



SORPTION AND REUSE OF CALCINED LAYERED DOUBLE HYDROXIDE FOR REMOVAL OF TEXTILE DYE

Syahidah Ghazali¹, Wardah Tahir² and Siti Mariam Sumari³

¹Faculty of Civil Engineering, Universiti Teknologi MARA, UiTM Shah Alam, 40150 Shah Alam, Selangor Darul Ehsan, Malaysia.

ABSTRACT

Adsorption techniques by using layered double hydroxide have been proven to be successful in removal of colors in wastewater especially in textile industries. The uptake of Reactive Orange 16 from aqueous solution by calcined layered double hydroxide (CLDH) has been investigated. CLDH was synthesized by using co-precipitation method to act as an alternative adsorbent to activated carbon which is more expensive and cannot be regenerated. The objective of this research is to investigate the regeneration efficiency of the CLDH in batch equilibrium study for Reactive Orange 16. The layered double hydroxide with Mg/Al molar ratio of 4:1 were synthesized by using co-precipitated method and their calcined product were obtained by heating at 600°C. The sorption cycle of CLDH was found out to be able to absorb Reactive Orange 16 dyes from an aqueous solution and the sorption efficiency and percentages removal were investigated. Next, the residue of the CLDH was re-calcined and the process was repeated for investigation of the percentage removal of each dyes. The results after recycling of the sorbent show that the most effective reuse of CLDH was at the second cycle with 50% removal of dye. The sorption of anions from dyes solution by structural reconstruction of CLDH was based on the special property material called as memory effects. The study proved that CLDH can be recycled and reused for dye removal effectively.

1. Introduction

The first indication of pollutant to be detected in polluted water is color (Darus *et al.*, 2007)[1]. Most industries involved in both dyes manufacturing and consumption created significant problems due to their discharges of colored wastewater. Dyes have been widely used in many industries including textile, paper printing, leather, color photography and cosmetics. However, the production of even small amounts of dyes in water is highly visible and affects the quality of water bodies. Dyes can be categorized based on their chemical structures including anionic, cationic, basic, and reactive dyes. Among these, reactive dyes are the most common type of dyes because of their distinctive properties such as bright color (Sumanjit *et al.*, 2007)[2].

Besides the effect to the environment, dyes can cause deterioration to public health. The dyes can become toxic by production that causes mutagenic and carcinogenic form (Chen *et al.*, 2003). The receiving water bodies can be affected and water supply can be contaminated when the dyes waste are discharged from the industries. Other health consequences of dye contaminated water is an allergy reactions, dermatitis, skin irritation, cancer and mutation both in babies and grown-ups (Darus *et al.*, 2007)[**Error! Reference source not found.**].

In addition, dyes problems can also cause bad impact to some of the vital activities such as fisheries, livestock, and agriculture since the water is polluted. Many regulations have been enacted to regulate the effluent discharge from the industries aiming to control and to limit several parameters in the effluent wastewater. For example, the Environmental Quality (Sewage and Industries Effluents) Regulation, 1979, limits the color present in the final discharge by the industries to 10 Hazen for the Standard A and 50 Hazen for the Standard B (Environmental Quality Act, 1974). The dyes discharges, mainly from textile industries, were often founds exceeding these limits along the other parameters such as BOD, COD, dissolved oxygen and total iron (Darus *et al.*, 2007)[**Error! Reference source not found.**].

There were several methods available for removing color from waste water which can be classified as physical, chemical and biological. The various conventional methods for removing dyes include flocculation, precipitation, ionic exchanges, membrane filtration, electrochemical destruction, irritation, ozonization, and adsorption on activated carbon

(Chaparadza *et al.*, 2011)[3]. Nevertheless, some of these methods have high cost and economic disadvantages such as the using of activated carbon. Biological color treatment utilizing fungi, bacteria or other biomass (either dead or alive) was widely accepted due to its economic advantages. However, the disadvantage for this method is the requirement for longer treatment period. Physical methods often using either membrane filtration or adsorption techniques. Based on these two methods, adsorption has been found to be superior due to the advantages it offers such as initial lower cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants (Sumari *et al.*, 2009)[4].

Adsorption technology that has been commonly applied to treat wastewater use various adsorbents such as activated carbon, peat, chitin, sludge, algae, clay, zeolite, fly ash and montmorillonite (Darus *et al.*, 2007)[**Error! Reference source not found.**]. The most common adsorbent materials used are alumina silica, metal hydroxide and activated carbon. As proven by many researchers, removal of dyes by layered double hydroxide (LDH) is economically preferable and technically easier (Yasin *et al.*, 2012)[5]. The LDH $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{m-}_{x/m-n}H_2O]$ is a compound with the hydrotacite (HT) structure. These materials consist of stacks mixed hydroxide layers of magnesium (Mg) and aluminium (Al), which are positively charged and require the presence of interlayer anions, most commonly carbonate, which can be exchanged with a wide range of inorganic and organic anion thereby the hydrotacite is also known as anionic clay. The Mg^{2+} and Al^{3+} ratio controlled the anion exchange capacity of the material (Chen *et al.*, 2006). The LDH anion exchange ability, large surface area and regeneration ability ensure that this adsorbent can be effectively utilized in wastewater purification before being discharged to water bodies. Since the LDH cost is relatively inexpensive to synthesize, it provides an alternative adsorbent to replace the expensive activated carbon.

Reactive dyes are commonly used in textile industries. The reactive dyes are important in coloring cellulosic and wool fibers. Reactive dyes typically contain chromophores combined with different types of reactive groups. They differ from all other classes of dyes in that they bind to the textile fibers to form strong covalent bonds (Zeynep *et al.*, 2005)[6]. During the coloration process, reactive dyes are combined covalently with the fibers through nucleophilic displacement.

The main objective of the study is to investigate the effectiveness of CLDH to remove the dye color in waste water, its regenerability and reuse.

2. Materials and Methods

The chemicals used in the study include Magnesium Nitrate Hydrate [$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and Aluminium Nitrate Hydrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], Sodium Hydroxide [NaOH], Nitrogen gas [N_2], Acid Hydrochloric [HCl], Reactive orange 16 dye [RO16] and deionized water.

The equipments used in this experiment are Powder X-Ray Diffractometry (XRD), Fourier Transform Infrared Spectroscopy (FTIR), UV-Visible Spectrophotometer, water bath, incubator shaker, centrifuge, hotplate stirrer, furnace, oven, volumetric flask, beaker, and microsieve 212 μ .

2.1 Preparation of LDH

LDH was prepared by using the co-precipitation method. The 5 M of sodium hydroxide (NaOH) were added until the pH water was pre adjusted to pH 10. Magnesium nitrate hydrate [$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and aluminium nitrate hydrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] solution were prepared with the total concentration of 1.0 M and the molar ratios of 4:1 of $\text{Mg}^{2+}/\text{Al}^{3+}$. The pH of 10 were maintained while the solution were added drop-wise into the vigorously-stirred deionized water in a reaction vessel. Besides that the 5 M Sodium Hydroxide (NaOH) was added simultaneously as needed until the solution reach pH 10 as also done by Wang *et al.*, (2006). Throughout the synthesis processes, this solution was kept under constant Nitrogen (N_2) gas purging flow at constant temperature at 25°C. Afterward, the resulting slurry was aged at 70°C for 24 hours in the oil bath. The precipitates were filtered and washed thoroughly with deionized water to eliminate or remove any dissolved salt until pH 7 was achieved. The resulting slurries were next dried in oven at 80°C for 24 hours. After drying, the resulting LDH was grinded and sieved into powder by using 212 micro sieves. The LDH was also calcined (heated) at temperature 600°C using a furnace. The products of Layered Double Hydroxide (LDH) and Calcined Layered Double Hydroxide (CLDH) were

kept tightly in the capped bottles for further use and characterization as also described in Sumari *et al.*,(2009)[4].

2.2 Characterization of LDH and CLDH by Powder X-Ray Diffractometer (XRD)

The powder diffraction method is ideally suitable for characterization and identification of polycrystalline phase. The X-Ray diffraction pattern of pure substances is like a fingerprint of the substance. When the X-Ray interacts with the crystalline substance, one gets a diffraction pattern. The same crystalline substance will always give the same pattern and in a mixture of substances, each substance produces its pattern independently of the others. According to Sumari *et al.*, (2009)[4], PXRD was performed by using a XRD Model PANalyticalX'Pert PRO Cu-K α radiation at wavelength, $\lambda= 1.54\text{\AA}$ at 60kV and 60mA via powder technique was determined by the solid sample mounted on alumina sample holder. Basal spacing (d spacing) of the LDH and CLDH were read from the reading of X-Ray Diffraction Pattern (Sumari *et al.*, 2009)[4].

2.3 Characterization of LDH and CLDH by Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) can be obtained by using a Perkin Elmer 1725X spectrophotometer Model Spectrum One as discussed in Sumari *et al.*,(2009)[4]. Spectroscopic grade KBr mixed was used to identify and obtain specific spectrum of LDH, CLDH, pure dye and dye loaded CLDH. This was done by mixing with the sample that was finely ground, and pressed into the disk. The spectrum sample was scanned at 2 cm^{-1} resolution between 400 and 4000 cm^{-1} . The FTIR was the method of infrared spectroscopy that was preferred by LDH and CLDH compounds.

2.4 Sorption Experiment

The sorption of Reactive Orange 16 (RO16) was studied by batch type equilibrium experiment at room temperature. The concentration dyes ranged from 100-2000 ppm were

prepared by dissolving the dye in deionized water. The pH of the solution was varied from 3.20 to 3.69 depending on the dyes concentration. The flask were shaken in a shaker at 25°C and allowed to equilibrium by leaving for 24 hours in the water bath. The suspensions were then filtered and analyzed for each dyes concentration by using ultraviolet-visible (UV-Vis) spectroscopy monitoring the each dyes adsorption peak range in 300 – 700 nm.

The amount of the adsorption Q was calculated by

$$\% \text{ Removal} = \frac{C_i - C_t}{C_i} \times 100 \quad \text{Equation (1)}$$

Where,

C_i is the initial concentration (ppm) of the RO16 dye

C_t is the concentration (ppm) RO16 of the dye in the supernatant at the equilibrium stage

$$Q = \frac{(C_i - C_t) V}{m} \quad \text{Equation (2)}$$

Where,

V is the volume of the RO16 dye solution (ml)

m is the mass of adsorbent employed (g)

(Allen *et al.*, 2003)[7].

2.5 Reuse Experiment

After the first equilibrium was achieved, the residue dry of LDH from sorption experiment was calcined at 600°C for 7 hours in the furnace. The procedure experiment of sorption was repeated to evaluate of removal of dyes in first cycle. The resulted solution was mixed with accurately weighted 0.2 g of CLDH in a secured capped bottles. The suspensions was shaken in a shaker at 25°C and allowed to equilibrium by placing in the water bath for 24 hours at 100rpm. The suspensions was then centrifuged at 3600 rpm for 10 minutes. The supernatant clear liquid was carefully pipetted and the value of the colour remaining in the supernatant liquid was measured by ultraviolet-visible (UV-Vis) spectroscopy monitoring the

each dyes adsorption peak range in 300-700 nm. In each cycle, the CLDH were filtered and repeatedly washed with deionized water. The suspensions after filtration was analyzed for each dyes concentration by using ultraviolet-visible (UV-Vis) spectroscopy monitoring each dyes adsorption peak range 300-700 nm. The residue of the CLDH was recalcined at 600°C. Next, the procedures of each sorption-reuse were repeated of each step. Finally, the CLDH was then characterized by PXRD.

2.6 Adsorption Capacity

Adsorption behavior of dye on Reactive Orange 16 (RO16) was investigated as a function of pH of the aqueous dye solution, concentration of the dye solution and adsorbent dosage. The adsorption capacity of Reactive Orange 16 (RO16) was studied by batch type equilibrium experiment at room temperature. The concentration dyes ranged from 50ppm were prepared by dissolving the dye in deoinized water. The pH of the solution was varied from 3.2 to 3.69 depending on the dye concentration. The flasks were shaken in a incubator shaker at 30°C and allowed to equilibrium, left for 24 hours in the incubator shaker. After each set of experiment, the adsorbent was recovered by centrifugation at 5,000 rpm for 5 minutes using SIGMA centrifuge. The absorbance was measured at 494nm and the concentration of the unabsorbed Reactive Orange 16 (RO16) was determined from Beer's Lamberts plot at 494nm with percentages removal of Reactive Orange 16 (RO16).

2.6.1 The pH of the Reactive Orange 16

Based on Kaur (2014)[8], all adsorption experiments were performed using 0.1 g of each adsorbent CLDH at 30°C. The objective of this experiment is to investigate the effect of pH on adsorption efficiency. The Reactive Orange 16 dye solution is 50 ppm having pH value 2,4,6,8 and 10. Each of the dye solution was treated with CLDH as an adsorbent at the equilibrium time (24hours)(Kaur and Datta ., 2014)[8].

2.6.2 Concentration of the Reactive Orange 16

Kaur (2014), investigated the effect of initial dye concentration on adsorption efficiency with Reactive Orange 16 dye solutions having 50 ppm until 300 ppm concentration range were prepared. Each of these solutions (50ml) maintained at natural pH was treated with the CLDH as a adsorbent at the equilibrium time (24hours)(Kaur and Datta ., 2014)[8].

2.6.3 Adsorbent Dosage

To study the effect of adsorbent dosage on adsorbent efficiency, 50ml of 50ppm of Reactive Orange 16 dye solution was prepared. The dye solution was maintained at natural pH with the CLDH as an adsorbent at the equilibrium time (24hours) (Kaur and Datta ., 2014)[8].

3. Results and Discussions

3.1 Characterization of LDH, CLDH and CLDH-Dye Using FTIR

The results of FTIR of CLDH and LDH are shown in Figure 1. As previously mentioned, CLDH was obtained from LDH that underwent heating at 600°C to reconstruct the material. The FTIR spectrums for CLDH show that the mono layered structure was destroyed by heating at 600°C and indicate only Magnesium Oxides (MgO) peaks. Besides, there was almost total decomposition of the Layered Double Hydroxide (LDH) and elimination of the interlayer nitrate (NO^{3+}) anions.. The infrared spectrum of LDH (Mg-Al- NO_3) resembles those of other hydrotalcite-like phase.

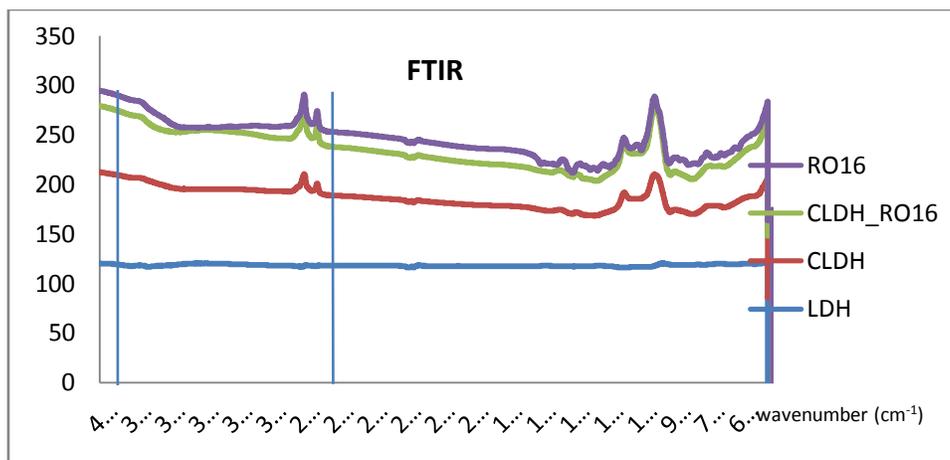


Figure 1: FTIR Spectra for LDH, CLDH, CLDH_RO16 and RO16

Figure 1 shows the FTIR spectra measured of LDH, CLDH, CLDH _Reactive Orange 16 and pure Reactive Orange 16 dye. Besides, the LDH shows broad peaks of 3465 cm^{-1} due to OH stretching and adsorbed molecules of water. The specific spectrums for the water were predominant in the regions of $3800\text{-}2600\text{ cm}^{-1}$ (OH stretching) and $1200\text{-}700\text{ cm}^{-1}$ (librations) (Wang *et al.*, 2006)[9]. The H_2O bonding band of water was observed at 1637 cm^{-1} that indicates close to that bulk water. Moreover, the nitrate (NO_3) and Magnesium Oxide (MgO) metal hydroxide stretching appeared at 1384 cm^{-1} and 590 cm^{-1} . According to Wang *et al.*, (2006)[9], the Layered Double Hydroxide (LDH) in water was observed by FTIR spectra, the presence of the strong water bands was expected and observed the OH stretching and deformations bands of the hydroxide layer and the N-O bonding band of interlayer nitrate (NO_3) ($\sim 820\text{ cm}^{-1}$). The nitrate (NO_3) and Magnesium Oxide (MgO) metal hydroxide were stretching at 1384.69 cm^{-1} and 587.29 cm^{-1} sequence. Furthermore, the FTIR spectrum of Reactive Orange 16 shows the broad peak at 3406 cm^{-1} . Similarly, the CLDH also shows the broad peak at 3467 cm^{-1} which is closed to value Reactive Orange 16 (Wang *et al.*, 2006)[9]. The asymmetric stretching vibration related to the S=O bond appears in the $1273\text{ - }1155\text{ cm}^{-1}$ region. The adsorption bands at 1674 and 1474 cm^{-1} are assigned to the stretching vibration of the C=C bond to the aromatic ring, while the bands at 1634 and 1128 cm^{-1} are assigned to those of C=O and respectively C-N bond (Elkhatabi *et al.*, 2013)[9]. Besides, the interlayer nitrate (NO_3) anions have been replaced. That shows the adsorption of dye occurs.

3.2 Characterizations of LDH, CLDH and CLDH-Dye Using XRD

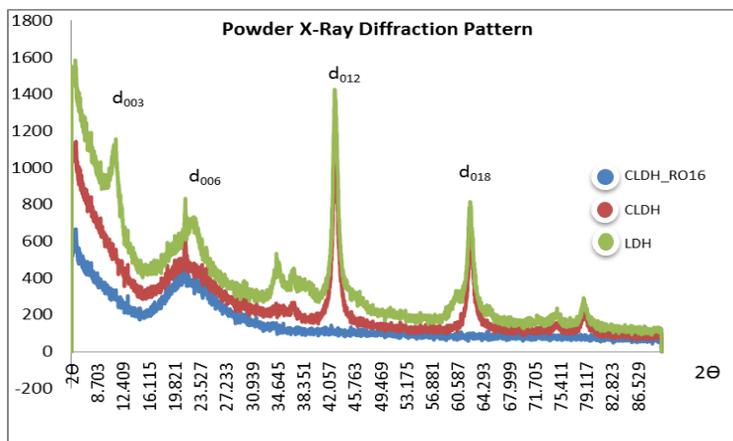


Figure 2: XRD Pattern of LDH, CLDH and CLDH_RO16

Figure 2 represents XRD patterns of Layered Double Hydroxide (LDH) before heating at 600°C, Calcined Layered Double Hydroxide (CLDH) after heating at 600°C and Calcined Layered Double Hydroxide (CLDH) loaded by Reactive Orange 16 dye. The basal spacing (d_{003}) was calculated from the average of peaks to be 4.16050 Å, 2.10569 Å and 7.85170 Å respectively for the LDH, CLDH and CLDH loaded with Reactive Orange 16 dye containing materials. The XRD pattern of the original LDH consists both sharp and symmetrical peaks with some asymmetrical peaks at high angle, indicating good crystallinity (Zhu, 2005)[11].

The XRD pattern of CLDH shows the layered of CLDH was destroyed by heating at 600°C. The peaks show the presence of the Magnesium Oxides (MgO) left in the CLDH. After Reactive Orange 16 dye sorption by CLDH, the layered structure of recovered products was reconstructed. The XRD pattern sharps peaks at 7.8517 Å were absence and replaced with the d-spacing. It is because the layered structure of the recovered products was reconstructed. The peaks become smaller and the intensity of the Calcined Layered Double Hydroxide (CLDH) peaks was become decreased. These results were indicating some decrease in crystallinity followed by calcinations and rehydration. The space between the layers of the CLDH was filled by Reactive Orange 16 dye during reaction that is why the sharp peaks of CLDH become smaller after contracting with the Reactive Orange 16 dye. This reaction process also called 'memory effect', which is the ability to regain the modified

structure of LDH after the calcinations products CLDH is exposed to water or anion in water (Sumari *et al.*, 2009)[4].

Furthermore, the adsorption process involved intercalation of anionic molecule of the dye into the CLDH structure. The intercalation of the dye anions makes an increase in the interlayer space from $d_{003} = 2.10569 \text{ \AA}$ to $d_{003} = 7.85170 \text{ \AA}$ for CLDH loaded by Reactive Orange 16 dye containing materials respectively. These results was a good evidences with values reported by other authors (Elkhatabi *et al.*, 2013)[9] and it was explained by the exchange of nitrate (NO₃) with the anions of Reactive Orange 16 dye.

According the XRD pattern, the CLDH structure was destroyed and can be evidenced only after the presence of Magnesium Oxides (MgO) at the next calcination of CLDH (Alexandrica *et al.*, 2015; You *et al.*, 2002)[12][13]. Based on the observation, there was almost total decomposition of CLDH and most of interlayer nitrate (NO₃) and Hydrogen Oxidex (OH) were eliminated. After dye adsorption process, the calcination process to make the CLDH has been reconstructed. It was also shown that the percentage of removal had become decreased compared with the first cycle.

3.3 Reuse of CLDH and the Percentages of Dye Removal

The amount of CLDH used was 0.2 g to adsorb 100 mL of 150 ppm of Reactive Orange 16. The pH was decided to be original and temperature of water bath was 25°C. The water bath was constantly was shaken at 100 rpm. All the adsorption experiment was conducted in duplicate and color remaining in solution was measured using UV Visible in which the maximum wavelength for Reactive Orange 16 dye was 494 nm. Under the effect of the calcinations temperature of CLDH the effectiveness of reuse of cycled CLDH as a sorbent was also investigated.

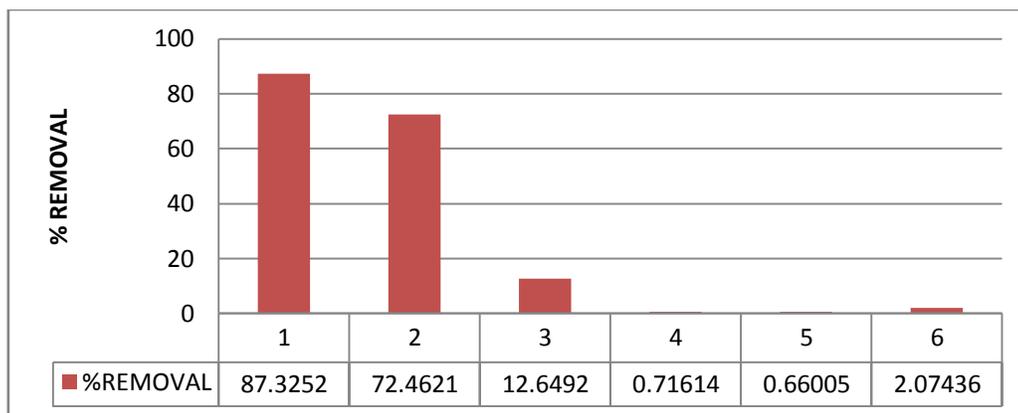


Figure 3: Percentage Removal of Reactive Orange 16 by Using CLDH for Each Cycle

As one can see, the CLDH was a very efficient sorbent for Reactive Orange 16 dyes. Figure 3 indicates that the first cycle has the highest percentages of removal of Reactive Orange 16 dye at 87.3%. After the sorption process, the dye was submitted to anion exchange with nitrate (NO_3) and calcined. The CLDH was in turn put in contact with the nitrate solution. The percentages of Reactive Orange 16 dye removal were reduced by 50% after the second cycle and that it did not change significantly subsequently. According to the results, for Reactive Orange 16 dye the 3th cycle 4th cycle have not produced significant dye removal with removal percentages of 12.6% and 0.7 % respectively. The results had agreed with the findings by Chrepaldi, et al (2002)[14] who found that the sorption capacity was decreased by 50% after the second cycle.

According to the XRD pattern, the CLDH structure is destroyed and can be evidenced only after the presence of Magnesium Oxides (MgO) at the next calcination of CLDH (Alexandria et al., 2015; You et al., 2002)[12][13]. Based on the observation, there was almost total decomposition CLDH and most of interlayer nitrate (NO_3) and (Hydrogen Oxides) OH were eliminated. After dye adsorption process, the calcination process of the CLDH has been reconstructed. It was shown that the percentage of removal had become decreased compared with the first cycle, suggesting that the cristallinity due to the calcination had decreased.

3.4 Adsorption Equilibrium Studies of Reactive Orange 16 on CLDH

3.4.1 pH of The Reactive Orange 16 on Adsorption Efficiency

There is no pronounced effect of pH Reactive Orange 16 dye on the adsorption efficiency. Based on Figure 4, the Reactive Orange 16 dye was almost 100% removed during the entire pH range studies especially at pH 10, in which almost 99.5% of dye was adsorbed by the CLDH. The effect of pH on sorption at an initial concentration of Reactive Orange 16 dye are 50 ppm and CLDH dosage 0.2 g is shown in Figure 4.

The adsorption efficiency with initial pH between 2,4,6,8 and 10 was investigated. Reactive Orange 16 sorption had increased from 98.6 to 99.5% percentage of removal. When the initial pH was at 10, the percent sorbed increased. It may be concluded that the effect of initial pH over a wide pH range (2.0–10.0) on anionic dye removal by CLDH is minimal probably due to OH⁻ release during the structural reconstruction of CLDH in aqueous environments.

The results show that the percentage removal by the CLDH with initial dye on pH 2,4,6,8 and 10 are 98.9%, 98.3%, 97.3%, 98.2% and 99.5 % respectively. The highest percentage removal of Reactive Orange 16 dye by CLDH was at pH 10. However as far as weak acid or acid dye solutions are concerned, the effect of pH on anionic dye sorption by CLDH may be insignificant because the pH values of the dye solutions are generally near 7.0. However, the effect of pH on both cationic and anionic dye sorption by many other adsorbents, for example, fly ash and acid-activated bentonite was pronounced, according to previous studies (Janos *et al.*, 2004)[15].

The difference between initial and final pH values after sorption experiments using CLDH is also shown in Figure 4. Generally, when initial pH values are lower than 10.0, final pH values can be enhanced and finally stabilized within a narrow alkaline range of 10.6–10.8. A similar phenomenon was reported by You *et al.*, (2001)[16]. This is environmentally meaningful for precipitation or co-precipitation of some co-existing metal cations like Ca²⁺, Pb²⁺ and Cd²⁺, which are attracting attention of environmental scientists (Kameda *et al.*, 2003)[17].

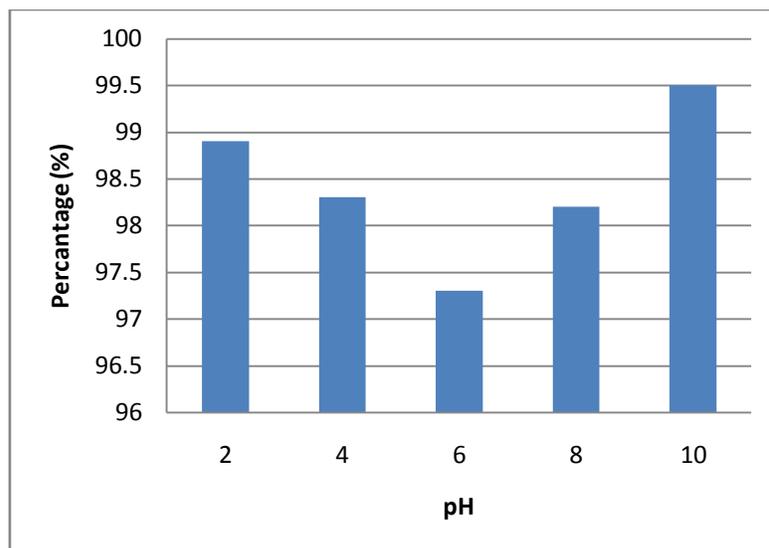


Figure 4: Percentage of Removal Reactive Orange 16 Dye for Different pH

3.4.2 Concentration of The Reactive Orange 16 on Adsorption Efficiency

Based on the results, if there is an increase in the initial concentration, the percentages removal decreases after achieving the saturation at the particular initial dye concentration if using CLDH as an adsorbent (Kaur and Datta, 2014)[8]. Figure 5 indicates that at concentration of 50ppm, 100ppm, 150ppm and 200ppm the percentages removal were higher and almost 100% that shown 96.5%, 99.4%, 99.6% and 96.2% respectively. Besides, for the low initial concentration the percentages removal almost achieves 100% removal because of the availability of the unoccupied sorption sites on the adsorbent. The adsorbent dosage of 0.1 g also effective used on initial concentration of dye between 50 – 200ppm to achieve the higher percentage removal of Reactive Orange 16 dye. Besides that, on the higher initial concentration the availability of the unoccupied sorption sites become lower. However, the increase of weight of CLDH can be used for high concentration of Reactive Orange 16 dye to achieve the effective removal for Reactive Orange 16 dye. Subsequently, percentages removal of Reactive Orange 16 dye had depended on the initial concentration of Reactive Orange 16 dye. The colour of Reactive Orange 16 dye was removed from orange to colourless. The changes of colour from Reactive Orange 16 dye to colourless depend on the concentration of Reactive Orange 16.

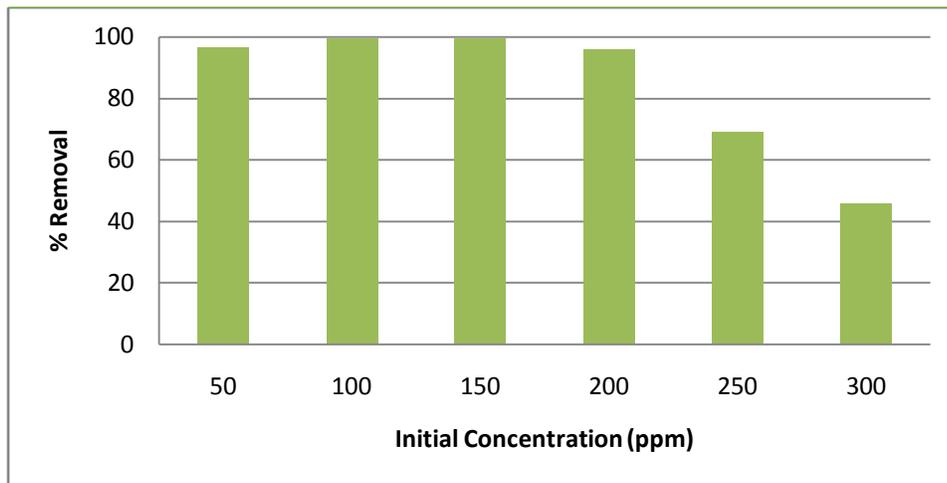


Figure 5: Percentage Removal of Reactive Orange 16 Dye for Different Initial Concentration

3.4.3 Adsorbent Dosage

The results show that if the mass of adsorbent dosage was increased from 0.1 g until 0.30 g, the percentage removal of the Reactive Orange 16 dye solution had been varying. The result on Figure 6 shows that if the dosages of CLDH were varied from 0.1 g, 0.15 g, 0.20 g, 0.25g, to 0.30 g the percentage removal of the Reactive Orange 16 dyes had varied at 99.7%, 98.9%, 95.7%, 98.6%, and 95.6% respectively. The effect of CLDH dosage on Reactive Orange 16 dye sorption was shown in Figure 6 and illustrated in Figure 7. The observation probably implies that the amount of sorption sites also increased linearly with increasing dosage of CLDH during structural reconstruction. When a 50 ppm of Reactive Orange 16 solutions was treated using 0.1 g of CLDH, the % Reactive Orange 16 sorbed can reached up to 99.7% that is almost achieving 100% removal of Reactive Orange 16 dyes.

These results suggest that CLDH are very efficient sorbents for anionic dyes and are particularly suitable to remove anionic dyes of relatively high concentrations. Efficiency of CLDH for anionic dye removal is much higher than that of most low-cost solid waste adsorbents and is somewhat higher than that of much more expensive activated carbon adsorbents produced from agricultural waste products. Efficiency of LDH is equivalent to that of some low-cost adsorbents.

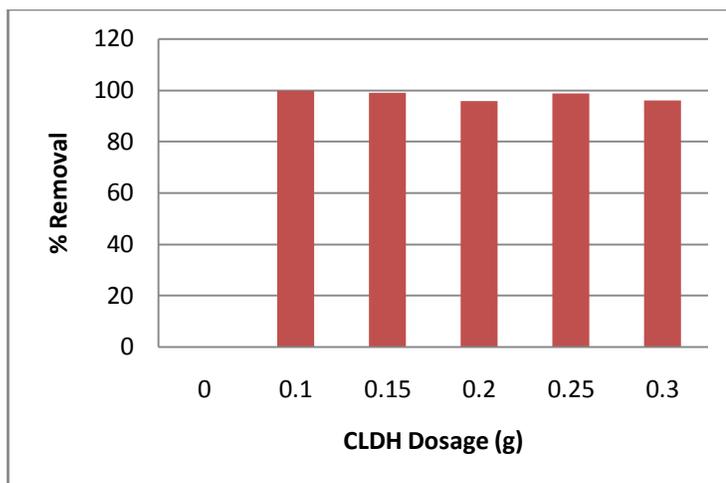


Figure 6: Percentage of Removal of RO16 for Varies Adsorbent Dosage

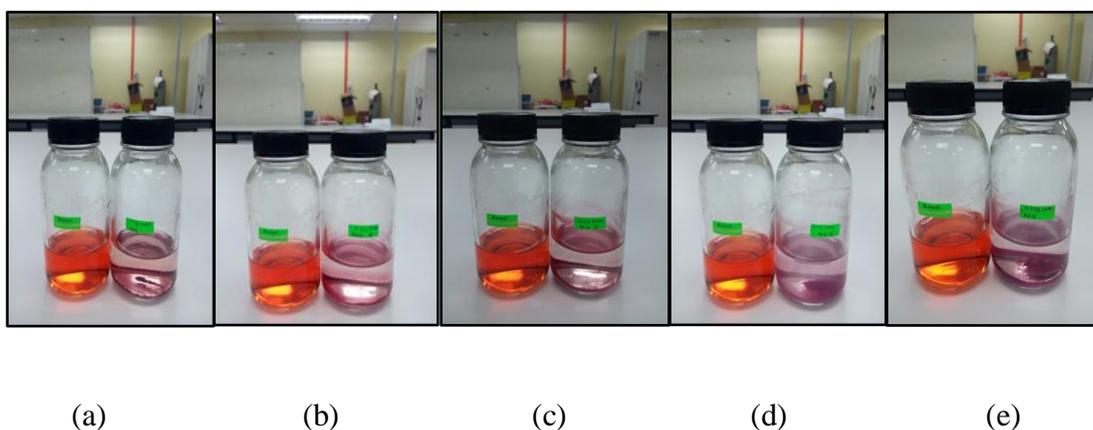


Figure 7 :Reactive Orange16 Dyes with Different Dosage of Adsorbent After 24 Hours :

a) 0.1g CLDH b) 0.15g CLDH c) 0.2g CLDH d) 0.25g CLDH e) 0.3g CLDH

4. Conclusions

In conclusion, the results had indicated a good crystalline pattern due to the appearance of sharp peaks as in the previous study of CLDH. The FTIR spectrum had confirmed the functional groups of CLDH and the differences between CLDH and LDH

The XRD pattern had shown the different pattern of peaks before CLDH made contact with Reactive Orange 16 dye and after the contact. Before the reaction between the CLDH and RO16 dyes, the peaks were clear and sharp. After the reaction, the peaks became exactly the same as the LDH peaks. It is because the dyes were entered between the layer of CLDH. As known, the structure of CLDH was double layer with space between the layer and

that area can be filled by the other molecules. These appearances of peaks were called memory effect of LDHs. This is the reason why the CLDH adsorbent can be used for the removal of colours of dyes.

The FTIR spectra had shown the differences of each band between CLDH and LDH. It had also shown the band of Reactive Orange 16 dye before and after the reaction with CLDH. The IR spectrum of CLDH and LDH had resembled those of other hydrotalcite-like phase. In addition, the broad peak at 3463 cm⁻¹ had indicated OH stretching and adsorbed molecules of water. The graph of CLDH had also shown wider and higher pattern than the LDH graph. Moreover, the graphs of the Reactive Orange 16 dye had more sharp peaks but after reacted with the CLDH, there were no sharp peaks observed.

Based on the reuse cycle results, it was found that the percentage of dyes removal was more than 50 % after the second cycle but went down to 2% after the fifth cycle. While the adsorption efficiency results had shown that the percentage of removal of Reactive Orange 16 was almost 100%. The pH behavior was not affected by the color removal. The results had also indicated that the increase of concentration will decrease the effectiveness of the 0.1g CLDH. In addition, the increasing of adsorbent dosage had shown the increasing of the removal of Reactive Orange 16 dye solution.

Finally, from the results obtained here it is possible to conclude that LDH is a highly potential alternative sorbent for dyes especially after calcinations. Based on this, the calcined material or CLDH had taken place as a fast reconstruction of the oxide with the intercalation of hydroxyl anion. The ion exchange process occurred where the changes of anion between N-O Nitrate (NO₃) with the dyes had occurred. The results indicated that the recycling of CLDH to restructure back for use in the next cycle offer potential effective alternative adsorbent for dyes removal.

REFERENCES

1. Darus, Fairus Muhamad, Rusdin Laiman, and Mohd Nizam Yusof. (2007) *The removal of basic dye (methylene blue) from aqueous solutions by adsorption on activated carbon prepared from palm oil fibre.* (2007): 1-10.
2. Sumanjit, Walia, TPS, Kaur, R. (2007) *Removal of health hazards causing acidic dyes from aqueous solutions by the process of adsorption.* Online J Health Allied Scs. 3:3

3. Chaparadza, A., Hossenlopp, J.M., (2011). *Removal of 2,4-dichlorophenoxyacetic acid by calcined Zn-Al-Zr layered double hydroxide*. J Colloid Interface Sci. 2011 Nov 1 ;363(1):92-7
4. Sumari, M., Yasin, Y., Hamzah, Z., (2009). *Adsorption Of Anionic AmidoBlack Dye By Layered Double Hydroxide, znalco₃-LDH*. The Malaysian Journal of Analytical Sciences, Vol 13 No 1 (2009): 120-128
5. Yasin, Y., Hafiz, A.M., and Sumari, S.M., (2010). *Adsorption of eriochrome black dye from aqueous solution onto anionic layered double hydroxides*. Oriental Journal of Chemistry Vol. 26(4), 1293-1298 (2010)
6. Zeynep, X., Chu, X., Jigong, Zhang, Y., Li, G., Yin, Q., and Ding, A., (2010). *Single calcination synthesis of polychlore free Pb(Mg_{1/3} Nb_{2/3}) O₃ powder using particle coating method*. J. Am. Ceram. Soc., 93[1] 18-21
7. Allen, S.J., Gan, Q., Matthews, R., Johnson, P.A., (2003). *Comparison of Optimised Isotherm Models for Basic Dye Adsorption by Kudzu*. Bioresource Technology, 88 (2003) 143-152.
8. Kaur, M., and Datta, M., (2014) *Adsorption behavior of Reactive Red 2 (RR2) Textile Dye Onto Clay : Equilibrium and Kinetic Studies*. Eur. Chem. Bull, 3(8), 838 - 849
9. Wang, S.L., Wang, P.C., (2006). *In Situ XRD and ATR-FTIR study on the molecular orientation of interlayer nitrate in Ma/Al layered double hydroxide in water*. Colloid Surf A 2007;292:131
10. Elkhatatabi, E.H., Lakraimi, M., Bedreddine, M., Legrouri A., Cherkaoui O., Berraho M., (2013). *Removal of Remazol Blue 19 from wastewater by zinc aluminium chloride layered double hydroxide*, Applied Water Science, 3, 431 – 438.
11. Zhu, M. X., Li, Y. P., Xie, M., Xin, H Z., (2004) *Sorption of an anionic dye by uncalcined and calcined layered double hydroxides*: Journal of Hazardous Materials B120 (2005) 163–1
12. Alexandrica, M. C., Sillion, M., Hrtcu, D., Popa M.I., (2015) *Layered Double Hydroxides as Adsorbents for anionic Dye Removal from Aqueous Solutions*. Environmental Engineering and Management Journal. Vol 14. No 2. 381-388
13. You, Y., Zhao, H., Vance, G.F, (2002) *Adsorption of dicamba (3,6-dichloro-2-methoxy benzoic acid) in aqueous solution by calcined-layered double hydroxide*, Appl. Clay Sci. 21 217–226.

14. Crepaldi, E.L., Tronto, J., Cardoso, L.P., Valin, J.B., (2002). *Sorption of terephthalate anions by calcined and uncalcined hydrotalcite-like compound*. *Colloids and Surfaces A Physicochemical and Engineering Aspects* 211(2-3):103-114 .
15. Janořs, P., Buchtov'a, H., R'yznarov'a, M.,(2004) *Sorption of dyes from aqueous solutions onto fly ash*, *Water Res.* 37 4938–4944.
16. You, Y., Vance, G.F., Zhao, H., (2001) *Selenium adsorption on Mg–Al and Zn–Al layered double hydroxides*, *Appl. Clay Sci.* 20 13–
17. Kameda, T., Yoshioka, T., Mitsuhashi, T., Uchida, M.,(2003) A. Okuwaki, *The simultaneous removal of calcium and chloride ions from calcium chloride solution using magnesium–aluminum oxide*, *Water Res.* 37 4045–4050.