

Synthesis of Nickel/Aluminium-Layered Double Hydroxide As Potential Adsorbent for Methyl Orange and Crystal Violet Dyes

Mazidah Mamat*, Mohd Aidil Adhha Abdullah, Adila Mohd Jaafar, Rosmadila Abd Rahman, Siti Syakirah Jamal Safuan

Abstract: in this study, nickel/aluminium-layered double hydroxide (NAL) was synthesized to be used as adsorbent to remove dyes in water. Two types of dyes which are anionic and cationic dyes, respectively, were chosen, namely methyl orange (MO), and crystal violet (CV). NAL was synthesized via co-precipitation method and characterized by using powder X-ray diffractometer (PXRD) and Fourier transform infra-red spectrophotometer (FTIR). The removal of MO and CV dyes were conducted using different dosages of NAL. As the amount of NAL increases, the removal percentage of both dyes increased. NAL was able to remove up to 99.9% of anionic dye (MO). However, only 31.5% of cationic dye (CV) was successfully removed from water after being in contact with NAL for 24 hours.

Index Terms: Layered Double Hydroxide, Dye Removal, Adsorption, Methyl Orange; Crystal Violet,

I. INTRODUCTION

Fast growing industrial sector has loaded environment with pollutants and toxicants which can cause adverse effects to human health and the surroundings. In Terengganu, Malaysia, dyes used in the processing of Batik textile were found to be one of the most concerning contaminants in wastewater. A number of studies have been carried out in order to remove dyes in wastewater by using various methods including precipitation, filtration, adsorption, coagulation and etc [1]. Adsorption is considered as the most popular method as it gives the best results and it can be used to remove different types of coloring materials [2]. However, activated carbon that commonly used as adsorbent is expensive thus, it is not preferable for developing countries [3]. Hence, the need for alternative adsorbent which can act effectively and is able to be produced at a low cost is uttermost necessary.

In this study, layered double hydroxide (LDH) was synthesized as an alternative adsorbent for the removal of anionic and cationic dyes from wastewater. LDHs are

classified as lamellar materials which have the structure of brucite ($Mg(OH)_2$) where Mg atom is surrounded by octahedral unit of hydroxyl groups. In the LDH, divalent metal (M^{2+}) ions will be partially replaced by trivalent metal (M^{3+}) ions, giving rise to the positive charge which is balanced by the anions and water molecules in the interlayer gallery [4]. LDHs have high anion exchange [5] and adsorption abilities [6] making it suitable candidate to be used as an alternative adsorbent. Two types of dyes namely anionic (methyl orange) and cationic (crystal violet) were used to study the ability of LDH in removing colorants in aqueous solution. Molecular structure of both dyes are shown in Figure 1.

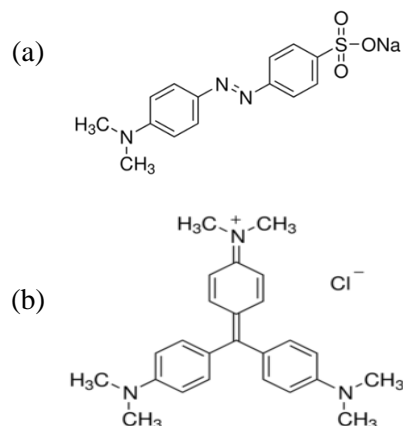


Figure 1. Molecular structure of (a) methyl orange and (b) crystal violet dyes

II. MATERIALS AND METHODS

2.1 Materials

The materials used are nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, Merck), aluminium nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Merck), sodium hydroxide (NaOH, Merck), methyl orange ($C_{14}H_{14}O_3N_3SNa$, Bendosen) and crystal violet ($C_{25}H_{30}N_3Cl$, Merck). All the chemicals were used without any further purification and the solutions were prepared using distilled water.

2.2 Preparation and characterization of NAL

Nickel/aluminium-layered double hydroxide (NAL) was prepared by co-precipitating mixed metal solutions of nickel nitrate and aluminium nitrate at $pH\ 6.00 \pm 0.05$ by dropwise addition of NaOH (2M) solution under vigorous stirring.

Revised Manuscript Received on December 30, 2018.

Mazidah Mamat, School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia

Mohd Aidil Adhha Abdullah, School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia.

Rosmadila Abd Rahman, School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia

Siti Syakirah Jamal Safuan, School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia

Adila Mohd Jaafar, Chemistry Department, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor.

The resulting slurry was then aged at 70°C for 18 hours, then filtered, and washed with excess distilled water and dried in an oven.

The obtained NAL was ground to fine powder and was then characterized using a powder x-ray diffraction (PXRD) (using a Rigaku, Miniflex II) and Fourier Transform Infrared Spectroscopy (FTIR) (using a Perkin Elmer Precisely, Spectrum 100 FT-IR Spectrophotometer).

2.3 Adsorption studies

Batch of adsorption studies were performed to evaluate the ability of NAL in the removal of both anionic and cationic dyes, namely methyl orange and crystal violet, respectively. The different dosages of NAL (0.01, 0.025, 0.05, 0.1, 0.2 and 0.5 g) were put in contact with the dye solutions and was then shaken with a Thermolyne Big Bill shaker at 100 rpm for 24 hours. The remaining dye concentrations were determined by using a UV-Vis spectrophotometer (Shimadzu Model: UV-1601 PC UV Visible Spectrophotometer).

III. RESULTS AND DISCUSSION

3.1 Characterization of NAL

The X-ray diffraction pattern of NAL (Figure 2) exhibits the typical characteristic of LDH with sharp and symmetrical peaks at low 2θ angles while at higher 2θ, it has weaker and less symmetrical peaks [7] and no other crystalline phases were present. The basal spacing of (003) plane is similar to the literature value which is 0.88 nm, corresponding to nitrate form LDH [8].

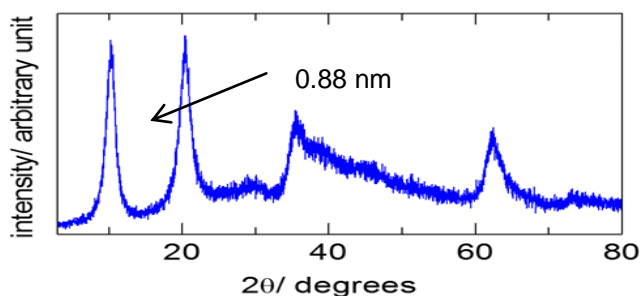


Figure 2. X-ray diffractogram of NAL.

A broad peak centered at around 3400 cm⁻¹ was observed in the FTIR spectrum (Figure 3) of NAL due to the presence of O-H stretching mode of the hydroxyl group present in the layers of NAL as well as interlayer water molecules [9] as commonly observed for the LDH materials. Peak attributed to nitrate anion located in the interlayer region of NAL can be noticed at 1384 cm⁻¹ while bands at low frequency region can be ascribed to M-O stretching modes and M-O-H bending vibrations (M = metal) [9]. The FTIR spectrum also showed that NAL is free from CO₂ contamination as no peak of carbonate anion was observed.

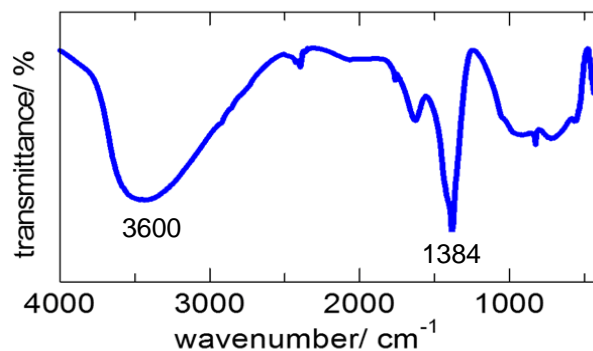


Figure 3. FTIR spectrum of NAL.

3.2 Adsorption of dyes by NAL

The adsorption studies of dyes were tested using different dosages of adsorbent (NAL) and the removal percentage of dyes by NAL was calculated using the following equation (1):

$$\text{Removal percentage} = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

Where C_0 is initial concentration (mg/L) of dyes and C_e is concentration (mg/L) of dyes at equilibrium. In general, the removal percentage of both MO and CV dyes increases, as the amount of NAL increased (Figure 4), which is due to the availability of greater number of vacant sites thus contributing to the larger surface area and number of adsorption sites [10, 11]. The uptake of both dyes drastically increased at initial stage as NAL dosage increases up to optimum mass (m_{opt}) and thereafter, becomes plateau over a certain amount of NAL. At m_{opt} , the NAL surfaces were saturated with adsorbed dyes, and the increase of NAL dosage beyond m_{opt} results in only small increment due to the overlapping of binding sites, owing to the overcrowded adsorbent particles [12]. Although the removal trend for both dyes was similar, the removal percentage of MO dye is much higher than CV dye. The underlying reason is due to LDH which consists of cationic layers resulting from the replacement of dimetal ions with trimetal ions in the hydroxyl octahedral structure. Anionic dye (MO) can be attracted to the surface of LDH as well as intercalated between the layers to compensate the positive charges generated by the replacement of metals as mentioned above. However cationic dye (CV) were only attracted to the edges of LDH containing free hydroxyl groups due to the electrostatic interaction, thus only small amount of CV can be adsorbed.

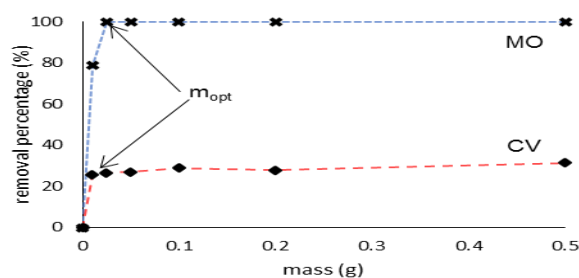


Figure 4. Effect of NAL dosage on MO and CV dyes removal

The experimental data were further tested using two isotherm models, namely Langmuir and Freundlich equations. Langmuir isotherm model assumes the adsorption takes place on homogeneous sites by monolayer adsorption while Freundlich model assumes the uptake of adsorbate occurs on heterogenous surface by multilayer adsorption [13]. The linearized Langmuir and Freundlich equations used in this study are expressed in equations (2) [14] and (3) [15], respectively.

$$\frac{Q_e}{C_e} = Q^o K_L - K_L Q_e \quad (2)$$

$$\log Q_e = \log K_F + (1/n) \log C_e \quad (3)$$

Where Q_e is the amount of dyes adsorbed per unit weight of NAL at equilibrium, C_e is equilibrium concentration of dyes, Q_o is the amount of dyes adsorbed at complete monolayer coverage, K_L is the Langmuir constant and both K_F and n are the Freundlich constants. Langmuir and Freundlich plots for both MO and CV dyes are illustrated in Figures 5 and 6, respectively. Correlation coefficients (R^2) were compared and used to evaluate the applicability of the tested isotherm models. Adsorption of MO favoured multilayer adsorption since the R^2 of Freundlich equation is higher than Langmuir equation (Figure 5). Whereas adsorption data of CV (Figure 6) fitted well with Langmuir isotherm ($R^2 = 0.9998$) which shows the adsorption process is governed by homogenous binding. The ability of anionic dye (MO) to adsorb on the layer surfaces and between the layers of LDH results in heterogeneous adsorption while the adsorption of cationic dye (CV) at the edge of LDH layers results in homogeneous attraction.

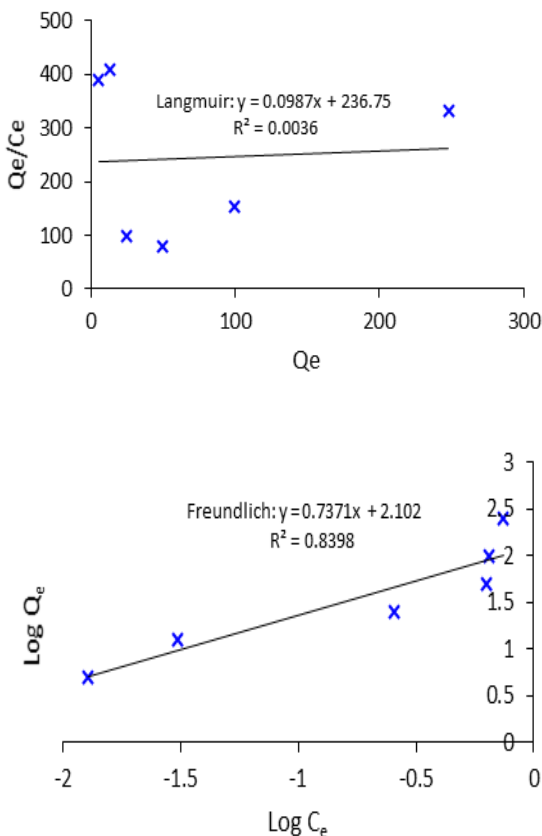


Figure 5. Langmuir and Freundlich adsorption isotherm plots for MO

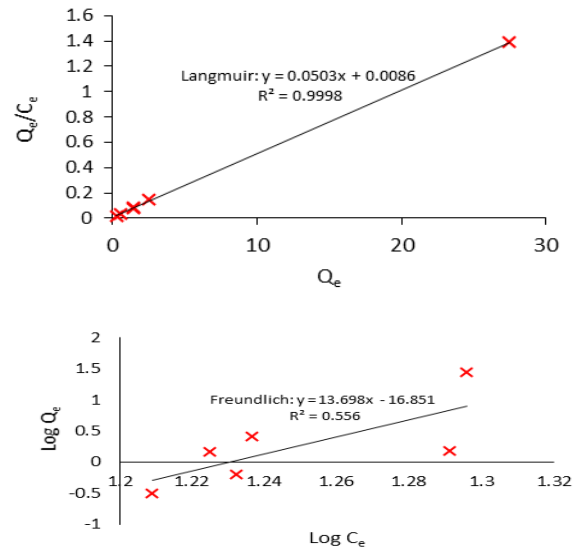


Figure 6. Langmuir and Freundlich adsorption isotherm plots for CV

IV. CONCLUSION

The LDH has the potential to be used as an adsorbent in removal of anionic and cationic dyes from aqueous solution. The experimental data shows the removal percentage of dyes by NAL is much higher for anionic dye (MO) when compared to cationic dye (CV). The mechanism of adsorption for MO dye give good fit for Freundlich isotherm while the equilibrium data for adsorption of CV dye obeys the Langmuir isotherm. It shows that the type of dye does affect the adsorption process, in which anionic dye shows heterogeneous binding while cationic dye shows homogenous binding.

V. ACKNOWLEDGEMENT

The authors are grateful to the Malaysian government for the funding (FRGS 59179) and Universiti Malaysia Terengganu for providing research facilities.

REFERENCES

1. Bi, B., et al., Heteropoly blue-intercalated layered double hydroxides for cationic dye removal from aqueous media. *Applied Clay Science*, 2011. 54: p. 242-247.
2. Rafatullah, M., et al., Adsorption of methylene blue on low-cost adsorbents: A review. *Journal of Hazardous Materials*, 2010. p. 177: 70-80.
3. Ertaş, M., et al., Removal of methylene blue from aqueous solution using cotton stalk, cotton waste and cotton dust. *Journal of Hazardous Materials*, 2010. 183: p. 421-427.
4. Vaccari, A., Preparation and catalytic properties of cationic and anionic clays. *Catalysis Today*, 1998. 41: p. 53 – 71.
5. Villegas, J. C., et al., New layered double hydroxide containing intercalated manganese oxide species: Synthesis and characterization. *Inorganic Chemistry*, 2003. 42(18): p. 5621-5631.
6. Hongo, T., et al., Synthesis and adsorption properties of nanosized Mg-Al layered double hydroxides with Cl^- , NO_3^- or SO_4^{2-} as interlayer anion. *Materials Science-Poland*, 2011. 29(2): p. 86 – 91.
7. Mamat, M., et al., Behavior of layered double hydroxides having different divalent transition metal groups. *Applied Mechanics and Materials*, 2014. 563: p. 94 – 101.

Synthesis of Nickel/Aluminium-Layered Double Hydroxide As Potential Adsorbent for Methyl Orange and Crystal Violet Dyes

8. Li, K.W., et al., The pH effects on the formation of Ni/Al nitrate form layered double hydroxides (LDHs) by chemical precipitation and hydrothermal method. *Materials Chemistry and Physics*, 2010. 121: p. 223 – 229.
9. Abdolmohammad-Zadeh, H., et al., Nickel-aluminium layered double hydroxide as a nanosorbent for selective solid-phase extraction and spectrofluorometric determination of salicylic acid in pharmaceutical and biological samples. *Talanta*, 2011. 84: p. 368-373.
10. Gullipali, CH. S., et al., Batch study, equilibrium and kinetics of adsorption of selenium using rice husk ash (RHA). *Journal of Engineering Science and Technology*, 2011. 6(5): p. 586-605.
11. As'ari, R., et al., Kinetic study of palm oil adsorption onto acetylation treated oil palm mesocarp fiber. *Journal of Applied Sciences Research*, 2015. 11(24): p. 22-26.
12. Mary, P.P., et al., Adsorption of copper (II) ions from aqueous solution on carbons from morinda citrifolia bark. *World Journal of Pharmaceutical Research*, 2015. 4(5): p. 1246-1253.
13. Ansari, R. and Mosayebzadeh, Z., Removal of Eosin Y, an Anionic dye, from aqueous solutions using Conducting Electroactive Polymers. *Iranian Polymer Journal*, 2010. 19(7): p. 541 – 551.
14. Li, Q., et al., A comparative study on the properties, mechanisms and process design for the adsorption of non-ionic or anionic dyes onto cationic-polymer / bentonite. *Journal of Environmental Management*, 2010. 91: p. 1601-1611.
15. Mittal, A., et al., Batch and Bulk Removal of a Triarylmethane Dye, Fast Green FCF, from Wastewater by Adsorption Over Waste Materials. *Journal of Hazardous Materials*, 2009. 163: p. 568 – 577.