4th International Conference on Process Engineering and Advanced Materials

Synthesis of Magnetite-Mg/Al Hydrotalcite and Its Application as Adsorbent for Navy Blue and Yellow F3G Dyes

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Abstract

Synthesis of magnetite-Mg/Al hydrotalcite (M-Mg/Al HT) and its utilization as adsorbent for mixture dyes (navy blue (NB) and yellow F3G (YF3G) dyes) have been studied. Magnetite, Mg/Al hydrotalcite (Mg/Al HT), and M-Mg/Al HT were synthesized by co-precipitation method. The results showed that M-Mg/Al HT was successfully synthesized by co-precipitation method. M-Mg/Al HT had a higher adsorption capacity for the mixture dyes than Mg/Al HT with adsorption capacity for M-Mg/Al HT was 63.75 mg/g and Mg/Al HT was 15.67 mg/g. Furthermore, the adsorbents possessed higher adsorption capacity after regenerated and reused. It was reported from the results of adsorption capacity of mixed dyes of both adsorbents before and after calcination process, which are M-Mg/Al HT increased from 63.75 to 81.67 mg/g, while Mg/Al HT increased from 15.67 to 81.58 mg/g.
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Peer-review under responsibility of the organizing committee of ICPEAM 2016

Keywords: M-Mg/Al HT; Adsorption; NB and YF3G Dyes

1. Introduction

Nowadays, synthetic dyes have been widely used as dye coloring in textile industry because they are inexpensive, stable, available in many colors, and easy to be prepared [1]. Almost 10-15% of the dyes lose during dyeing process [2]. Thereby, wastewater which is produced by textile industry contains a considerable amount of dyes. These dyes give negative impact to the environment, such as causing aesthetic problem, reduce light penetration into aquatic system and generate toxicity to organism [3]. Synthetic dyes are also difficult to biodegrade in the environment due to their resistance to light, heat, chemical and water [4]. In order to reduce the existence of the dyes, there are various conventional methods which were developed in wastewater treatment, such as bio-sludge [5], biosorption [6], adsorption [7, 8 and 9] and photocatalytic degradation [10]. Among these methods, adsorption was found to be an effective method because of its low cost, high efficiency, and simplicity of the design/operation [11].

Hydrotalcite (HT) is anionic clay, which has similarity structure with brucite ($Mg(OH)_2$). General formula of HT is $[M(II)_{1-x}M(III)_x(OH)_2]^{x+} (A^{n-})_{x/n}.mH_2O$, where M(II) and M(III) are divalent and trivalent cations and A^{n-} is an anion. Due to partial substitution of M(II) with M(III), the hydroxide sheets of HT have net positive charge. The positive charge will compensate the exchangeable anions, which are present in the interlayer space. HT has received a lot of interest as it has a large surface area, a high anion retention capacity and also a simple thermal regeneration procedure. HT is able to regenerated using

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simple thermal procedure because it can reconstruct its structure after thermal damage. The reconstruction process can be performed by introducing HT into an anion-containing solution then the anion will be intercalated. This process is called 'memory effect' [12]. The memory effect makes HT become a promising material in adsorption processes because as less side products will be produced. In order to increase its performance, HT can be modified with magnetic properties by composting it with magnetite particles in order to facilitate the easy separation of adsorbent from the remaining adsorbate in an adsorption process [13]. This composite material is called magnetite-hydrotalcite (M-HT) and its application in various processes increasingly received more attention recently.

A composite materials of magnetite and Mg/Al HT (M-Mg/Al HT) is one of M-HT materials. The application of M-Mg/Al HT as material adsorbent in dye removal is still limited. Some studies that reported M-Mg/Al HT as material adsorbent in dye removal, such as organic dye removal (Congo Red, Orange II, Methyl Orange, Rose Bengal, and Eosin B) [13], Acid Flavine 2G dye removal [14], and C.I. Acid Yellow 219 (AY219) dye removal [15]. In this paper, M-Mg/Al HT was carefully synthesized and its performance as adsorbent for navy blue (NB) and yellow F3G (YF3G) mixed dyes was examined.

2. Materials and Method

2.1. Materials and instrumentation

All chemical used in this research, i.e. $Mg(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, $FeCl_3.6H_2O$, $FeSO_4.7H_2O$, NaOH, and CH_3COOH were analytical grade (Merck Co. Inc., Germany) and used without further purification. Dyes NB and YF3G were donated by CV. Maju Mapan (Tulungagung, East Java) Textile Industry and N_2 gas were purchased from CV. Perkasa, Yogyakarta.

All of the synthetic materials were identified by XRD using Shimadzu 6000 diffractometer with Cu Kα radiation at 40 kV and 30 mA. In order to examine the successful synthesis of M-Mg/Al HT, the infrared spectra of magnetite, Mg/Al HT and M-Mg/Al HT were identified using Shimadzu FTIR Prestige 21 with KBr disc method. The morphology and content analysis of materials were observed with Jeol JSM-6510 SEM EDS.

2.2. Synthesis of Materials

Magnetite. Magnetite was basically synthesized according to the procedure described by Lasalle et al. [16]. The solution was prepared by dissolving 3.254 g of $FeCl_3.6H_2O$ and 1.789 g of $FeSO_4.7H_2O$ in 100 mL of aquadest at a closed beaker, deoxygenating for 25 minutes under N_2 atmosphere and maintaining the temperature at 70°C. NaOH solution was added into the solution at a constant rate in order to reach pH 10. The mixture was allowed to complete the magnetite formation by stirring the mixture for 30 minutes. In order to purify the magnetic particles, the products were washed three times and dried at 70°C until constant weight was achieved.

Mg/Al HT. Mg/Al HT was prepared by dissolving of 12.8 g of $Mg(NO_3)_2.6H_2O$ and 9.4 g of $Al(NO_3)_3.9H_2O$ in 100 mL of aquadest followed by addition of NaOH solution until pH 10 under N_2 atmosphere. The mixture was then hydrothermally treated at 120°C for 5 hours. The suspension was filtered, washed and then dried at 70°C until constant weight was achieved.

M-Mg/Al HT. M-Mg/Al HT was synthesized as follows [17]. First, preparation of dispersion of Fe_3O_4 was done by dispersing 1.3 g of Fe_3O_4 in 100 mL of aquadest. Second, preparation of mixed solution of Mg and Al nitrates by 12.8 g of $Mg(NO_3)_2.6H_2O$ and 9.4 g of $Al(NO_3)_3.9H_2O$ in 100 mL of aquadest. Third, preparation of NaOH solution by dissolving 6.6 g of NaOH in 100 mL aquadest. The mixed solution of Mg and Al nitrates and the solution of NaOH were then added to the dispersion of Fe_3O_4 at constant rate under N_2 atmosphere. After reached pH 10, the suspension was hydrothermally treated at 120°C for 5 hours. The suspension was filtered, washed and then dried at 70°C until constant weight was achieved.

2.3. Adsorption Experiments for Single Dye

A batch method was used to evaluate the effects of pH, contact time and concentration on the adsorption of single dye (NB and YF3G dyes). The effects of the initial pH solution on dye adsorption was evaluated by contacting 12.5 mL dye solutions (NB and YF3G) at pH 4, 6, 8 dan 10 with 25 mg adsorbent and then shaking for 2 hours. The suspension was filtered (M-Mg/Al HT was separated from solution by external magnetic field) and dye concentration was determined using UV-Vis spectrophotometer at a wavelength giving maximum absorbance.

The effect of contact time was evaluated by dispersing 12.5 mg adsorbent with 12.5 mL dye solution. The initial pH was adjusted at the optimum pH. The mixture was shaken with contact times of 5, 10, 15, 30, 60, 90, 120 and 180 minutes. The suspension was filtered (M-Mg/Al HT was separated from solution by external magnetic field) and dye concentration was determined using UV-Vis spectrophotometer.

The effect of initial concentration of dye was carried out at room temperature by contacting 12.5 mg adsorbent with 12.5 mL dye solution at initial concentration of 40, 60, 80, 100, 120, 160, 200 and 240 mg/L. The initial pH and contact time were adjusted at the optimum condition. The suspension was filtered (M-Mg/Al HT was separated from solution by external magnetic field) and dye concentration was determined using UV-Vis spectrophotometer.

2.4. Adsorption Experiments for Mixed Dyes

The adsorption of mixed dyes (NB and YF3G) in solution was investigated by contacting 12.5 mg adsorbent with 12.5 mL mixed dye solution containing 0.267 and 0.533 mg/mL NB and YF3G, respectively, at optimum condition obtained from the adsorption of single dye. The suspension was filtered (M-Mg/Al HT was separated from solution by external magnetic field) and the remaining dye concentration in supernatant was determined using UV-Vis spectrophotometer at wavelength giving maximum absorbance.

2.5. Regeneration of Adsorbents

The effectiveness of the adsorbents that were going to be reused was conducted by first regenerating them via calcination process at 450°C for 3 hours [17]. The calcined adsorbents were then contacted with the mixture of dye solutions. The suspension was filtered (M-Mg/Al HT was separated from solution by external magnetic field) and the dye concentrations were determined using UV-Vis spectrophotometer.
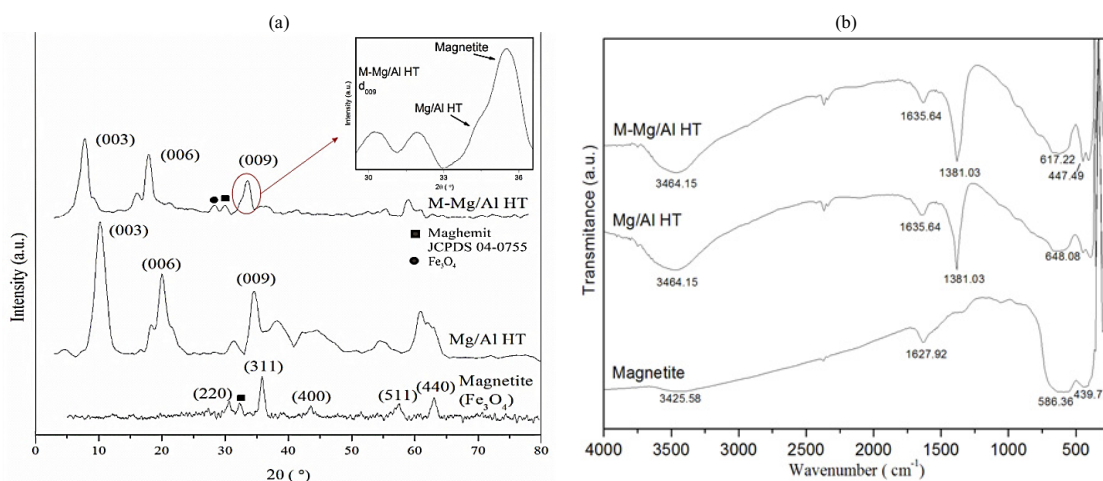
3. Results and Discussion

Fig. 1. (a) XRD pattern of synthesized materials; (b) FTIR spectra of synthesized materials

The XRD pattern of M-Mg/Al HT is dominated by characteristic peaks of Mg/Al HT and few characteristic peaks of magnetite at 2θ: 30.25° and 35.4° (Fig. 1 (a)). The characteristic peaks of M-Mg/Al HT and Mg/Al HT indicated that both adsorbents have layered structure. The peak, which is corresponding to basal spacing (009) of M-Mg/Al HT contains two overlapping sub-peaks, the first one is at smaller diffraction angle, which corresponds to the basal spacing (009) of Mg/Al HT and the second one is at slightly greater diffraction angle, which corresponds to the magnetite particle that was incorporated on Mg/Al HT surface (see inset of Fig. 1. (a)).

FTIR spectra of magnetite, Mg/Al HT and M-Mg/Al HT are shown in Fig. 1. (b). The broad band around 3463.15 cm^{-1} was due to the stretching vibration of -OH groups from M-OH (Al-OH, Mg-OH and Fe-OH), the lattice, and the interlayer of water; 1635.64 cm^{-1} due to the bending vibration of water at magnetite lattice and Mg/Al HT and also at Mg/Al HT interlayers; 1381.03 cm^{-1} due to the stretching vibration of nitrate ion from Mg/Al HT interlayer [18], 617.22, 447.49 and 408.91 cm^{-1} due to the stretching vibration of M-O (Al-O, Mg-O and Fe-O).

The particle morphology of M-Mg/Al HT is shown in Fig. 2. As from EDS analysis (Table 1), it can be concluded that Mg/Al HT and M-Mg/Al HT have the same elemental composition except for Fe element in M-Mg/Al HT owing to magnetite particle.

Table 1. Elemental composition of materials.

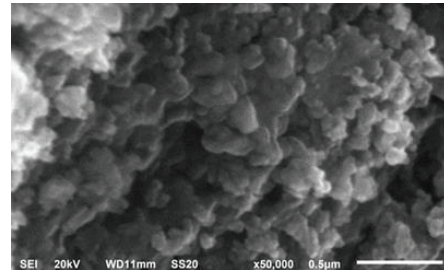|	% mol						
	N	O	C	Fe	Mg	Al	Mg : Al
M-Mg/Al HT	0.38	2.87	0.67	0.49	0.36	0.14	2.57
Mg/Al HT	0.54	3.98	0.28	-	0.73	0.29	2.52
Magnetite	-	2.68	3.01	0.36	-	-	-

Fig. 2. SEM image of M-Mg/Al HT

Structure of NB and YF3G dyes that has been used in this experiment was shown in Fig. 4. UV-Vis spectroscopy analysis of NB, YF3G and the mixture of these dyes revealed that the maximum absorbance was observed at 410 nm for YF3G, 602 nm for NB and 430 nm for mixture of dyes.

Medium acidity is one of the very important parameters in adsorption since it can affect the ionization degree of the functional groups of adsorbate and adsorbent. Effect of this pH medium on the removal of NB and YF3G was given in Fig. 3. (a). The adsorption at pH below 4 was not done because there is a huge risk that the adsorbents may dissolve at low pH values [19]. Moreover, it was observed that pH 4 was the optimum condition for adsorption of NB and YF3G dyes using both Mg/Al HT and M-Mg/Al HT. The explanation of this matter is that the functional groups of adsorbent at acidic pH were protonated ($-OH_2^+$) [19, 20], therefore it can interact with electron rich functional groups of dyes using hydrogen bond. The adsorption process of dyes using both adsorbents was low at neutral pH because the hydrogen bond was diminished. At basic pH, the functional groups of adsorbent became deprotonated ($-O^-$), which induce repulsive force to the electron rich functional groups of dyes.

Effect of contact time for adsorption of dyes using both adsorbent was shown in Fig. 3. (b), showed that M-Mg/Al HT need a shorter time than Mg/Al HT to reach equilibrium. Mg/Al HT need 120 min to reach equilibrium while M-Mg/Al HT only need 60 min. The removal of dyes onto both adsorbent was fast at the beginning and went down gradually until reaching the equilibrium time, which gave no significant increase of the dye removal. There were three kinetic models that have been used to understand the adsorption characteristics of dyes onto adsorbent, i.e. Lagergren pseudo-first order, Ho pseudo-second order [21] and Santosa [22].

Lagergren pseudo-first order kinetic model can be expressed as follow:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{1}$$

Where q_t (mol/g) and q_e (mol/g) represent the amount of adsorbed dye onto adsorbent at time t and at equilibrium time; k_1 (min^{-1}) represents adsorption rate constant, which is calculated from the plot of $\ln(q_e-q_t)$ against t.

Ho pseudo-second order kinetic model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

Where k_2 (g/mol·min) represents pseudo-second order adsorption rate constant, which is calculated from the plot $\frac{t}{q_t}$ against t.

Santosa kinetic model can be expressed as:

$$\frac{1}{C_{Ae}} \ln\left(\frac{C_A(C_{Ao} - C_{Ae})}{C_{Ao}(C_A - C_{Ae})} \right) = k_s t \tag{3}$$

Where C_{Ao} (mol/L) represents initial concentration, C_A (mol/L) and C_{Ae} (mol/L) are the concentration of adsorbate at t and equilibrium, respectively; k_s $\{(mol/L)^{-1}.min^{-1}\}$ represents Santosa adsorption rate constant, which is calculated from plot $\frac{1}{C_{Ae}} \ln\left(\frac{C_A(C_{Ao} - C_{Ae})}{C_{Ao}(C_A - C_{Ae})} \right)$ against *t*. The results showed that Ho pseudo-second order kinetic model fits the best to the data because it gives the highest value of coefficient correlation (R^2) with k_2 value 53,146 g/(mol.min).
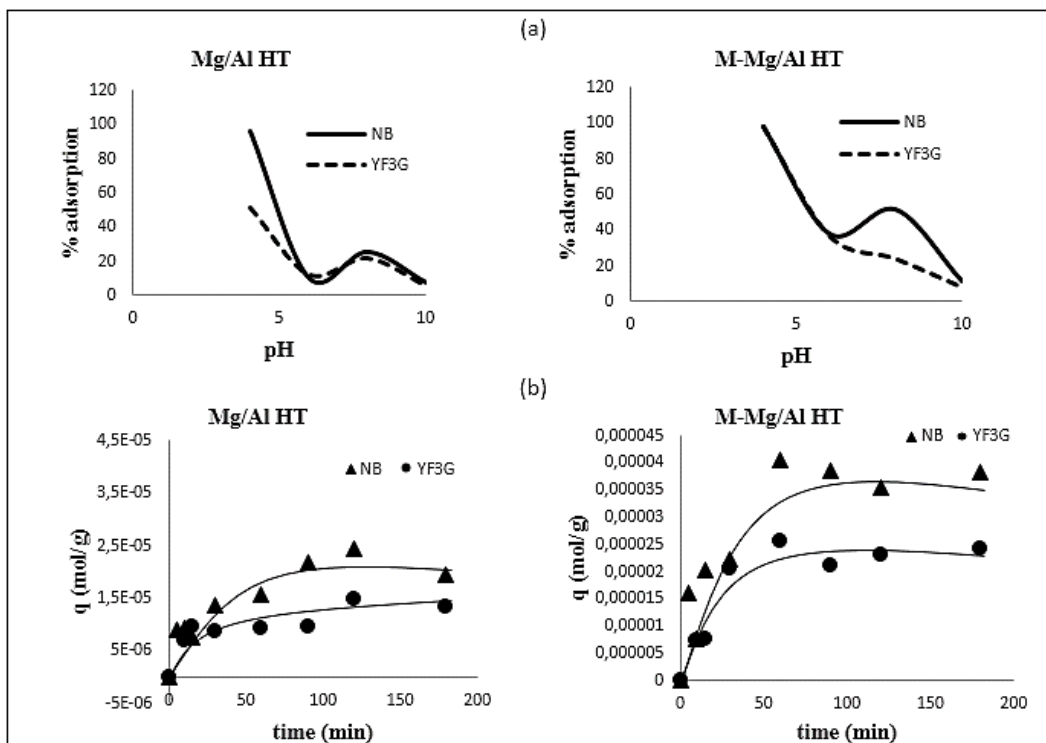
Fig. 3. The effect of (a) initial pH solution and (b) contact time on the adsorption of NB and YF3G using Mg/Al HT and M-Mg/Al HT

Table 2. Adsorption isotherm models.

Adsorbent	Dye	Freundlich isotherm model			Langmuir isotherm model		
		R^2	K_F (L/g)	n	R^2	K_L (L/mol)	q_{max} (10^{-3} mol/g)
Mg/Al HT	NB	0.593	0.003	4.975	0.923	159,700	0.626
	YF3G	0.134	0.001	6.098	0.952	72,300	0.346
M-Mg/Al HT	NB	0.454	0.009	4.065	0.990	1,831,000	0.546
	YF3G	0.106	0.005	4.202	0.928	318,500	0.392

Table 2 shows the adsorption isotherm of NB and YF3G onto adsorbent. As shown from the R^2 values, the Langmuir isotherm model fits better to the data than the Freundlich isotherm model. From the data, there was slightly different adsorption capacity of M-Mg/Al HT and Mg/Al HT. At the same weight of the applied adsorbents, M-Mg/Al HT has a smaller amount of Mg/Al HT content than Mg/Al HT, but they have relatively the same adsorption capacity. Therefore, with the same Mg/Al content, M-Mg/Al HT has a higher adsorption capacity than Mg/Al HT. From these results, it can also be concluded that magnetite, which is incorporated in Mg/Al HT to form M-Mg/Al HT adsorbent, has an ability to enhance the adsorption capacity of Mg/Al HT. As seen in the Table 2, both adsorbents give a higher adsorption capacity for NB dye than YF3G dye. It can be explained that YF3G has a bigger volume than NB (Fig. 5); hence, it was rather difficult for YF3G to adsorb onto adsorbents.
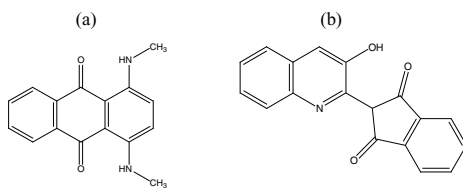

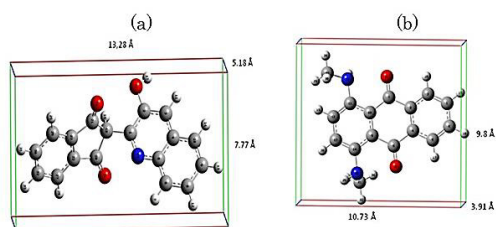Fig. 4. Structure of (a) NB and (b) YF3G dyes

Fig. 5. Size and shape of (a) YF3G and (b) NB dyes simulated by Gauss View 4

The optimum condition for the adsorption of single dye had been used as an adsorption condition in mixed dyes. With this adsorption condition, M-Mg/Al HT gave a better adsorption capacity (63.75 mg/g) than Mg/Al HT (15.67 mg/g).

Table 3. Spacing parameter of adsorbent after adsorption process

Adsorbent	M-Mg/Al HT	M-Mg/Al HT A[a]	Mg/Al HT	Mg/Al HT A[a]
d-spacing (Å)	8.927	8.531	8.579	7.979

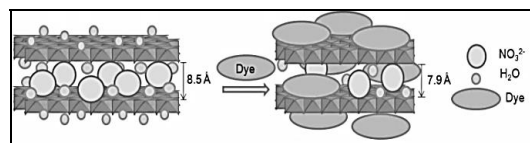A[a] = after being used to adsorb mixed dyes

Fig. 6. Interlayer width before and after the adsorption of the mixed YF3G and NB dyes

From XRD pattern, the basal spacing of both adsorbents after being used to adsorb the mixed dyes decreased (Table 3). Because the adsorbed dyes were categorized as hydrophobic compounds, hence the adsorbents became more hydrophobic than before the adsorption. Hydrophobic condition made the adsorbent lost their anion and water, which were initially incorporated in the interlayer and therefore reduced interlayer width as illustrated in Fig. 6.

Before and after being used to adsorp the mixed dyes, both adsorbents were calcined at 450°C for 3 h. The purpose of the calcination was to remove all dyes that were adsorbed and hopefully the calcined adsorbent could be reused. XRD pattern of Mg/Al HT (Fig. 7. (a)) shown that after calcination, some characteristic peaks of Mg/Al HT were destroyed. This fact can be explained by the Mg/Al HT structure layers that were collapsing due to the loss of water molecules and perhaps also the anion and dyes in interlayer. As it is known that calcination will eliminate water and anion, which are incorporated and intercalated as well by three mechanism steps: evaporation of surface-absorbed water and interlayer water, dehydroxylation of the brucite-like octahedral layers of Mg/Al HT, and elimination of anion intercalated in interlayer [23].

The thermal decomposition was also confirmed by FTIR spectra of both adsorbents after calcination where the intensity peaks of water and anion at around 3400, 1630 and 1380 cm^{-1} (Fig. 7. (b)) were seemed to decrease. Kameda et. al. [23] reported that calcination process can not elliminate all nitrate ions that intercalated at interlayer of HT, it only reduces the amount of nitrate ions. Hence, nitrate ion peak still remain in FTIR spectra after calcination process. The fact of dyes lost after calcination was indicated by color change of solid materials from green (after adsorption of the mixed dyes) to white (original color of Mg/Al HT) and brownish-red (color of the calcined M-Mg/Al HT). SEM image of Mg/Al HT (Fig. 8) shows the morphology alteration after calcination process.
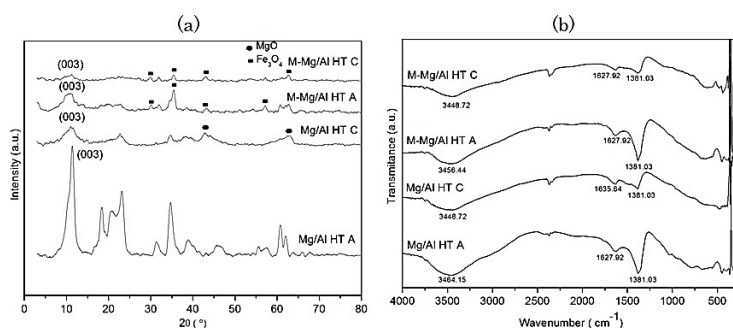

Fig. 7. (a) Diffractogram and (b) FTIR spectra of adsorbents after adsorption process (symbolized as A) and calcination at 450°C (symbolized as C)
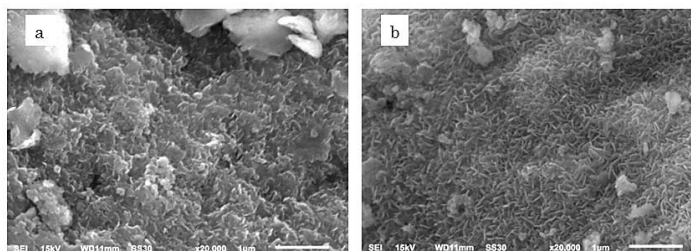
Fig. 8. SEM image of (a) synthesized Mg/Al HT and (b) Mg/Al HT after calcination at 450°C
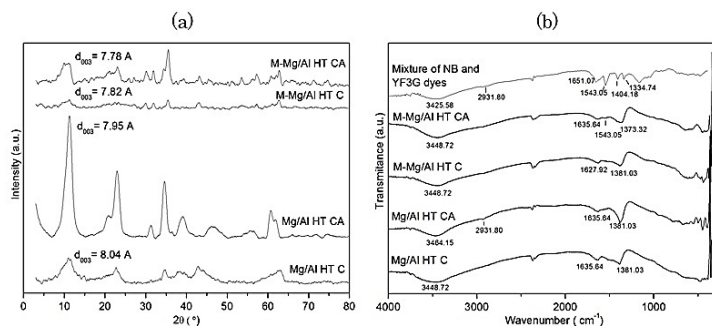

Fig. 9. (a) Diffractogram and (b) FTIR spectra of adsorbent after calcined at 450°C symbolized as (C) and after being reused symbolized as (CA)

The calcined adsorbents then were reused as adsorbents in the adsorption of the mixed dyes. The adsorption capacities of both adsorbents in this second usage were significantly higher compared to those of the adsorbents in the first usage. The adsorption capacity of M-Mg/Al HT increased from 63.75 to 81.67 mg/g, while Mg/Al HT increased from 15.67 to 81.58 mg/g. After calcination, some anions and waters that were adsorbed or intercalated in adsorbent appeared to be lost, and these empty spaces were filled with mixture of dyes when the calcined adsorbent interacted with the mixed dyes. XRD pattern of both adsorbents (Fig. 9. (a)) shows a reconstruction after adsorption process. From the XRD pattern, it is clear that Mg/Al HT shows better reconstruction than M-Mg/Al HT. Spectra FTIR after the second usage of both adsorbents (Fig. 9. (b)) did not appear to be different from the spectra after the first usage although it shows an increase in adsorption capacity. This indicates that the reason of both adsorbents reconstructed after reused was mainly due to the adsorbed mixture of dyes. It was confirmed by some characteristic peaks of the mixed dye at 2931.80 and 1543.05 cm^{-1} and also peak of nitrate ion at 1381 cm^{-1} became broader indicating that there was interaction between nitrate ion and other compounds, which probably the dyes.

4. Conclusion

M-Mg/Al HT was successfully synthesized using co-precipitation method at pH 10. The application of both M-Mg/Al HT and Mg/Al HT for adsorption of NB and YF3G was optimum at pH 4. The optimum interaction time for the adsorption of NB and YF3G on Mg/Al HT was 120 min and it shortened to 60 min when M-Mg/Al HT was used instead of Mg/Al HT. In addition, the presence of magnetite on Mg/Al HT in the form of M-Mg/Al HT made this composite not only easier to be separated but also generating a higher adsorption capacity than Mg/Al HT itself. The regeneration of Mg/Al HT and M-Mg/Al HT using simple thermal method enhanced the adsorption capacity of the calcined adsorbent compared to the adsorbents before calcination owing to the memory effect.

Acknowledgements

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