Synthesis and modification of Zn-Al LDHs for the adsorption of cationic and anionic dyes and phosphates

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Abstract

Phosphates and dyes are two common water pollutants. The discharge of excess phosphates results in eutrophication, while the discharge of dyes into water bodies leads to pollution, making the water unsafe for consumption. Thus, there is a need to remove both phosphates and dyes from water bodies. This study proposes the use of Zn-Al Layered Double Hydroxides (LDHs) to adsorb both dyes and phosphates. In this study, chloride intercalated Zn-Al LDHs which can adsorb anionic species such as methyl orange and phosphate were synthesised by co-precipitation. The Zn-Al LDH was modified with sodium dodecyl sulfate (SDS) to allow it to remove cationic dyes such as methylene blue. The LDHs synthesized were characterised using Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). The effects of initial dye and phosphate concentration and pH on adsorption by the LDHs were studied. Reusability tests were also carried out on methyl orange to evaluate the efficacy of the LDHs after continuous cycles of regeneration. Zn-Al LDH has a maximum adsorption capacity of 1110 mgg^{-1} and 262 mgg^{-1} on methyl orange and phosphate respectively, outperforming several other LDHs. Modifying the Zn-Al LDH with SDS enhances its maximum adsorption capacity on methylene blue, attaining a maximum adsorption capacity of 149 mgg^{-1} which is greater than several other LDHs. Zn-Al LDH is able to remove more than 95% of both methyl orange and phosphate at pH 4 and above. Both Zn-Al LDH and SDS-Zn-Al LDH show great potential to be used to remove dyes and phosphate from industrial effluent.

1. INTRODUCTION

Rapid population growth and industrialisation have resulted in the large-scale pollution of water bodies with various pollutants via wastewater discharge (Yassen & Scholz, 2018). Textile industries are a major culprit of water pollution as they release undesirable dye effluents. Dyes such as methyl orange and methylene blue are widely used in textile, paper and pharmaceutical industries and are often discharged into water bodies (Edris, Zarei, Nadi & Mohammad, 2014). Wastewater containing these dyes is toxic, carcinogenic and mutagenic to life forms mainly due to carcinogens like benzedrine, naphthalene and other aromatic compounds (Carmen & Daniela,

2012). Thus, this has resulted in high cancer rates and diseases such as diarrhea in many communities that rely on such water bodies.

Eutrophication of water bodies is another major environmental problem. Water bodies are polluted with phosphate ions due to sewage discharge and fertiliser runoffs (Maryna, 2016). Phosphorus is a key element causing eutrophication, which leads to the excessive growth of algae (Subha, Sasikala, & Muthuraman, 2015). This directly affects water quality and harms aquatic life through oxygen depletion. Consequently, the removal of phosphates from surface waters is necessary. Waste containing phosphates must meet the maximum discharge limits, which is typically between 0.5 and 1.0 mg P/litre (Subha, Sasikala, & Muthuraman, 2015).

The conventional methods for treating dye-containing wastewater are coagulation, flocculation, reverse osmosis and adsorption on various adsorbents. Adsorption by activated carbon is the preferred method because of its efficiency, capacity and scalability for commercial usage (Mattson & Mark, 1971). However, activated carbon is expensive, which limits its application. On the other hand, major treatment processes to remove phosphate from water include ion exchange, chemical precipitation, biological treatment, and adsorption (Jiang, & Wu, 2010; Long et al., 2011). However, both biological treatment and chemical precipitation require high operational costs. Chemical precipitation results in the problem of sludge handling while biological treatment is slow and not effective due to variability in temperature of wastewater that would make the execution of this process inaccessible for wastewater treatment (Long et al., 2011).

Layered double hydroxides (LDHs) are naturally occurring and synthetic anionic clays, in which divalent cations within brucite-like layers are replaced with trivalent cations. The general chemical composition of LDHs can be described by the following formula (Goh, Lim, & Dong, 2017):

$[M^{2+}_{(1-\alpha)}\ N^{3+}(OH)_2]^{\alpha+}[A^{n-}]_{\alpha/n} \bullet mH_2O$, where M^{2+} is the divalent cation, N^{3+} is the trivalent cation, A^{n-} is the interlayer anion and α is the molar ratio of $N^{3+}/(M^{2+}+N^{3+})$.

The resulting positive charge is balanced by hydrated anions found in the interlayer space between the brucite sheets (Cai et al., 2012). One application of LDHs is their ability to be used as sorbents for the removal of anions from aqueous solutions (Theiss, 2012). There has been an increasing interest in the synthesis of layered double hydroxides (LDHs) in the past few years due to its flexibility, low operational costs, ease of operation as well as the possibility to recover phosphate, which can be used in biological fertilizers, as researchers have already pointed out that the world's phosphate reserves may be depleted before 2050 (Theiss, 2012).

While many studies have used CO_3^{2-} as their intercalated anion, few have used Cl^- ions (Forano, 2004). In addition, conventional LDHs synthesized by co-precipitation are hydrophilic and have a low affinity for organic pollutants including dyes (Fernandez et al., 2017).

Objectives

This study proposes the use of chloride intercalated Zn-Al LDH as a novel method to adsorb both dyes and phosphates. In order to adsorb organic dyes, the LDH will be modified with sodium dodecyl sulfate (SDS). The effectiveness of the Zn-Al LDH in the removal of anionic methyl orange dye and phosphates ions, as compared to other studies was investigated. In addition, the effectiveness of the modified SDS-LDH in the removal of cationic methylene blue compared to other studies was investigated. Finally, the effect of pH, and initial concentration of dye/phosphate on their adsorption by LDH was investigated.

Hypothesis

This study hypothesizes that the Zn-Al LDH intercalated with Cl^- ions can be modified with sodium dodecyl sulfate (SDS). Zn-Al LDH is comparable to other studies in the removal of methyl orange dye and phosphates. SDS-Zn-Al LDH is comparable to other studies in the removal of methylene blue dye.

2. MATERIALS & METHODS

2.1 Materials

Zinc chloride, aluminium chloride, sodium hydroxide, and sodium dihydrogen phosphate were procured from GCE Chemicals. SDS (sodium dodecyl sulfate) is purchased from Sigma Aldrich.

2.2 Synthesis of Zn-Al LDH

A solution (150ml) containing 0.2 mol of $ZnCl_2$ and 0.1 mol of $AlCl_3$ was slowly added to a second solution containing 300 ml of 2.0 mol dm^{-3} NaOH by a burette for 150 minutes under constant vigorous stirring at 250 rpm at room temperature. After the mixing, a thick slurry was obtained. It was then aged at 85^{o}C for 2 hours using a hot plate. After the ageing process, the precipitates were centrifuged, filtered, washed with deionized water and dried in an oven until constant mass. The Zn-Al LDH obtained was then crushed into a powder using mortar and pestle.

2.3 Modification of Zn-Al LDH

The Zn-Al LDHs were modified with SDS ($CH_3(CH_2)_{11}SO_4Na$) by reconstruction method. Zn-Al LDHs were calcined at 450 °C for 2 hours to destroy the layered structure. 1g of LDH was added to 50 ml of 0.500 mol dm^{-3} SDS and the mixture was stirred at room temperature for 24 hours.

SO_4^{2-} anions in the SDS were exchanged with the Cl^- anions to be intercalated between layers of cations.

2.4 Batch Adsorption Studies

20 ml of dye or phosphate of varying concentrations (from 200 ppm to 1200 ppm) were stirred with 0.020g of LDH/SDS-LDH for 24 hours. The mixture was centrifuged, and the supernatant was obtained. The remaining concentration of the dye was then determined using a UV-VIS Spectrophotometer (Shimadzu UV1800) at 664 nm (for methylene blue) and 465 nm (for methyl orange). The remaining concentration of phosphate was determined using a colorimeter (HACH DR 890). The adsorption capacity was then calculated using the formula below.

$$q_e = \frac{(C_0 - C_e)V}{m}$$

C_o = initial dye/phosphate concentration in mgL^{-1};
C_e = equilibrium dye/phosphate concentration in mgL^{-1};
m = mass of LDH used (in g) and V = volume of dye/phosphate used (in L)

To determine the adsorption mechanism and maximum adsorption capacity, the equilibrium concentration data was fitted into two most common isotherms – Freundlich and Langmuir isotherms (Appendix, page 14 to 17).

2.5 Effect of pH

20 ml of 50 ppm concentration of dyes/phosphates at pH 2, 4, 6, 8,10 were mixed with 0.020g of LDH for 24h. pH was adjusted using HCl and NaOH. Adsorption was carried out as described in section 2.4. The remaining concentration of dye or phosphate was then determined and percentage removal (%) was calculated

2.6 Reusability tests

LDH was regenerated through calcination at 400°C. LDH was then reused to adsorb 50 ppm of dyes/phosphates. Remaining concentration of the dye or phosphate was then determined and percentage removal was calculated. A total of 4 cycles of regeneration were carried out.

3. RESULTS AND DISCUSSIONS

3.1 Characterisation of Chloride Intercalated Zn-Al LDH

3.1.1 By XRD

The X-Ray Diffraction (XRD) pattern of Zn-Al LDH (figure 1) reveals two Theta peaks at 11.3°, 22.6°, 34.4°, which corresponded with the symmetrical basal reflections of the (003), (006) and (009) planes respectively. On the other hand, two Theta peaks at 38.8° and 46.0° corresponded with the asymmetrical basal reflection of the (015) and (018) planes respectively, which are

characteristic of the rhombohedral structure exhibited by the LDHs. The XRD patterns of Zn-Al LDH were similar to those reported in literature. (Qu et al., 2017), confirming the successful synthesis of Zn-Al LDH.

Figure 2 reveals two Theta peaks at 11.2º, 13.7º, 16.4º and 21.3º which correspond with the formation of a superlattice with ordered dodecyl sulfate anions intercalated between layers (Starukh, Rozovik & Oranska, 2017), confirming the successful synthesis of SDS-LDH by reconstruction.

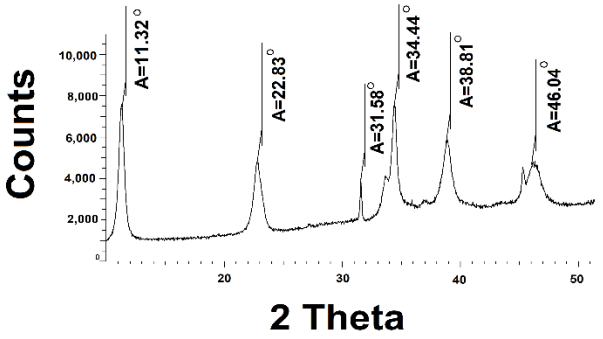

Figure 1: XRD of Zn-Al LDH

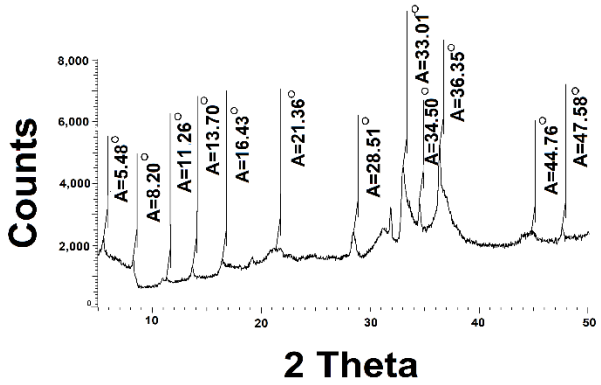

Figure 2: XRD of SDS Zn-Al LDH

3.1.2 By SEM

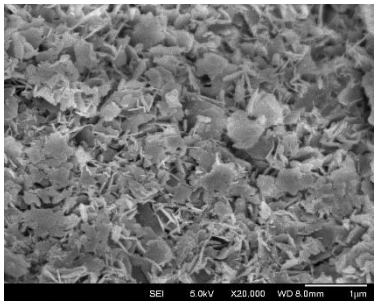

Figure 3: SEM of Zn-Al LDH

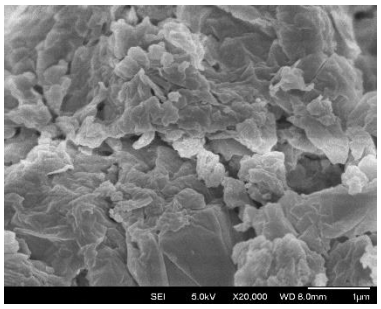

Figure 4: SEM of SDS-Zn-Al LDH

The surface morphologies of the LDHs were visualised with a Scanning Electron Microscope (SEM). The morphology of the LDHs were similar to those reported in literature (Qu et al., 2017). Both LDH have flake-like structures that form agglomerates. The particles of SDS-Zn-Al LDH are bigger than that of Zn-Al LDH.

3.2 Adsorption Studies

3.2.1 Effect of initial concentration of methyl orange (MO) and phosphate ions on the adsorption capacity of Zn-Al LDH

Figures 5 and 6 show the effect of initial concentration of methyl orange and phosphate on the adsorption capacity on Zn-Al LDH respectively. The general trend observed is that adsorption capacity increases as the initial concentration of methyl orange and phosphates increases. This could be due to the fact that as phosphate and methyl orange concentration increases, more phosphate ions and methyl orange molecules are available for sorption by the active sites of LDH.

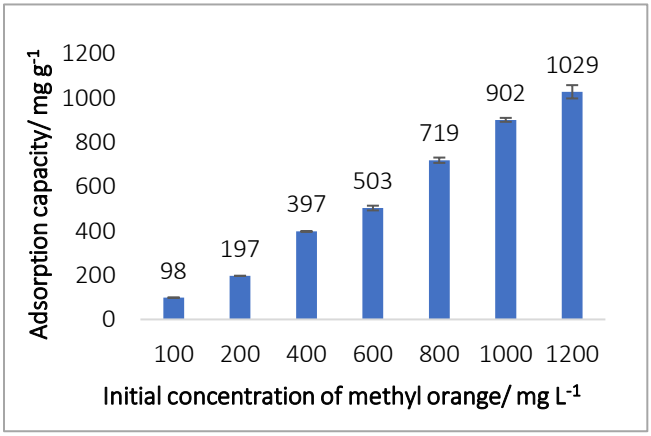

Figure 5: Effect of initial concentration of methyl orange on adsorption capacity of Zn-Al LDH

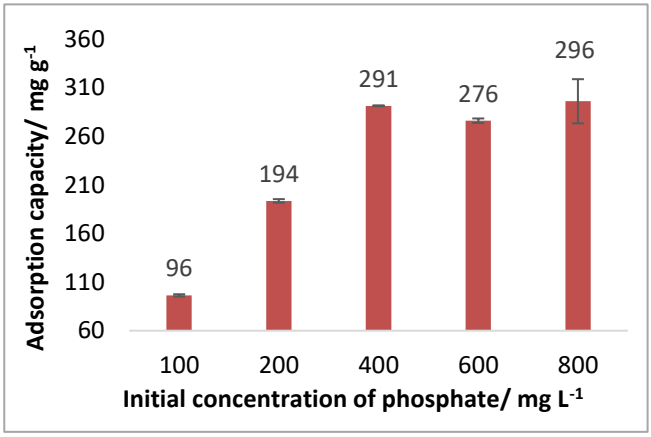

Figure 6: Effect of initial concentration of phosphate on adsorption capacity of Zn-Al LDH

LDH adsorbed methyl orange and phosphate ions through electrostatic forces of attraction as the metal cations in the LDH attract the SO_3^{2-} anions in methyl orange and the phosphate anions. Phosphate anions and methyl orange containing SO_3^{2-} can also be exchanged with the Cl^- ions intercalated within the LDH via ion exchange (Almoisheer, Alseroury, Kumar, Aslam, & Barakat, 2019). Thus, there are various pathways for adsorption to occur, increasing the efficacy of Zn-Al LDH for adsorption of methyl orange and phosphates.

Equilibrium concentration data for methyl orange and phosphate was fitted into Langmuir and Freundlich isotherm (Appendix, page 14-17). Langmuir isotherm was determined to be a better fit for the adsorption of both methyl orange and phosphate, with an R^2 value of 0.970 and 0.998 respectively. The results suggest that methyl orange and phosphates are adsorbed over a uniform adsorbent surface. The maximum adsorption capacities were then derived from the gradient of the linear plots of Langmuir isotherm and were compared with the maximum adsorption capacity of other adsorbents (Table 1 and 2).

Table 1: Maximum adsorption capacity (Q_{max}) of different adsorbents on methyl orange

Type of adsorbent	Q_{max}/(mg/g)	Reference
Zn-Al intercalated with chloride ions	1110	This study
Zn-Al intercalated with carbonate ions	684	Zheng, Li & Zhang, 2012
Zn-Al LDO	182	Ni, Xia, Wang & Xing, 2007
Modified chitosan magnetic composite	758	Yang, Qiu & Yang, 2016

LDO: Layered double oxide

Table 2: Maximum adsorption capacity (Q_{max}) of different adsorbents on phosphate

Type of adsorbent	Q_{max}/(mg/g)	Reference
Zn-Al intercalated with chloride ions	263	This study
Zn-Al intercalated with nitrate ions	78	Zhou, Yang, Yu & Shu, 2011
Ni-Al LDH	27	Yan et al., 2015
Mg-Al LDH	128	Wang & Li, 2015
Fe_3O_4-SiO_2-LDH	57	Li et al., 2020

For both methyl orange and phosphate, Zn-Al LDH synthesised in this study outperforms other forms of LDH and other adsorbents. Zn-Al LDH intercalated with chloride ions is more effective than Zn-Al LDH intercalated with carbonate ions at adsorbing methyl orange (Table 1). Similarly, Zn-Al LDH intercalated with chloride ions is also more effective than Zn-Al LDH intercalated with nitrate ions at adsorbing phosphates (Table 2). This could be due to the chloride ions having a smaller ionic radius, decreasing the interlayer spacing (Mahjoubi, Khalidi, Abdennouri & Barka, 2017), allowing more chloride ions to be intercalated between the layers, increasing the ion exchange capabilities of the LDH.

As shown in table 2, Zn-Al LDH is more effective at adsorbing phosphates compared to Ni-Al and Mg-Al LDH. This could be due to the divalent ions having affinity to phosphate in the following order $Zn^{2+} > Cu^{2+} > Mg^{2+} > Ni^{2+}$ (Almojil & Othman, 2019). Thus, Zn-Al LDH intercalated with chloride ions is the most effective at adsorbing both methyl orange and phosphates.

3.2.2 Effect of initial concentration of methylene blue (MB) on the adsorption capacity of SDS-Zn-Al LDH

Figure 7 shows the effect of initial concentration of methylene blue on the adsorption capacity on SDS-Zn-Al LDH. The general trend observed is that adsorption capacity of SDS-Zn-Al LDH increases as the initial concentration of methylene blue increases.

Dodecyl sulfate (SDS) anions occupied the interlayer regions and resulted in the formation of hydrophobic interactions between the alkyl chains of SDS and methylene blue, allowing the LDH to adsorb methylene blue(Kong, Huang, Meng, & Zhang, 2018).

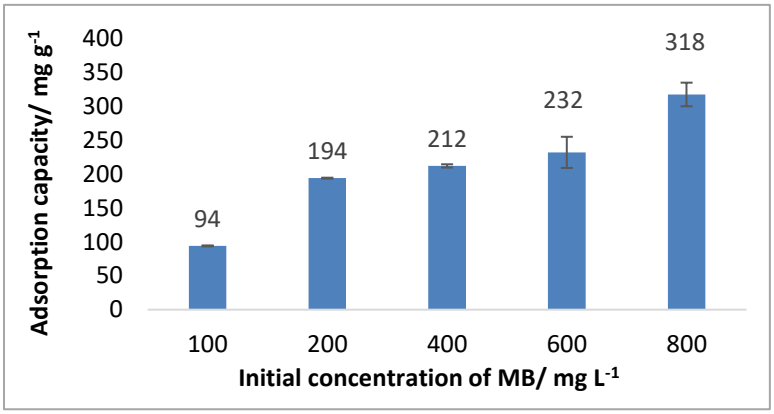

Figure 7: Effect of initial concentration of MB on adsorption capacity of SDS-Zn-Al LDH

Equilibrium concentration data of methylene blue was fitted into Langmuir and Freundlich isotherm. Langmuir isotherm was a better fit with an R^2 value of 0.947. This shows that the adsorption methylene blue was monolayer. The maximum adsorption capacity was then derived and was compared with the maximum adsorption capacity of other researchers (Table 3).

Table 3: Maximum adsorption capacity (Q_{max}) of different adsorbents on methylene blue

Type of adsorbent	Q_{max}/(mg/g)	Reference
SDS Zn-Al LDH	149	This study
Zn-Al LDH	31	Bi, Xu & Liu, 2011
SDS Mg-Al LDH with iron oxide	110	Miranda et al., 2014
Mg-Al LDH	44	Aguiar et al., 2012

The modification of LDH with SDS enhances the adsorption capacity of the LDH due to the increased hydrophobic interactions (Kong et al., 2018) as compared to Zn-Al LDH without modification. Zn-Al LDH modified with SDS also outperforms other LDHs synthesised by other researchers.

3.2.3 Effect of pH of methylene blue (MB) & phosphate solution on adsorption of methylene blue (MB) & phosphate by LDH.

As shown in figure 8, percentage removal of phosphate is lowest at pH 2. From pH 4-10, the percentage removal of phosphate remains relatively constant. There is a significant difference in percentage removal of phosphate when pH varies as the p-value of Kruskal Wallis test at a significance level of 0.05 was 0.01208 which is less than 0.05. This could be due to the disordering of the LDH structure at low pH, resulting in the leaching of Al^{3+} and Zn^{2+} ions into the solution

(Barrado, 2015), reducing the efficacy of the LDH as positively charged Zn^{2+} and Al^{3+} ions attract the negatively charged PO_4^{3-} ions through electrostatic forces of attraction.

A similar trend was observed in figure 9. Percentage removal of methylene blue was also lowest at pH 2. The difference in percentage removal when pH varies is not significant (p-value of Kruskal-Wallis test= 0.4067 >0.05). This could be due to low pH promoting hydrophilic interaction rather than hydrophobic interactions, reducing the efficacy of the SDS-LDH in adsorbing methylene blue. Additionally, large amounts of H_3O^+ ions exist at low pH which can compete with methylene blue, a cationic dye in adsorbing on the active sites of the SDS-LDH (Tang et al., 2017), resulting in a significant decrease in efficacy of the SDS-LDH in adsorbing methylene blue.

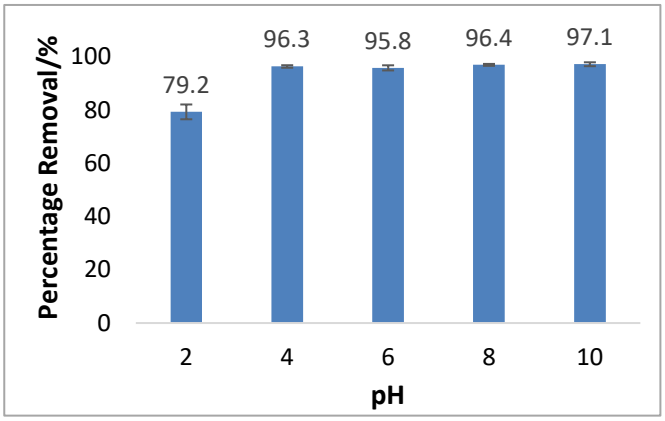

Figure 8: Effect of pH on adsorption of phosphate

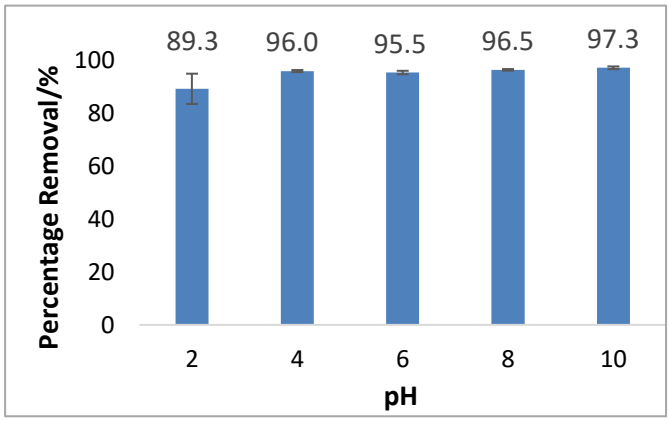

Figure 9: Effect of pH on adsorption of methylene blue

3.3 Reusability Studies

As shown in figure 10, Zn-Al LDH is able to sustain more than 95% removal of methyl orange across 4 cycles of regeneration. This is because calcination at 400 °C degrades the methyl orange intercalated between layers of the LDH. Although the high temperature breaks down the layered structure of the LDH, forming LDOs (Layered Double Oxides), due to its “memory effect”, after being added to the dyes, it was rehydrated and underwent structural reconstruction and formed LDH again, thus it can be regenerated and sustain its ability to adsorb methyl orange dye (Wang, 2019).

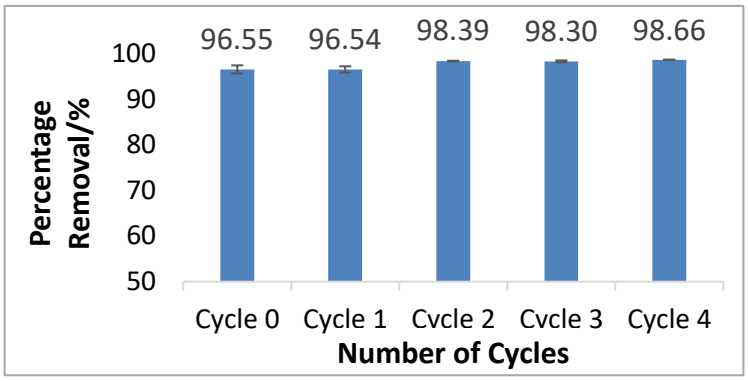

Figure 10: Effect of number of cycles of regeneration of MO on the percentage removal of methyl orange

4. Conclusion and Future Work

Zn-Al LDH has been successfully synthesized via co-precipitation reaction involving sodium hydroxide with $ZnCl_2$ and $AlCl_3$ salts in a 2:1 mole ratio. Zn-Al LDH has also been successfully modified with SDS via reconstruction method to obtain SDS-Zn-Al LDH. The adsorption of methyl orange, phosphate and methylene blue fits the Langmuir isotherm model, suggesting that the adsorption is monolayer. Zn-Al LDH has a greater maximum adsorption capacity on methyl orange dye and phosphates as compared to several other forms of LDH and adsorbents. Modifying the Zn-Al LDH with SDS enhances its maximum adsorption capacity on methylene blue. SDS-Zn-Al LDH also has a greater maximum adsorption capacity on methylene blue dye as compared to other forms of LDH. Zn-Al LDH is able to remove more than 95% of both methyl orange and phosphate at pH 4 and above. Zn-Al LDH can be modified easily to effectively adsorb both cationic and anionic dyes and phosphates and thus it is a convenient and novel alternative to conventional methods of removing dyes. In addition, Zn-Al LDH can be reused multiple times to adsorb methyl orange, rendering it a suitable and eco-friendly alternative to conventional adsorbents.

In the future, the desorption and recyclability of phosphate can be studied as phosphate reserves in the world are being depleted. In addition, the effectiveness of LDH in removing phosphate can be compared with lime, another chemical used to remove phosphate. In real life, wastewater contains more than one type of pollutant. Hence it would be interesting to find out if the presence of other pollutants would affect the ability of Zn-Al LDH in adsorbing dyes and phosphates.
Finally, both the Zn-Al LDH and SDS-Zn-Al-LDH can be incorporated into filters to remove both cationic dyes, anionic dyes and anions such as phosphate from wastewater.

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Appendix: Adsorption Isotherms of Zn-Al LDH and SDS-Zn-Al LDH

The equilibrium concentration data obtained from adsorption isotherm studies on methyl orange (MO), phosphate and methylene blue (MB) were fitted into Langmuir isotherm and Freundlich isotherm.

The Langmuir isotherm assumes that adsorbed material (such as phosphate) is adsorbed over a uniform adsorbent surface at a constant temperature.

The linear form of Langmuir isotherm equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

Where C_e is the equilibrium concentration of phosphate/MO/MB (mg/L), q_e is the equilibrium capacity of the sorbents (mg/g), b is the Langmuir constant that indicates the sorption intensity and q_m is the maximum sorption capacity (mg/g).

From the Langmuir constant, b, a dimensionless equilibrium parameter (R_L) can be obtained.

$$R_L = \frac{1}{1+bC_o}$$

Where C_o is the highest concentration (mg/L). The value of R_L indicates the type of the isotherm to be either unfavourable (R_L>1), favourable (0< R_L<1), or irreversible (R_L=0). The Freundlich isotherm assumes that the adsorption occurs on a heterogeneous surface.

The linear form of Freundlich equation is given by:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

Where C_e is the equilibrium concentration of methylene blue/methyl orange/phosphate (mg/L), q_e is the equilibrium capacity of the sorbents (mg/g), K_F, a constant, is related to sorption capacity and n corresponds to sorption intensity. The n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if n=1, then adsorption is linear; if n<1, then adsorption is a chemical process; if n>1, then adsorption is a physical process. Values of n in the range 1<n<10 also indicate favourable sorption (Mulu, 2013).

The Langmuir and Freundlich isotherm plots are shown below:

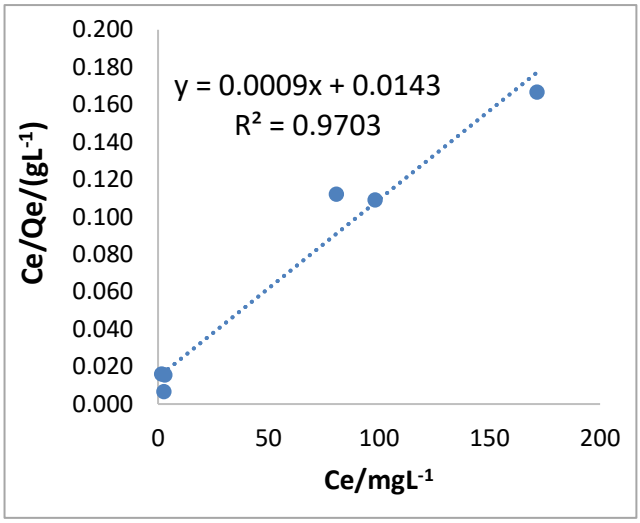

Figure 11: Langmuir isotherm for Zn-Al LDH on methyl orange

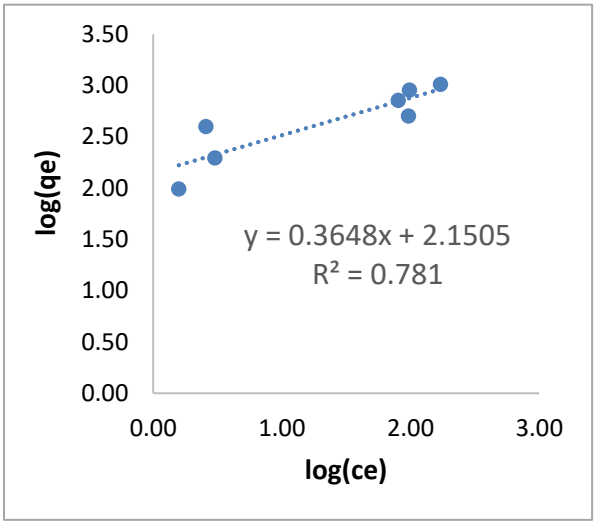

Figure 12: Freundlich isotherm for Zn-Al LDH on methyl orange

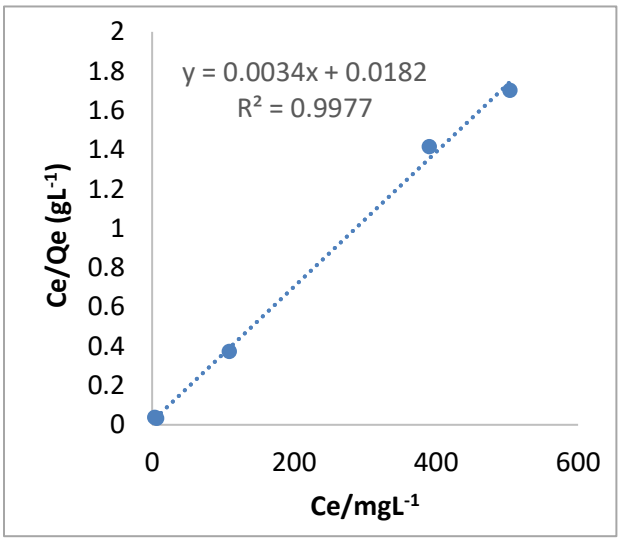

Figure 13: Langmuir isotherm for Zn-Al LDH on phosphate

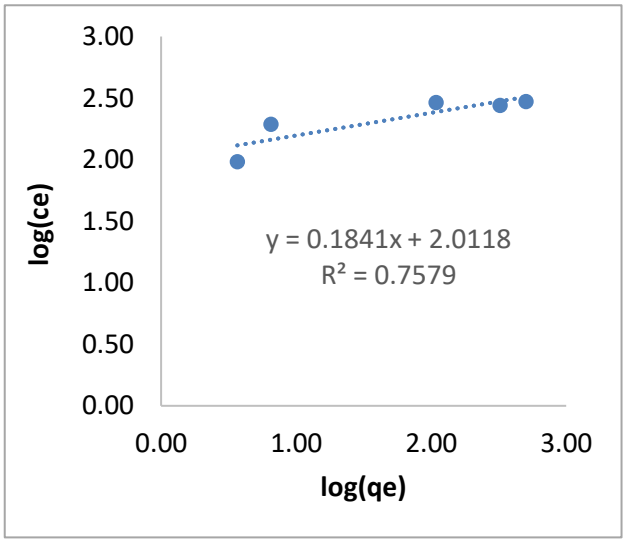

Figure 14: Freundlich isotherm for Zn-Al LDH on phosphate

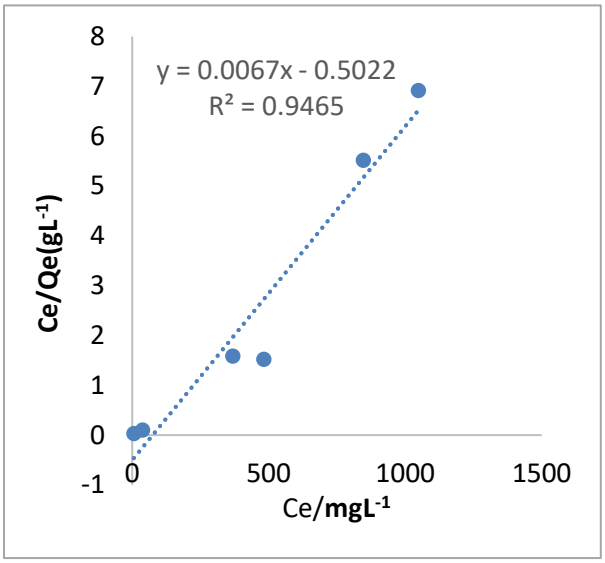

Figure 15: Langmuir isotherm for Zn-Al LDH on methylene blue

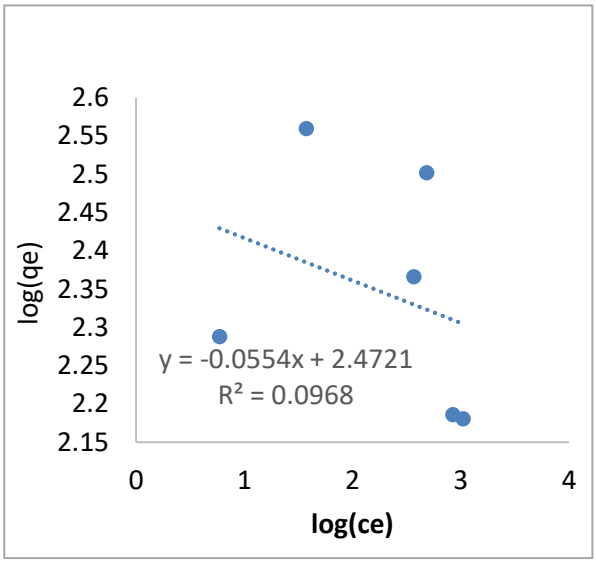

Figure 16: Freundlich isotherm for Zn-Al LDH on methylene blue

The values of b and Q_{max} were computed from the slope and intercept of Langmuir isotherm plots respectively. Similarly the values of K_F and n were computed from the intercept and slope of the Freundlich plot of $\log(q_e)$ versus $\log(C_e)$ respectively.

The isotherm parameters obtained are summarized in table 4

Table 4: Isotherm parameters for Zn-Al and SDS-Zn-Al LDH

Langmuir isotherm parameters						**Freundlich isotherm parameters**		
		Q_{max} (mg/g)	b (L/mg)	R_L	R^2	K_f $(mgg^{-1})(Lmg^{-1})^{1/n}$	n	R^2
Zn-Al LDH	Methyl orange	1110	0.0629	0.0131	0.970	141	2.74	0.7810
	Phosphate	263	0.137	0.00906	0.943	109	6.47	0.6065
SDS Zn-Al LDH	Methylene blue	149	-0.0133	-0.0668	0.947	297	-18.1	0.0968

Comparison of the coefficient of determination (R^2) of the linearised forms of both isotherms suggests that the Langmuir model yields a better fit for the equilibrium adsorption data of methyl orange, methylene blue and phosphate onto both Zn-Al LDH and SDS-Zn-Al-LDH. R_L values for Zn-Al LDH on adsorption of methyl orange and phosphate were in the range of 0-1, indicating that the Langmuir isotherm adsorption was favourable. The values of n for methyl orange and phosphate were also between 0-10, indicating that adsorption was favourable. The maximum adsorption capacity, Q_{max}, of Zn-Al LDH on the adsorption of methyl orange was the highest, followed by the Q_{max} of Zn-Al LDH on the adsorption of phosphate, and the Q_m of SDS-Zn-Al on the adsorption of methylene blue.