. The nanocomposite was washed with distilled water and dried for 2 hours at 110 °C. The nanocomposite was then crushed and filtered with a 60 µm nylon mesh. The FTIR, XRD, nitrogen adsorption, transmission electron microscopy (TEM), and vibrating sample magnetometry (VSM) methods were used to characterize the clay-magnetite nanocomposite.

Adsorptive Removal of Synthetic Dye in Batik Wastewater

Adsorptive removal of the synthetic dye from *Benang Bintik* batik wastewater was carried out using three different types of adsorbents, i.e., natural clay, activated clay, and clay-magnetite nanocomposite in the batch system. Firstly, 25 mL of wastewater was measured for absorbance by UV-Vis spectrophotometer at a wavelength of 400 nm to 700 nm. Furthermore, the effects of adsorption parameters, i.e., pH and contact time were studied. The effect of pH was investigated by varying the initial pH of wastewater from 1 to 6. The pH value was adjusted by 0.1 M HNO_3 and 0.1 M NaOH solutions. The 0.05 grams of natural clay, activated clay and clay-magnetite nanocomposite were used to adsorb 50 mL of wastewater at different initial pH values. The adsorptive removal process was conducted using a shaker at 100 rpm for 3 hours at room temperature. The solution was collected from the mixture to determine the removal efficiency of the synthetic dye. The solutions from the mixtures of natural and activated clays were collected by a filtration method, while the solution from the clay-magnetite nanocomposite mixture was collected by a magnetic separation method. Similar to the procedure of the pH effect, the effect of contact time was also investigated using three different types of adsorbents. The contact time was in the range from 5 to 420 minutes. The 0.05 grams of each adsorbent was added into 50 mL of wastewater at optimum pH value. Then, the mixture was shaken at 100 rpm in room temperature with different contact times. The solution was collected from the mixture by the same procedure as above.

The removal efficiency of synthetic dye in batik wastewater was determined by UV-Vis Spectrophotometry method. All of the adsorption results were corrected by blank tests in which no adsorbent was added into the wastewater. The removal efficiency of NBB dye (%), was calculated using the equation:

$$\text{Removal efficiency (\%)} = \frac{A_0 - A_t}{A_0} \times 100$$

where A_0 and A_t are the absorbance of NBB dye in the wastewater before and after treatment, respectively.

Separation studies were also studied on the activated clay and clay-magnetite nanocomposite adsorbents in this part. The adsorbents of activated clay and clay-magnetite nanocomposite added to 20 mL of wastewater. These suspensions were then shaken at room temperature for 90 min. Finally, from these suspensions, the activated clay was separated by sedimentation process, while clay-magnetite nanocomposite was separated by magnetic separation process.

RESULTS AND DISCUSSION

Based on its mineral content, natural clay consists of four main groups, namely montmorillonite-smectite, kaolinite, halloysite, and chlorite. These minerals are usually combined with the impurity minerals, such as quartz, illite, biotite, chrysotile, anatase, etc. Among them, montmorillonite and kaolinite are minerals that can be used to adsorb dye molecules. They are minerals with the layered structures that have various of active sites, such as aluminol hydroxyl and silanol hydroxyl sites. The general structure of the montmorillonite group consists of three layers with a ratio of 2:1 for tetrahedral silica and octahedral alumina units. Meanwhile, the kaolinite group consists of two layers by 1:1 ratio of tetrahedral silica and octahedral alumina units (Adeyemo et al., 2017; Kausar et al., 2018). To eliminate the impurity minerals and increase its specific surface area, the natural clay from Central Kalimantan was first activated with chemical and physical treatments. The activated clay was then synthesized with magnetic material to form the clay-magnetite nanocomposite using co-precipitation method. This method is chosen because of it easily reproducible, high product purity, high yield, low cost, and the lack of necessity to use organic solvents (Rane et al., 2018). This method was carried out by simultaneously interacting the activated clay with Fe^{2+} and Fe^{3+} solutions at mole ratio of 1:2 (Cottet et al., 2004; Chen et al., 2016). These ions would be entered into the layered structure of clay minerals by ion exchange process. Then, Fe^{2+} and Fe^{3+} ions within clay mineral structure formed $Fe(OH)_2$ and $Fe(OH)_3$ due to the addition of NH_4OH solution. These compounds were then oxidized and formed magnetite (Fe_3O_4) particles (Sadiana et al., 2018).

The obtained natural clay, activated clay, and clay-magnetite nanocomposite were further characterized by an FTIR spectrometer to confirm its functional groups. The infrared spectra of natural clay, activated clay, and clay-magnetite nanocomposite are shown in **Figure 1**. The infrared spectrum in **Figure 1**(**a**) shows the presence of several sharp absorption peaks in the wavenumbers of 3691.48, 1627.80, 999.05, 906.48, 794.61, 748.33, 671.18, and 563.17 cm^{-1}. These peaks are associated to OH-stretching of aluminol hydroxyl, OH-bending of water molecule, Si-O-stretching, Al-O-stretching, O-Si-O-stretching of quartz, Si-O-Si-simestris from the tetrahedral silica unit, Si-O-stretching, and Si-O-Al^{VI}-stretching from the octahedral alumina unit (Eren et al., 2009, Holtzer et al., 2011; Wang et al., 2011; Lou et al., 2015). Therefore, based on data from all absorption peaks showed that this sample is a family of aluminosilicate minerals.

Furthermore, the infrared spectral patterns of natural clay (**Figure 1a**) and activated clay (**Figure 1b**) do not show any significant changes. A slight shift in the spectrum occurred in the wavenumber of 999.05 cm^{-1} which indicated that there is dealumination in the crystal structure of clay minerals. The wavenumber of 906.48 cm^{-1} also experienced a shift towards a larger wavenumber. It indicates that the more homogeneous environment of the Al-OH structure which is caused by the dissolution of metal atoms in the outside of the clay mineral framework (non-octahedral). This result suggests that the activation process was able to remove impurities that are still trapped in the crystal lattices of clay minerals. The infrared spectral pattern of the clay-magnetite nanocomposite shows in **Figure 1**(**c**). The wavenumber of 671.18 cm^{-1} has shifted towards a smaller wavenumber. This shift indicates that the Si-O bond was in less free due to the attractive competition between Si-O and Fe from the magnetite particles. This result is also supported by the shape of the spectrum at wavenumber of 400-500 cm^{-1} which is gentler when compared to the infrared spectral pattern of activated clay (**Figure1b**).

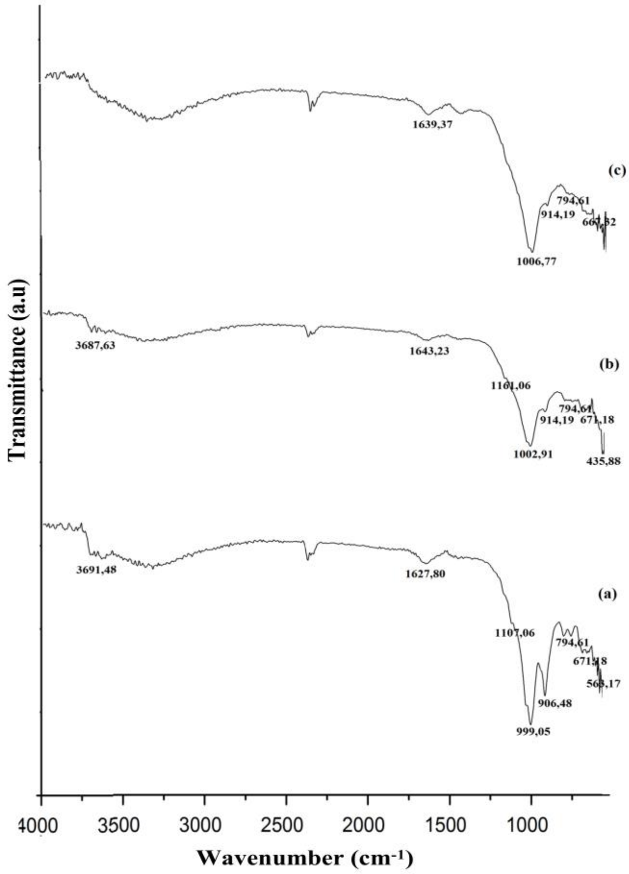


Figure 1. FTIR of natural clay (a), activated clay (b), and clay-magnetite nanocomposite (c).

An X-ray diffractometer is also used in the present study to characterize the samples. The XRD data are required to verify the content mineral of clay samples. The X-ray diffractograms of the natural clay, activated clay, and clay-magnetite nanocomposite are shown in Figure 2. Based on the Joint Committee on Powder Diffraction standard (JCPDS), the natural clay contained minerals of montmorillonite (JCPDS file no. 29-1498), chrysotile (JCPDS file no. 10-0381), quartz (JCPDS file no.46-1045), anatase (JCPDS file no. 21-1272), and biotite (JCPDS file no. 80–1110). The Figures 2(a) and 2(b) showed that the peaks of chrysotile, anatase, and biotite in the clay disappeared after the activation treatments. These results suggest that activation could remove impurity minerals, such as chrysotile, oligoclase, and biotite. Then, Figure 2(c) showed a change in the diffraction pattern of the clay-magnetite nanocomposite with the appearance of a new peak at 35.35°. This peak is related to the magnetite (Fe_3O_4) particles (JCPDS file no. 19-0629). This result indicates that the co-precipitation method has successfully synthesized magnetite particles in the network structure of activated clay. On the other hand, some characteristics peaks for montmorillonite in the diffractogram of clay-magnetite nanocomposite (Figure 2c) appeared highly reduced or disappeared completely in the diffractogram of activated clay (Figure 2b), which can give an indication that magnetite particles have completely precipitated on the surface of montmorillonite so that the characteristics peaks for montmorillonite are not detected by XRD. In addition, another cause may be due to some montmorillonite layers are dealuminated after being composited with magnetite particles.

The results of nitrogen adsorption analysis using a gas sorption analyzer based on the Brunauer–Emmett–Teller (BET) and Dubinin-Radushkevich (DR) equations from three types of clay samples are shown in Table 1. The BET equation shows that the that activation and synthesis of natural clay with magnetite particles can increase the specific surface area of clay minerals. According to DR equation, the surface area, volume, and radius of pores are also increased in the activated clay minerals. It suggests that the activation process has succeeded in dissolving the impurities so that the pores become more open. On the other hand, the surface area and volume of pores on the clay-magnetite nanocomposite are smaller than natural and activated clays. It may be caused by the formed magnetite particles trapped in the pores of clay minerals.

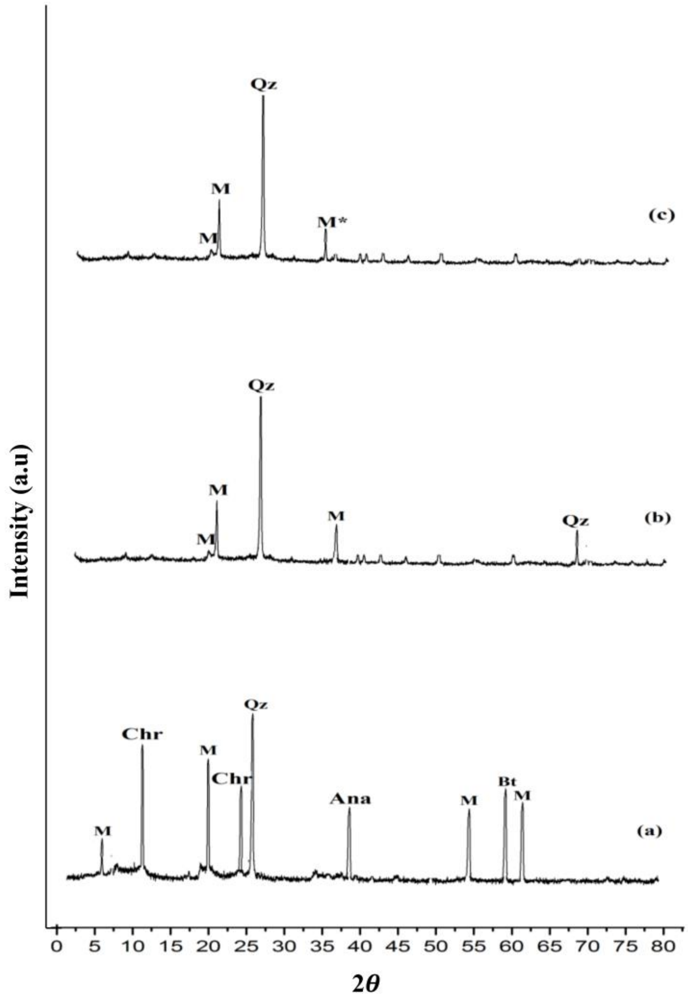


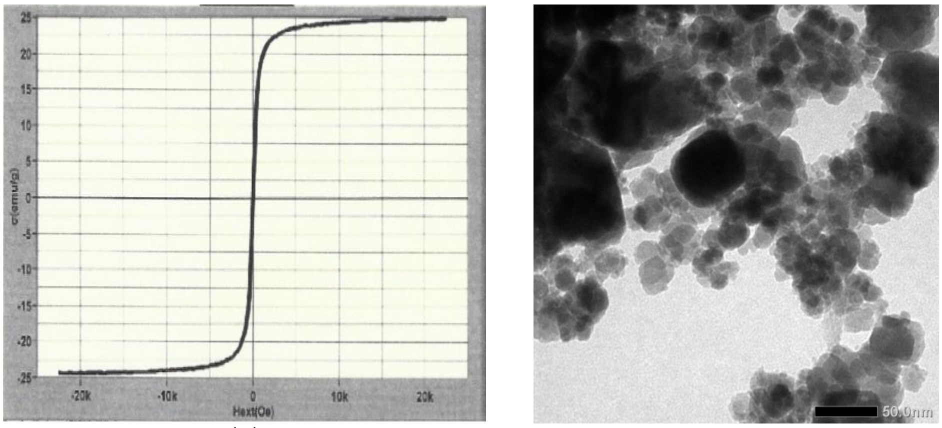
Figure 2. The X-ray diffractograms of natural clay (**a**), activated clay (**b**), and clay-magnetite nanocomposite (**c**). Note: M, monmorillonite; Chr, chrysotile; Qz, quartz; Ana, anatase; Bt, biotite; M*, magnetite.

The magnetization value of the clay-magnetite nanocomposite was investigated using the VSM instrument. The result is presented as the hysteresis curve (**Figure 3a**). The formed nanocomposite was superparamagnetic with a magnetization value at 24.91emu/g. It suggests that the clay-magnetite nanocomposite had magnetic property that can be used to facilitate the separation between the clay and liquid phase using an external magnetic field after adsorptive removal process. Moreover, the clay-magnetitev nanocomposite was also characterized with a TEM instrument. This is intended to confirm the size of the magnetite particles formed in the framework structure of clay. The micro structural image of clay-magnetite nanocomposite is presented in **Figure 3**(**b**). Thisv result vshowsv that the nanocomposite had similar vsize and morphology. The particle image of the TEM was then measured with the J image software. The result showed that the particle size of the composite was about 50 nm. It indicates that the synthesis of magnetite particles in the clay using the coprecipitation method has successfully produced a nanoscale composite. The smaller particle size wouldv produce larger surface areas that benefit to increasev the vadsorptive removal vefficiency of dyes by clay.

Adsorptive removal of the synthetic dye from *Benang Bintik* batik wastewater was carried out on the natural clay, activated clay, and clay-magnetite nanocomposite using a batch system. The effects of adsorption parameters were investigated in the present study, including pH and contact time. However, beforev these vstudy vare vcarried vout, determining the maximum wavelength of the synthetic dye of batik wastewater would be firstly conducted to to obtain the wavelength that provides the highest measurement sensitivity and semi-qualitative identification of the synthetic vdye contained in batik wastewater. The result shows that the UV-Vis spectrum of batik wastewater provides maximum absorbance at a wavelength of 610 nm (**Figure 4**). Fitriani (2016) was reportedv that the wavelength of 610 nm is correspond to the maximum wavelength of Naphthol Blue Black (NBB) dye.

Table 1. The results of nitrogen adsorption analysis based on the BET and DR equations from three types of clay samples.

Sample	Specific surface area (S_{BET})	Pore surface area (S_{DR})	Pore volume (V_{DR})	Pore radius (D_{DR})
Natural clay	36.415 m^2/g	46.085 m^2/g	0.016 cc/g	14.972 Å
Activated clay	36.712 m^2/g	48.230 m^2/g	0.017 cc/g	15.052 Å
Clay-magnetite nanocomposite	37.458 m^2/g	46.006 m^2/g	0.016 cc/g	15.070 Å



(a) (b)

Figure 3. Hysteresis curve (**a**) and TEM image (**b**) of the clay-magnetite nanocomposite.

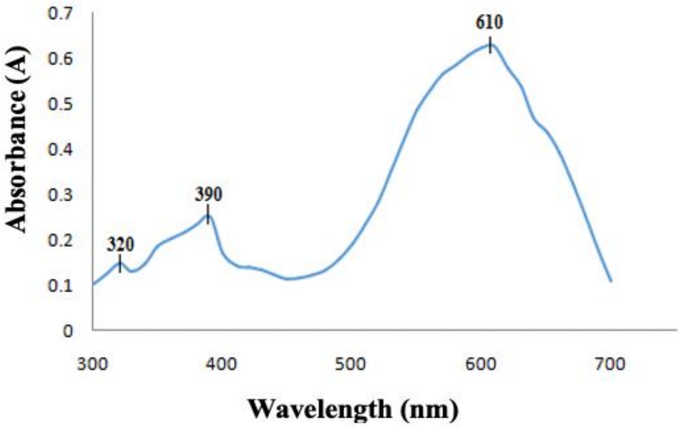


Figure 4. UV-Vis spectrum of batik wastewater

In addition, the UV-vis spectrum also showed absorption peaks at wavelengths of 320 nm and 390 nm which are characterized with nitrobenzene and azo (-N=N-) groups, respectively. These are also present in the molecular structure of NBB dye (Fitriani, 2016). This wavelength was then used to measure the absorbance of the batik wastewater before and after the adsorptive removal process.

The pH effect on the removal efficiency (%) of NBB dye in batik wastewater by the three types of adsorbents can be seen in **Figure 5**. The removal efficiency of the natural clay, activated clay, and clay-magnetite nanocomposite have almost the same pattern, where the pH optimums of adsorptive removal process were 2 (**Figure 5**). The pH value is known to affect the adsorbate species. At low pH, the adsorbate species of NBB dye can undergo protonation to form a positively charged dye due to the presence of H^+ ions. The generated positive charge of the dye is then bond to the negatively charged active sites of montmorillonite contained in the clay through electrostatic force. These active sites are generated by the isomorphic substitution in the montmorillonite structure (Adeyemo et al., 2017; Kausar et al., 2018). On the other hand, a high pH will reduce the presence of H^+ ions, so that the molecules of NBB dye tend to be negatively charged and the possibility of electrostatic interactions with the montmorillonite active sites will be difficult because of the negative charge repulsion generated by the molecules of NBB dye with the montmorillonite active site.

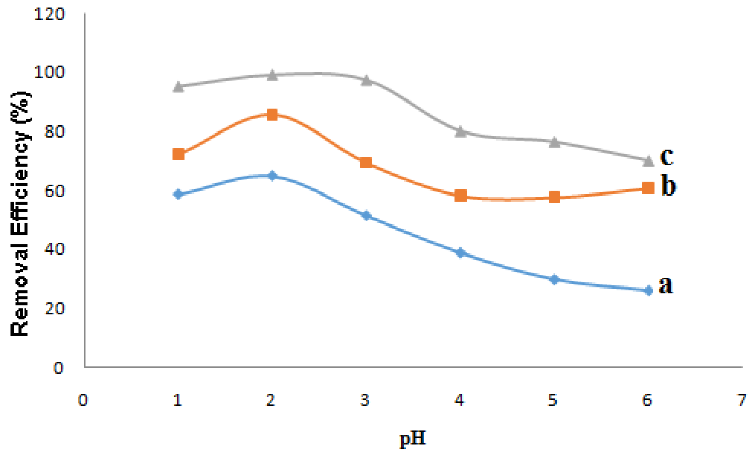


Figure 5. Effects of pH on the removal efficiency (%) of NBB dye in batik wastewater: natural clay (**a**), activated clay (**b**), clay-magnetite nanocomposite (**c**).

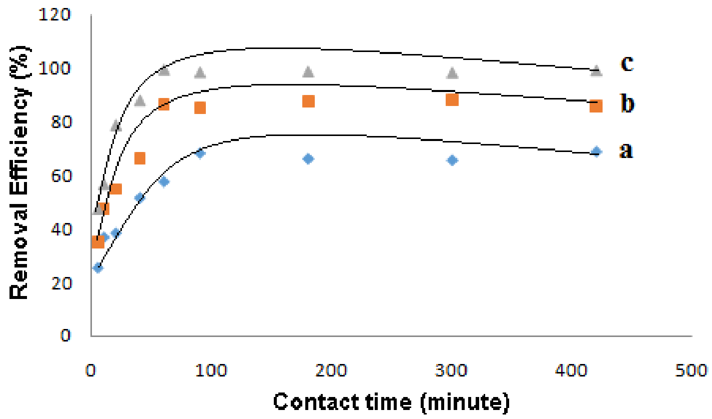


Figure 6. Effects of contact time on the removal efficiency (%) of NBB dye in batik wastewater: natural clay (**a**), activated clay (**b**), and clay-magnetite nanocomposite (**c**).

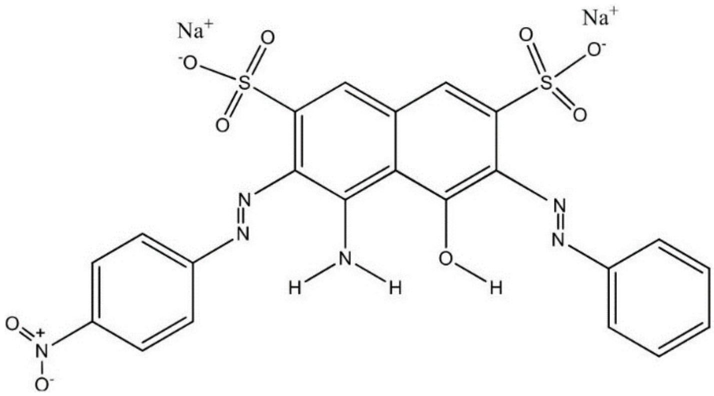


Figure 7. Molecular structure of naphthol blue black (NBB) dye.

(a) (b) (c)

Figure 8. Separation studies of the adsorbents from the batik wastewater: the batik wastewater (**a**), the clay-magnetite nanocomposite in the batik wastewater (**b**), the activated clay in the batik wastewater (**c**).

Furthermore, Figure 6 shows the contact time effect on the removal efficiency of NBB dye from batik wastewater on the three types of adsorbents. The results showed that adsorptive removal of NBB dye in batik wastewater by clay takes quite a long time. The optimum contact times of natural clay, activated clay, and clay-magnetite nanocomposite were 90, 60, and 60 minutes, respectively. The results from Figure 6 indicate that the interaction between the NBB dye and clay takes a relatively long time to achieve bond stability. This is because the NBB dye has a relatively large molecular size (Figure 7) so that it takes quite a long time to regulate itself for interacting and binding to the active site of the clay. The results also showed that the time required for activated clay and clay-magnetite nanocomposite to adsorb NBB dye was faster than natural clay. This is because the clay without activation treatment still contains impurity minerals. As a result, some of the active sites of the clay mineral are still hidden so that the dye takes a long time to find the active site and bind it until finally it can achieve bond stability.

Based on the data on the percentage of removal efficiency, the activation treatment in the clay was able to increase their adsorption abilities against NBB dye. This is because the activation treatment can dissolve impurities so that the pore of clay mineral becomes more open. It can increase the surface area and radius of clay mineral pores (Table 1). Consequently, the percentage of removal efficiency against NBB dye for the activated clay (86.28%) to be greater than natural clay (68.27%). Moreover, the combination of activated clay with magnetite particles was also able to increase its percentage of removal efficiency against NBB dye of 99.58%. This combination would produce a two-dimensional porous material with a larger surface area (Table 1). The percentage removal efficiency of clay-magnetite nanocomposite for this dye was also found to be greater than other dyes, such as methylene blue (99.47%; Chang et al., 2016) and bismark brown-Y (98.60%; Akar et al., 2021).

Separation studies were also carried out on the activated clay and clay-magnetite nanocomposite adsorbents. The solid phase of the adsorbent was separated from the mixture of adsorbent and wastewater. The activated clay was separated by sedimentation process, while clay-magnetite nanocomposite was separated by magnetic separation process. Figure 8 shows that the solid phase of clay-magnetite nanocomposite was easily and quickly separated from the liquid phase using an external magnetic field.

CONCLUSIONS

A co-precipitation method has successfully produced the clay-magnetite nanocomposite with specific surface area, saturation magnetization, and particle size were 37.458 m^2/g, 24.910 emu/g, and 50 nm, respectively. The obtained natural clay, activated clay, and clay-magnetite nanocomposite were also able to adsorptive remove NBB dye from the wastewater of *Benang Bintik* batik using batch system with optimum pH was 2, and the optimum contact times for natural clay, activated clay, and clay-magnetite nanocomposite were 90, 60, and 60 minutes, respectively. The clay-magnetite nanocomposite also showed a much better removal efficiency (99.58%) than activated clay (86.28%) and natural clay (68.27%). These results suggest that the presence of magnetite particles in the clay can increase the removal efficiency against NBB dye in the wastewater of *Benang Bintik* batik. The utilization of clay-magnetite nanocomposite as adsorbent not only can increase its removal efficiency against NBB dye, but also can facilitate the separation of the adsorbent solid phase from wastewater using an external magnetic field after the adsorptive removal process. These fundamental results demonstrate that the synthesized clay-magnetite nanocomposite can be a promising application for the removal of synthetic dyes such as NBB in wastewater of *Benang Bintik* batik.

ACKNOWLEDGEMENTS

The authors were grateful for financial support from Directorate of Research and Community Services, *DIKTI* under the grant of Applied Products in 2018.

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