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PREPARATION OF LAYERED DOUBLE HYDROXIDES WITH DIFFERENT DIVALENT METALS FOR THE ADSORPTION OF METHYL ORANGE DYE FROM AQUEOUS SOLUTIONS

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ABSTRACT

In this study, layered double hydroxides (LDHs) with different divalent metal cations were prepared and then utilized as adsorbent for the removal of dye from aqueous solutions. LDHs are positively charged lamellar solids consisting of divalent and trivalent metallic cations and exchangeable interlayer anions. The potential combinatorial series of M/aluminum (M=Ca, Mn and Zn) LDHs for the removal of methyl orange (MO) dye from aqueous solutions were investigated. LDHs were synthesized via a co-precipitation method and characterized using powder X-Ray diffraction (PXRD) and Fourier-transform infrared spectrophotometer (FTIR). The LDHs were then used as adsorbent for the removal of MO dye at different LDH dosages. As the LDH dosage increased, the removal percentage of MO dye also increased. CaAl, MnAl and ZnAl LDHs were able to adsorb up to 96.6%, 97.9% and 99.8% of MO dye, respectively, after being put in contact with the LDHs for 24h. Their adsorption ability was further analyzed by using Langmuir and Freundlich isotherm models in which the adsorption mechanism was determined. Adsorption of MO by CaAl, and ZnAl LDHs was governed by the Langmuir isotherm model while the adsorption data for MnAl LDH was found to fit well with the Freundlich isotherm model.

Keywords: Adsorption; Anionic clay; Methyl orange dye; Layered double hydroxide

1. INTRODUCTION

Anionic clay, layered double hydroxide (LDH), is a synthetic clay mineral that can be easily synthesized in the laboratory. LDH is a synthetic solid with positive charged brucite-like layers of mixed metal hydroxides separated by interlayer hydrated anions (Lafi et al., 2016). It consists of piles of positively-charged metal cations octahedrally surrounded by oxygen in the form of a hydroxide group (Figure 1). Through edge sharing, this octahedral unit forms infinite sheets and stack of layers which give rise to a positive charge that requires the existence of interlayer anions to retain the overall neutrality charge.

The chemical structure of LDH can be portrayed by the general formula (Peligro et al., 2016)

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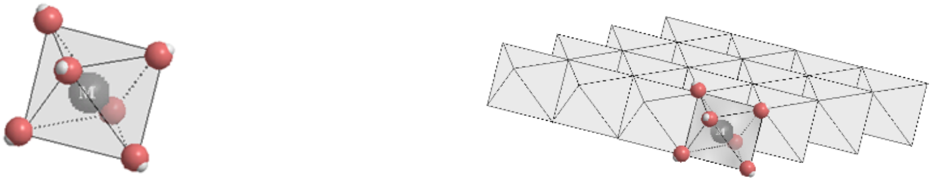

(a) (b)

Figure 1 Structure of LDH: (a) metal (M) octahedrally surrounded by a hydroxide group; (b) Edge sharing of octahedral units forming infinite sheets

$$[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}A^{n-}_{x/n}.mH_2O$$

where M^{2+} is the divalent ion, M^{3+} is the trivalent ion and A^{n-} is the interlayer anion. Due to the high charge density of the sheets and the exchangeability of the interlayer anions, many studies have been conducted on the removal of heavy metals (Peligro et al., 2016), dyes (Saiah et al., 2009) and oil (Wang et al., 2016). Several studies have examined LDHs and their derivatives as low budget adsorbents, which are promising for the remediation of dyes. LDHs are seen as potential adsorbents for wastewater treatment in the future (Zubair et al., 2017). LDHs have relatively weak interlayer bonding, which gives them an outstanding ability to trap organic and inorganic anions (Goh et al., 2008).

Methyl orange (MO) dye is an acid azo dye that is classified as an anionic dye. It may be released into the environment through the discharge of wastewater due to its wide range of applications, such as pH indicator, textile dyestuffs, paper printing, cosmetic dyes and more (Teixeira et al., 2014). MO has moderate mobility in soil due to its ionic nature, which helps it cling to clay particles in soil by ion exchange processes and leads to adsorption on sediment surfaces (Chequer et al., 2013). It is found to be nonvolatile in water due to its ionic nature and aerobic non-biodegradability; hence, it will persist in water for a long period, lead to bioaccumulation (Teixeira et al., 2014) and can cause stress to aquatic organisms (Zaharia et al., 2009). The molecular structure of MO dye is shown in Figure 2.

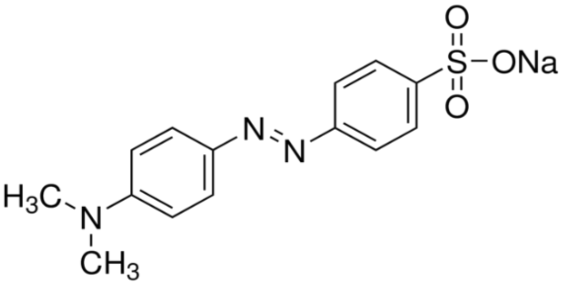

Figure 2 Molecular structure of MO dye

In this study, we report the synthesis of novel LDHs with different divalent metals: Ca, Mn and Zn. Since LDH materials exhibit different stabilities in pH range (Wang & Gao, 2006) and metal ratios, it is difficult to synthesize LDHs with the same pH and ratio. Therefore, the LDHs in this study were prepared at different ratios and pH values. The synthesized LDHs were then used as potential adsorbents for the removal of MO dye from aqueous solutions.

2. EXPERIMENTAL AND METHOD

2.1. Synthesis and Characterization of LDHs

All the chemicals utilized in this study were used as received from the suppliers without further purification. The chemicals involved were aluminum nitrate nonahydrate [$Al(NO_3)_3.9H_2O$, Merck], calcium nitrate hexahydrate [$Ca(NO_3)_2.6H_2O$, Merck], manganese nitrate tetrahydrate [$Mn(NO_3)_2.4H_2O$, Merck], zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$, Bendosen], sodium hydroxide [NaOH, Merck] and methyl orange [$C_{14}H_{14}N_3NaO_3S$, Sigma Aldrich].

All LDHs were prepared via a co-precipitation method. The solution of 2M NaOH was added dropwise into the mixed nitrate solution of M^{2+}/Al^{3+} ($M^{2+} = Ca^{2+}, Mn^{2+}, Zn^{2+}$) at a preset molar ratio until the mixture reached the constant appointed pH, as shown in Table 1. The process was performed under N_2 flow while the solution was stirred constantly. The resulting slurry was aged at 70°C for 18 hours. The precipitate was filtered, washed with distilled water and dried in an oven at 70°C. The obtained sample were then ground into fine powder and kept in sample bottles for further use as adsorbent for methyl orange dye. The synthesized LDHs were characterized by powder X-ray diffractometer (PXRD) using a Rigaku Miniflex II desktop X-ray diffractometer and a Fourier-transform infrared spectrophotometer (FTIR), a Perkin Elmer Spectrum 100 FT-IR spectrophotometer in the range of 4000–400 cm^{-1}.

Table 1 Preset molar ratio and pH of LDHs

LDH	Group of M^{2+}	Ratio of M^{2+}/Al^{3+}	pH
CaAl	2	4	12
MnAl	7	2	8
ZnAl	12	3	7

2.2. Adsorption Studies

Adsorption studies were performed using a batch method to evaluate the ability of LDHs as adsorbent for MO dye. The different dosages of LDHs (0.01, 0.025, 0.05, 0.1, 0.2 and 0.5 g) were put in contact with a 150 ppm MO dye solution and were then shaken with a Thermolyne Big Bill orbital shaker at 100 rpm for 24 hours. The remaining MO dye concentrations were determined by using a UV-Vis spectrophotometer (Shimadzu Model: UV-1601 PC UV/Visible spectrophotometer).

3. RESULTS AND DISCUSSION

3.1. Characterization of LDHs

The diffraction planes in the X-ray diffractograms (Figure 3) of the synthesized LDHs were indexed on the basis of a hexagonal unit cell with $R\bar{3}m$ rhombohedral symmetry (Zheng & Chen, 2017). All of them have typical XRD patterns with sharp and symmetrical peaks at the lower 2θ angle, showing that the LDHs have well-ordered layered structures with a high degree of crystallinity (Mamat et al., 2013). The basal spacing, *d* for (003) plane of LDHs depicted in Table 2, signifies the thickness of a single LDH layer and relates to the size and orientation of the interlayer anions (Olfs et al., 2009), which in this study are nitrate ions.

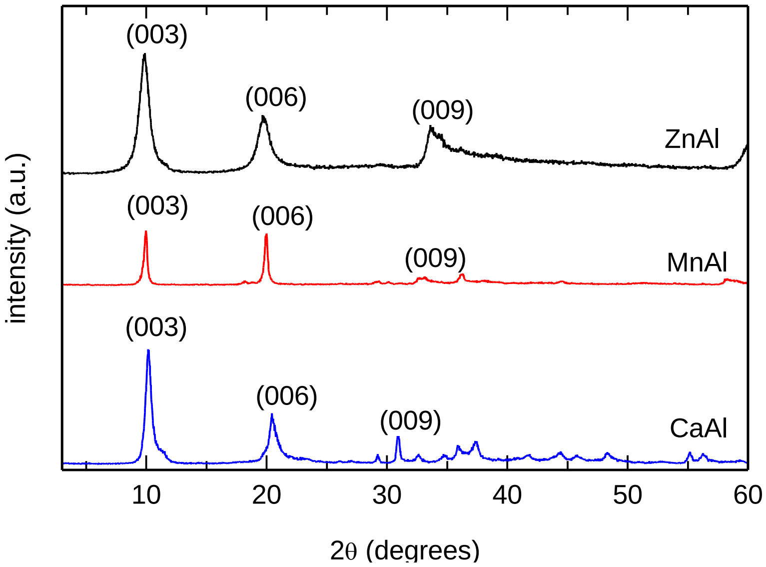

Figure 3 PXRD diffractograms for LDHs

Table 2 Relationship between the basal spacing values and divalent metal cations of LDHs

LDH	Group of M^{2+}	Type of M^{2+}	Basal spacing, *d* (nm)	*Ionic radii of M^{2+} (nm)
CaAl	2	Ca^{2+}	0.87	0.100
MnAl	7	Mn^{2+}	0.89	0.083
ZnAl	12	Zn^{2+}	0.90	0.074

*Ionic radii in octahedral coordination (Shannon, 1976)

Although all the LDHs have nitrate in the interlayer region, the basal spacing is slightly different. This is due to the different ionic radii of divalent metal ions used in the LDHs (Table 2). The oxygen atom in the metal-hydroxide (M–OH) octahedral structure is bound preferentially to a metal cation in the LDH layers with a small radius, making the hydrogen ion more easily dissociated from the oxygen atom (El Shafei, 1996). The effect weakens the bonding between the layer and the interlayer anions, causing the expansion of interlayer spacing for small metal cations (Teixeira et al., 2014). The metal ion of Zn^{2+} in ZnAl LDH thus has the smallest ionic radii, as expected, and it has the highest basal spacing value followed by MnAl and CaAl. This finding is in agreement with the previous report stating that the trend of the ionic radius has a reverse relationship to the *d* values (Mamat et al., 2014).

All the synthesized LDHs have typical FTIR (Figure 4) spectra for the LDH compounds with no significant differences between them. They have a broad band centered at around 3440 cm^{-1}, which is attributed to the OH stretching mode of the inter-hydrogen bonding of the hydroxyl groups of the LDH layers and the interlayer water molecules (Wang et al., 2007; Abdolmohammad-Zadeh et al., 2011). The weak band observed at around 1623 cm^{-1} is the bending mode of water molecules while the sharp and obvious peak at 1384 cm^{-1} is attributed to nitrate anions, thus confirming the success of synthesizing the M^{2+}/Al-nitrate LDH system. The peaks observed at lower wavenumbers below 1000 cm^{-1} are attributed to the vibrations of metal-oxygen bonding (M-O, M-O-M, O-M-O) in the layers (Kloprogge et al., 2006).

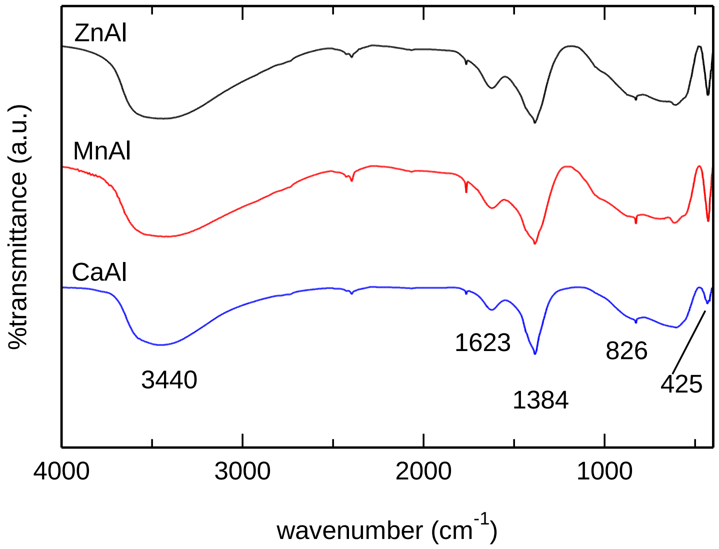

Figure 4 FTIR spectra for LDHs

3.2. Adsorption Studies

The abilities of LDHs as adsorbent towards MO dye were tested using different LDH dosages. The removal percentage of MO dye by LDHs was calculated using the following equation:

$$removal\ percentage = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

where C_o is the initial concentration (mg/L) of MO and C_e is the concentration (mg/L) of MO at equilibrium.

Generally, the removal trend for all LDHs was found to be almost similar (Figure 5). As the amount of LDHs increases, the removal percentage of MO increases due to the great availability of vacant sites, thus contributing to the larger surface area and number of adsorption sites (Gulipalli et al., 2011; As'ari et al., 2015). The removal of MO drastically increased as LDHs were introduced to the MO solution and kept increasing up to optimum mass (m_{opt}), thereafter plateauing. At m_{opt}, the LDHs surfaces were saturated with adsorbed MO, and the increase of LDHs dosage beyond m_{opt} resulted in only small increments due to the overlapping of binding sites caused by the overcrowded adsorbent particles (Pamila et al., 2015).

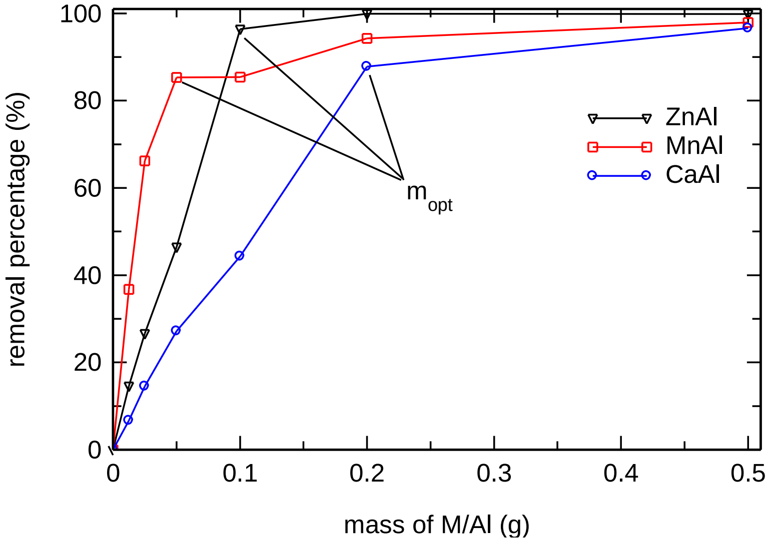

Figure 5 Adsorption of MO dye onto M/Al-LDHs

All the chosen divalent metals in the LDH system are located in period 3 of the periodic table; the size of the ionic radii of M^{2+} decreases across the period. As the size of M^{2+} in M/Al LDHs decreases, the removal percentage of MO onto LDHs increases. This is due to the increase of the effective nuclear charge (Z_{eff}) across the period and thus the decrease of the size of M^{2+}. The smaller size of M^{2+} packed in the octahedral unit of the LDH layers contributed to the higher attractive forces of LDH towards MO dye. Hence, as the amount of the LDHs increases to 0.5 g, the removal percentage of MO dye onto CaAl, MnAl and ZnAl LDHs increases (Table 3).

Table 3 Comparison of removal percentage at 0.5 g LDHs

LDH	Ionic radii of M^{2+} (nm)	Removal percentage (%)
CaAl	0.100	96.6
MnAl	0.083	97.9
ZnAl	0.074	99.8

The adsorption data were then tested using two common isotherm models, the Langmuir and Freundlich equations. The Langmuir isotherm model relates to the monolayer adsorption that takes place on homogeneous sites. As for the Freundlich model, it assumes that the multilayer adsorption of adsorbate occurs on heterogenous surfaces (Ansari & Mosayebzadeh, 2010).

The linearized Langmuir and Freundlich equations are expressed in Equations 2 and 3 (Mittal et al., 2009), respectively.

$$\frac{C_e}{Q_e} = \frac{1}{Q_\circ K_L} + \frac{1}{Q_\circ} C_e \tag{2}$$

$$\log Q_e = \log K_F + (1/n) \log C_e \tag{3}$$

where Q_e is the amount of MO adsorbed per unit weight of LDHs at equilibrium, C_e is the equilibrium concentration of MO, Q_o is the amount of MO adsorbed at complete monolayer coverage, K_L is the Langmuir constant and both K_F and n are the Freundlich constants.

Correlation coefficients (R^2) of both the Langmuir (Figure 6) and Freundlich (Figure 7) plots were compared and used to evaluate the applicability of the tested isotherm equations. Adsorption of MO onto CaAl and ZnAl fitted well with the Langmuir isotherm, showing that the process is governed by homogenous adsorption, whereas MnAl LDH favored multilayer adsorption since the R^2 of Freundlich equation is higher than for the Langmuir equation (Table 4).

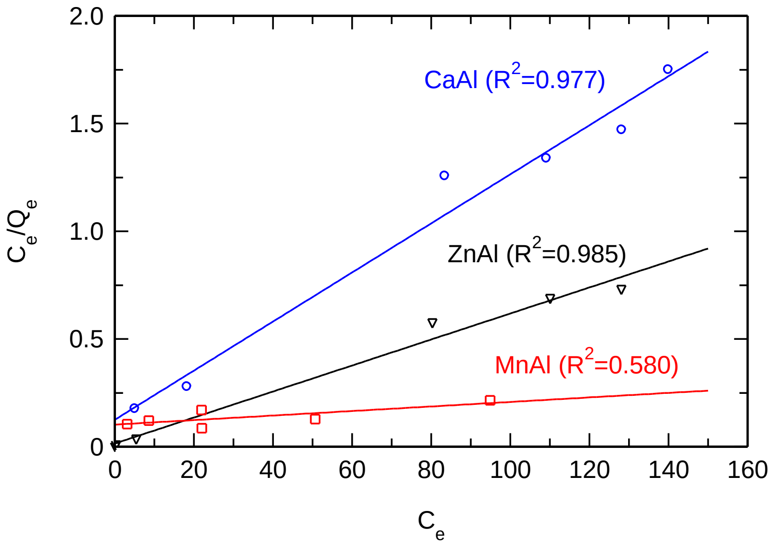

Figure 6 Fitting the data to the Langmuir isotherm model

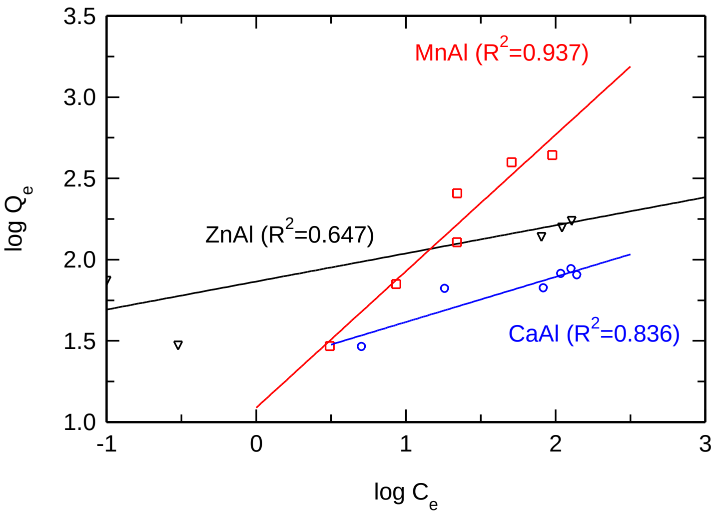

Figure 7 Fitting the data to the Freundlich isotherm model

Table 4 Comparison of R^2 values

LDH	Langmuir	Freundlich
CaAl	0.977	0.836
MnAl	0.580	0.937
ZnAl	0.985	0.647

4. CONCLUSION

The M/Al LDHs (M=Ca, Mn and Zn) were successfully synthesized via the co-precipitation method and were utilized as an adsorbent for the MO dye. The adsorption data for CaAl and ZnAl fitted well with the Langmuir isotherm model, showing that the process is governed by homogeneous adsorption, while the MnAl data fitted with the Freundlich equation due to the multilayer adsorption of MO by MnAl.

5. ACKNOWLEDGEMENT

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