

Entry to the Stockholm Junior Water Prize 2019

**Novel Hybrid
Regeneration Process for Adsorbent
used in Wastewater Treatment**

Wang Haiyi

National Junior College

Country: Singapore

Summary

A waste is not considered a resource as it is contaminated with other pollutants or has too low a concentration to be considered a resource. This project looks at a novel way of synthesizing a powerful adsorbent layered double hydroxide (LDH) to purify wastewater. It also develops an innovative method called electrochemical (EC) regeneration to regenerate the adsorbed products. An optimized voltage of -0.6V has been identified to repel the intercalated pollutants out of the interlayer of LDH without causing material degradation. It demonstrated a 185% boost in recovery rate compared to conventional desorption method. This environmentally friendly process can be operated on-site since little energy is consumed. A second method, calcination is optimized as activation and regeneration method. It was discovered that LDH activated at 400°C has a remarkable adsorption capacity of 418 mg/g for Congo Red which is 60 times than that of activated carbon. Fourier Transform Infrared (FTIR) showed that the “memory effect” of LDH is triggered which accounts for the drastic increase in capacity. Exhausted LDH was regenerated afterwards and it was found that 400°C is the most suitable temperature. The reusability of LDH was studied using 400°C calcination and recovery rate was above 95% up till the 6th cycle. It reduces capacity loss per cycle by 80%. SEM images and FTIR spectrum of LDH were obtained to study the degradation mechanism. Calcination is as an effective method to be employed in regenerating exhausted LDH. This project successfully develops effective regeneration methods, thus turning wastewater and adsorbed products into resources again.

Table of Content

| | |
|--|----------|
| 1.1 Literature Review | 3 |
| 1.1 Background..... | 3 |
| 1.2 Regeneration of adsorbent | 3 |
| 1.3 Use of thin film LDH | 4 |
| 1.4 Scope and objectives | 5 |
| 2. Materials and methods | 5 |
| 2.1 Synthesis of thin film LDH | 5 |
| 2.2 Removal of pollutant..... | 6 |
| 2.3 Regeneration of LDH..... | 6 |
| 3. Results and Discussion | |
| 3.1 Synthesis of adsorbent..... | 7 |
| 3.1.1 Synthetic mechanism of thin film LDH | 7 |
| 3.1.2 Refining synthetic conditions | 8 |
| 3.1.3 Physical characterization of thin film LDH | 10 |
| 3.2 Initial adsorption of pollutants | 11 |
| 3.3 Electrochemical (EC) Regeneration | 11 |

| | |
|---|-----------|
| 3.4 Regeneration through calcination..... | 13 |
| 3.4.1 Effect of calcinations as an activation process for newly synthesized films | 13 |
| 3.4.2 Regeneration of pollutant loaded LDH at various temperatures | 14 |
| 3.4.3 Successive Regeneration at 400°C | 16 |
| 4. Conclusion and future work..... | 18 |
| 5. Reference list | 18 |

Abbreviations and Acronyms

| | |
|-----------------------------------|---|
| LDH | Layered double hydroxide |
| EC Regeneration | Electrochemical regeneration |
| Zn-Al LDH | Layered double hydroxide with Zn ²⁺ and Al ³⁺ as divalent and trivalent cations |
| Zn(NO ₃) ₂ | Zinc nitrate |
| Al(NO ₃) ₃ | Aluminium nitrate |
| SEM | Scanning electron microscope |
| Mg/L | Milligram per litre (=1ppm) |
| rpm | Revolution per minute |
| CV | Cyclic voltammetry |
| KCl | Potassium chloride |
| C ₀ | Adsorption capacity (mass of pollutant adsorbed by per gram of adsorbent) |
| FTIR | Fourier-transform infrared spectroscopy |
| OCP | Open circuit potential |

Acknowledgement

I would like to take this opportunity to show my utmost gratitude to my research mentor Dr Ren Yi from IMRE, A*STAR for providing technical guidance throughout my research journey, and teacher advisor Dr Adrian Loh Sin Loy and Ms Jasmine Tan from National Junior College and Dr Guo Huiling from Ngee Ann Polytechnic for their constant help and invaluable advice in report writing and presentation.

Novel Hybrid Regeneration Process for Adsorbent used in Wastewater Treatment

1. Literature Review

1.1 Background

Wastewater treatment is an increasingly important solution to mitigate scarcity of clean water and environmental pollution. Many techniques have been developed to remove soluble pollutants in tertiary wastewater treatment. They can be classified into biological, chemical and physical methods. Conventional biological methods are not effective for treatment of all contaminants as each method targets at a certain type.¹ Chemical treatments are less favorable due to the additional costs involved in treating by-products formed.² Different physical methods are widely used in tertiary wastewater treatment but adsorption has been found to be superior to other techniques in terms of flexibility and simplicity of design, high cost-efficiency, non-selective to toxic pollutants and ease of operation.³ Operation is simple and quick since pollutants can be removed easily by soaking the adsorbents in wastewater for a short period of time.

Layered double hydroxide (LDH) has been intensively studied due to its excellent adsorption capacities and ease of production.⁵ LDH consists of multiple metal hydroxide layers. Since the pollutants can be adsorbed into the interlayer spacing, LDH has high adsorption capacity.

1.2 Regeneration of adsorbent

One problem that is still plaguing the use of LDH is the lack of effective regeneration process. Reusing the pollutant-loaded adsorbent, being the most difficult and expensive part of the adsorption technology, is often overlooked.⁶ Disposal of a large amount of exhausted adsorbents causes a lot of other environmental issues. Moreover, it does not solve the issue since it is merely changing the pollutants from liquid to solid phase. Therefore, this project aimed to develop simple and effective regeneration methods to reuse LDH in eliminating soluble pollutants from wastewater,

It is reported that adsorption capacity of pollutant loaded LDH can be recovered by soaking it in salt solution.^{7,8} Ions in the salt solution can replace adsorbed pollutants since they are in higher concentration. However, it can only recover 10-20% of the LDH's initial capacity. Moreover, volume of salt solution is large, making it impractical for the industry to apply.

In this project, a novel method called electrochemical (EC) regeneration is proposed. Design of the process remains straightforward, but it could greatly boost the recovery rate of pollutant loaded LDH. By applying electrical potential to the LDH which is immersed in salt solution, pollutants could be repelled easily within a short period of time. Little energy is consumed since potential used is low, making the process cost effective. Moreover, this method could allow recycling and reuse of pollutants, hence it is environmentally-friendly. All these advantages make it a practical regeneration method for the industry to apply.

It is found that calcination can recover capacity of pollutant loaded LDH.⁹ However, the process is not optimized (there is 20% reduction in adsorption capacity every cycle of regeneration).^{9,10} Pollutants could be easily broken down and eliminated by simply heating the pollutant loaded LDH in air. Structure of LDH changes under high temperature, but it is capable of regaining original structure after being immersed in wastewater again.⁵ Furthermore, the process could be energy intensive as it requires prolonged heating at relatively high temperature. Therefore, there is a need to fine tune the process such that it could be more effective and cost-efficient.⁵

Hybrid regeneration could be done to boost the number of cycle that the LDH could be reused. EC regeneration could be carried for multiple cycles on-site until adsorption capacity is fully exhausted. The capacity could be fully recovered by calcination again. The multiplier effect could allow reuse of LDH for many cycles.

1.3 Use of Thin Film LDH

Adsorbents are usually prepared in the form of powder, granule and nanoparticles to increase surface contact area with pollutants.⁴ However, this is counter-productive. It increases the operating cost as filtering system is needed for subsequent solid/liquid separation process. Problems arise such as blockage of the filter and secondary contamination. Fine particles could slip through the membrane, and the presences of these nanoparticles in treated water could cause detrimental health effect when it is consumed.

LDH could not only exist as fine particles, it can also be prepared in the form of thin film (Figure 1). It is coated on a continuous piece of flat and conductive substrate via an one-step electrochemical procedure under low synthesis (room) temperature.¹⁸ Adsorption can be just as efficient since pollutants can be adsorbed into the interlayer region (bulk adsorption). Moreover, this allows EC regeneration to be conducted at ease since LDH is coated on a piece of conductive substrate. Hence, thin film LDH is used in this project as ease of synthesis,

separation of adsorbents from treated water and regeneration make LDHs practical for industry to apply.

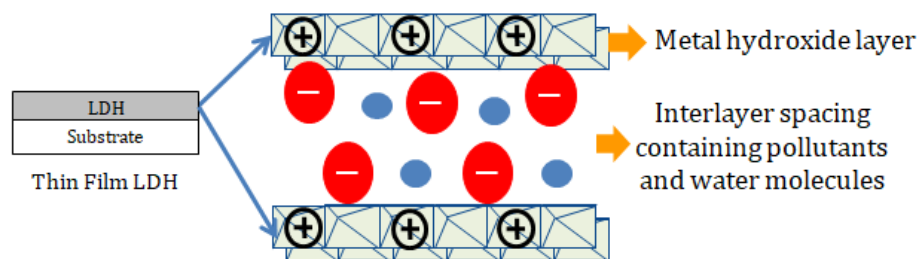


Figure 1. Schematic representation of thin film LDH

1.4 Scope and Objectives

To explore different methods of regenerating pollutant-loaded LDH, this work aims to:

1. Propose and optimize conditions for a novel regeneration method -- electrochemical regeneration
2. Investigate the effect of calcination on regeneration of LDH

With non-complicated and effective regeneration methods at hand, LDH can be easily reused over and over again to eliminate pollutants from wastewater. Therefore, wastewater can be cleaned effectively with high cost efficiency, producing larger amount of clean water.

2. Materials and Methods

All reagents used were of analytical grade and were purchased from Sigma Aldrich. All water used was distilled and further purified (elimination of ions and organic compounds) using a Millipore MilliQ system.

2.1 Synthesis of thin film LDH

In this work, Zn-Al LDH was chosen since it is a good adsorbent of organic and inorganic pollutants such as dyes and selenium.¹¹⁻¹³ Electrodeposition was carried out using potentiostat with a three electrode setup comprising of a 3M Ag/AgCl reference electrode, a Pt foil counter electrode and a Ni foam substrate as the working electrode (Figure 2). The electrolyte can be prepared by dissolving $Zn(NO_3)_2$ and $Al(NO_3)_3$ salts.¹⁴ Voltage within the range of -1.1V to -1.6V were investigated.¹⁴ The morphology and surface characteristics of films was examined using the Nova NanoSEM 450 Scanning Electron Microscope (SEM).

2.2 Removal of pollutant

The performance and regeneration of LDH in removing Congo Red ($C_{32}H_{22}N_6Na_2O_6S_2$), a common azo dye, was investigated. Films were immersed in 10 mL of Congo Red solutions with concentration of 50-100 mg/L for one hour and were shaken using orbital shaker (200 rpm) to ensure homogeneous solution. Peak absorbance values were taken at 498 nm from UV-Vis spectra, measured by the spectrophotometer with a quartz cuvette filled with DI water as the reference. The adsorption capacity (mg/g) of the LDH film were calculated using the following equation:

$$q_e = (C_o - C_e)V/W \text{----- (1)}$$

where C_o is the initial concentration, C_e is the final concentration (mg/L), V is the volume of solution used (L) and W is the mass of the film (g).

2.3 Regeneration of LDH

Electrochemical Regeneration: To find out the voltage range that can be applied without triggering reaction, cyclic voltammetry (CV) was done on a clean film. Exhausted films were regenerated within voltages identified by CV. Tri-electrode setup was used which is similar to that of electrodeposition and 0.1M of KCl was used as the electrolyte for both experiments (Figure 2).

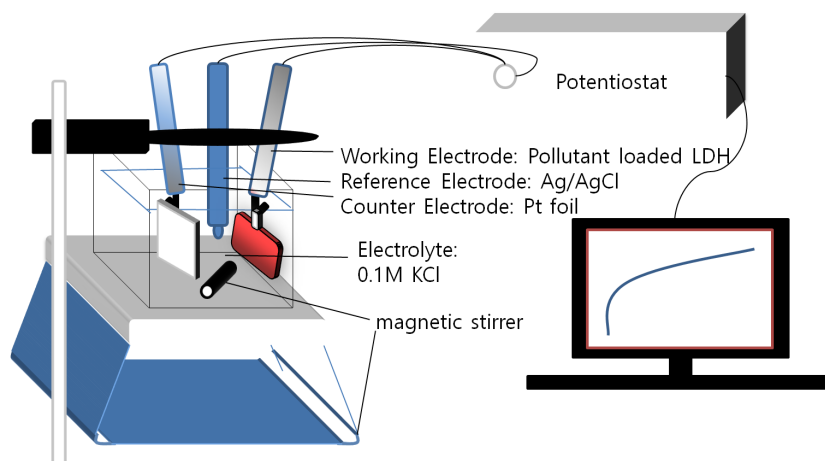


Figure 2. Schematic representation of EC regeneration setup

Calcination as activation and regeneration: The optimum activation temperature which improves the initial adsorption capacity was firstly investigated. Newly synthesized films were calcinated in air for 2 hours in tube furnace. The pollutant loaded films were then calcinated again at respective temperature for 2 hours and the regenerated capacity was measured to find the optimum regeneration temperature. The regeneration rate of each sample was calculated with the following common formula:

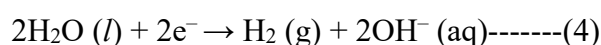
$$[\text{film capacity from } n^{\text{th}} \text{ adsorption (mg/g)} / \text{film initial capacity (mg/g)}] \times 100\% \text{ -----(2)}$$

3. Results & Discussions

3.1 Synthesis of adsorbent

3.1.1 Synthetic Mechanism of Thin Film LDH

The voltage used for electrodeposition should be sufficient to reduce nitrate ions and trigger water splitting but not enough to reduce Zn^{2+} ions in the electrolyte. During electrodeposition, NO_3^- ions and water are reduced to OH^- ions at the cathode:



The reaction occurring at the cathode increases the local pH, hence Zn^{2+} and Al^{3+} ions can precipitate at the surface of the substrate concurrently forming LDH. Initially, the original sample preparation procedure and deposition conditions which comprise of voltage applied and electrolyte concentration were used, but films were deposited on flat substrates in the literature instead of porous substrates.²⁴ Since shape of the surface of porous substrate was irregular, stress on the film was higher compared to that of flat surface. This may limit the greatest thickness grown on porous substrates. As such, procedure of sample preparation was refined. Moreover, it was thought that electrolyte may not be able to diffuse freely into the pores which affects uniformity of films deposited, hence amendments were made to optimize the deposition conditions of LDH on porous substrates.

Initially, clean and dry substrates were directly used for electrodeposition. However, mass of LDH deposited was inconsistent. It was also observed that air was trapped inside the pores of the substrate and air was trapped inside the pores of substrate when voltage was applied. This could impede uniform films being grown since the electrolyte cannot diffuse into the pores freely. As such, substrates were placed in ultrasonic bath for 5 minutes before being used for electrodeposition for subsequent experiments to fully saturate them.

3.1.2 Refining Synthetic Conditions

Subsequently, electrodeposition conditions, which consist of concentration of electrolyte, voltage and duration, were varied to find the optimum combination that can consistently deposit thick and uniform films with good adhesion to the substrates. Changing any one of the parameters could affect the thickness of the films grown.

Firstly, concentration of electrolyte was varied (voltage was fixed to be -1.2V). It is thought that higher concentration could result in more uniform film grown since there were more reactants in the pores and less diffusion is needed during deposition. However, results showed that little film was deposited (table 1, sample number 2), this could be due to difference in pH level. Electrolyte with higher concentration was too acidic for co-precipitation of zinc and aluminium hydroxide. As such, concentration of electrolyte used for subsequent deposition was fixed to be 12.5mM of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 7.5mM of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

Table 1. Average mass of LDH deposited in different concentration of electrolyte

| Number | Concentration (mM) | | pH Level | Mass of LDH deposited (g) | | | |
|----------|--|--|----------|---------------------------|---------|---------|---------|
| | $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ | $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ | | Trial 1 | Trial 2 | Trial 3 | Average |
| 1 | 12.5 | 7.5 | 3.62 | 0.0025 | 0.0028 | 0.0023 | 0.0025 |
| 2 | 62.5 | 37.5 | 3.00 | 0.0002 | 0.0005 | 0.0006 | 0.0004 |

Various voltages were tested within the range of voltage that can be used as proposed by Yarger (2008). Lower voltage normally means slower growth rate, which may give more time for reactant to diffuse into pore, thus resulting in better film quality and adhesion. However, longer deposition duration was needed such that same amount of charge would pass through the cathode, hence films with similar thickness could be deposited. Voltages between -0.9V and -1.3V were firstly tested. Newly synthesized films were loaded with Congo Red (as described in 2.3) and soaked in 10 mL of DI water overnight to check if pollutant loaded films peel off. This tested the adhesion of LDH to the substrates. Results showed that little film was deposited when -0.9V was applied, indicating that it was insufficient to trigger reaction at the working electrode (table 2, sample 1). When -1.3V was applied, pollutant loaded film peeled off upon overnight soaking (table 2, sample 2). This indicates that adhesion of film to the substrate was poor since the growth rate was too fast. Moreover, many bubbles were observed on the surface of the substrate during deposition, they could be H_2 gas as a product of water splitting (equation 4). Bubbles could impede the diffusion of electrolyte into the porous substrate, as such the film deposited is not uniform. Therefore, only voltages within the range of -0.9V and -1.3V were considered.

When $-1.0\text{V}(1000\text{s})$, $-1.1\text{V}(700\text{s})$ and $-1.2\text{V}(500\text{s})$ were applied, masses of film grown were consistent and peel-off of pollutant loaded film did not occur upon overnight soaking in DI water (table 2, sample 2, 3 & 4). This indicates good adhesion of the film to the substrate. Subsequently, duration of electrodeposition was lengthened to deposit thicker film. When -1.1V and -1.2V was applied for a longer period of time, thicker films were grown (table 2. sample 6 & 7). However, peel-off occurred for all films upon overnight soaking. This suggests that the adhesion of films to the substrates did not improve with lower voltage applied. Peel-off occurs as long as the films are thick (above 0.0030g) regardless of voltage applied during deposition. Since films with consistent mass and good adhesion were deposited for $-1.0\text{V}(1000\text{s})$, $-1.1\text{V}(700\text{s})$ and $-1.2\text{V}(500\text{s})$, $-1.2\text{V}(500\text{s})$ was chosen for subsequent synthesis of films to shorten the duration needed.

Table 2. Average mass of LDH deposited with different voltage applied

| Sample | Estimated charge passing through cathode (C) | Voltage applied (V) | Duration (s) | Mass of LDH deposited (g) | Peel off upon overnight soaking |
|--------|--|---------------------|--------------|---------------------------|---------------------------------|
| 1 | 13.5 | -0.9 | 1200 | 0.0020 | No |
| 2 | 14.0 | -1.0 | 1000 | 0.0027 | No |
| 3 | 14.0 | -1.1 | 700 | 0.0029 | No |
| 4 | 13.5 | -1.2 | 500 | 0.0028 | No |
| 5 | 13.5 | -1.3 | 400 | 0.0029 | Yes |
| 6 | 20.0 | -1.1 | 1000 | 0.0042 | Yes |
| 7 | 18.9 | -1.2 | 700 | 0.0035 | Yes |

Finally, post electrodeposition process was fine-tuned. Initially, newly synthesized films were rinsed, soaked in DI water for 5 minutes and blow-dried with N_2 gas immediately after electrodeposition. However, Congo Red solution darkened when films were sent for subsequent adsorption test. Congo red is pH sensitive, hence residual electrolyte on the film which was acidic could change the color of the solution. This made it interferes with the determination of Congo Red concentration using a spectrophotometer. Therefore, cleaning of the freshly prepared samples in this work was optimized as follow. Immediately after electrodeposition, films were soaked in DI water for 10 minutes and rinsed thrice. The liquid on the surface was removed by blowing them with a gentle stream of N_2 gas. Subsequently

they were soaked in DI water again for 10 minutes and blow-dried with N₂ gas. This process was standardized and used for subsequent cleaning and drying steps.

Table 3. Summary of Synthetic Conditions

| Factors | Deposition voltage/V | Zn(NO ₃) ₂ ·6H ₂ O concentration/mM | Al(NO ₃) ₃ ·9H ₂ O Concentration/mM | Deposition period/s |
|-------------------|----------------------|---|---|---------------------|
| Conditions | -1.2 | 12.5 | 7.5 | 500 |

3.1.3 Physical Characterization of Thin Film LDH

Physical characterization of films deposited using conditions mentioned above was performed. SEM was used to examine the morphology of LDH deposited on the Ni foam substrate. As can be seen from figure 3 (b), LDH was deposited uniformly on the substrate. The morphology of the film deposited was rougher compared to that of the substrate surface (Figure 3).

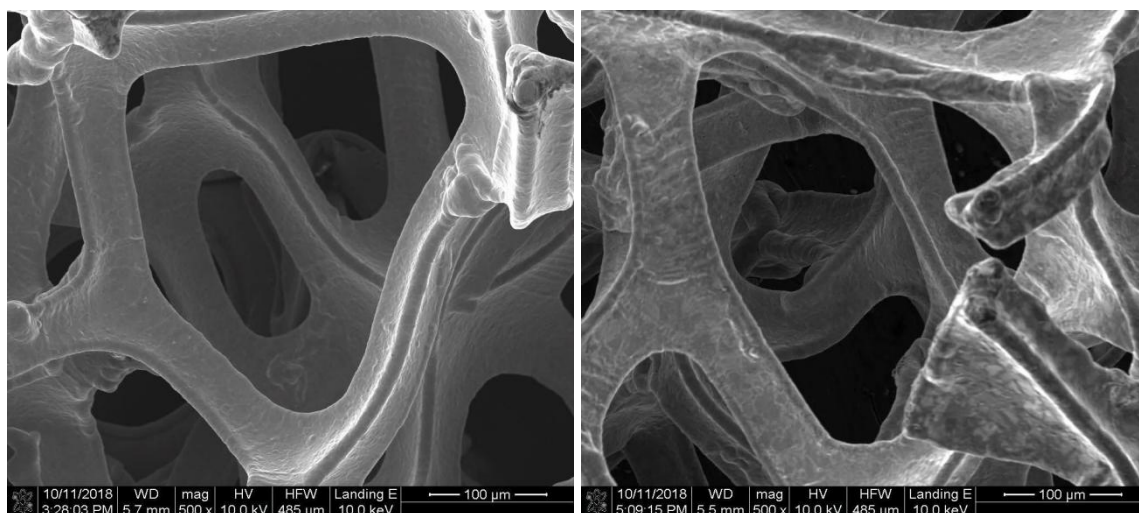


Figure 3. SEM images of (a) Plain Ni foam and (b) LDH deposited on Ni foam at 500X magnification

Conventional method of synthesizing powder LDH is more expensive and time consuming as it typically requires heating and stirring of reagents for about 70 hours.^{9,17} The fabrication process of thin film LDH is simple, quick and low-cost. It can be done in one step at room temperature within 10 minutes. Moreover, thin film LDH could be handled and regenerated at a greater ease compared to powder LDH, making it applicable for large scale application.

3.2 Initial adsorption of pollutants

Concentration of Congo Red was set to be 50mg/L as it is within the range of concentration of industrial effluent. Rapid decolourization of Congo Red occurred within 1 hour and the average initial adsorption capacity is found to be 105 mg/L which is 17 times than that of activated carbon.⁴

3.3 Electrochemical (EC) regeneration

A novel regeneration called electrochemical regeneration was proposed and optimized in this project. It could easily recover the capacity of the pollutant loaded LDH with low cost and simple setup. A negative potential was applied to the pollutant loaded LDH such that the metal hydroxide layers become negatively charged. It was therefore capable of repelling anionic Congo Red in the interlayer. When the voltage was cut off, ions in vicinity in the electrolyte could easily go back to the interlayer and occupy the active adsorption sites, thereby regenerating the LDH (Figure 4).

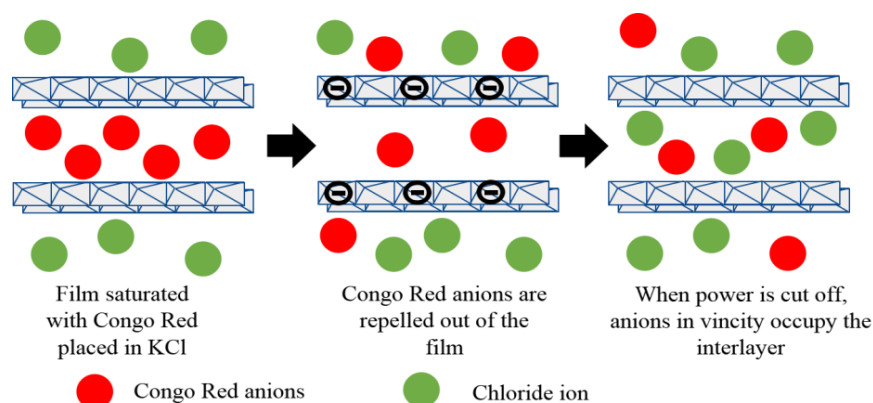


Figure 4. Schematic representation of proposed mechanism of electrochemical regeneration

Voltage applied was low since it just needed to repel the pollutants, hence cyclic voltammetry was performed to determine the range of voltage that can be applied without triggering any reaction. Only voltages between -0.6V and 0.1V were investigated since current passing through the film is negligible (Figure 5). Current surged outside of this range could be due to the LDH experiencing reactions such as degradation of intercalated Congo Red and water splitting.

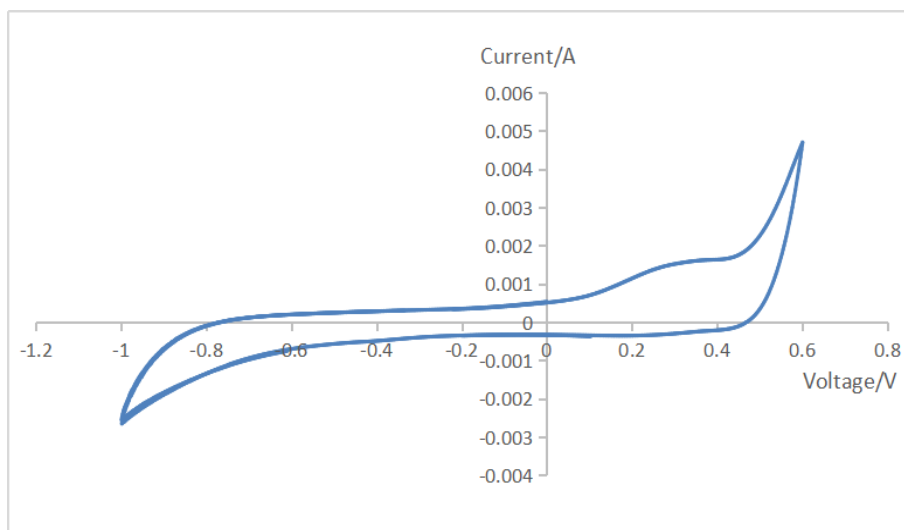


Figure 5. Cyclic Voltammetry(CV) graph of pollutant loaded film in 0.1M of KCl

Initially, experiments were conducted with absence of magnetic stirrer. However, the recovery rate did not improve regardless of voltage applied (Figure 6). This suggests that when power was cut off, Congo Red molecules that were repelled can easily go back to the interlayer since their diffusion is too slow to move them away from the LDH. As such, a magnetic stirrer was subsequently used (600 rpm) to assist the transfer of repelled Congo Red molecules to the bulk of solution.

Open circuit potential (OCP) was about -0.15V where no current flows, and when voltages higher than OCP are applied (0V and 0.4V), the film was charged positive and the repelling effect does not come into play. Hence, recovery rate is about the same as that of the control experiment where sample is soaked in the same electrolyte without current. As voltage applied becomes more negative, the recovery rate increases since the repelling effect is more pronounced (Figure 6). The results obtained show that electrochemical regeneration is able to regenerate up to 57% of the pollutant loaded LDH which is a 185% boost in recovery rate. The low current consumption makes it a cost-efficient regeneration method. It is 6 times cheaper than conventional desorption in salt. No harmful by-products are produced and it could allow potential reuse of adsorbate. Moreover, simple setup allows on-site regeneration. All these advantages make it practical regeneration for the industry to apply.

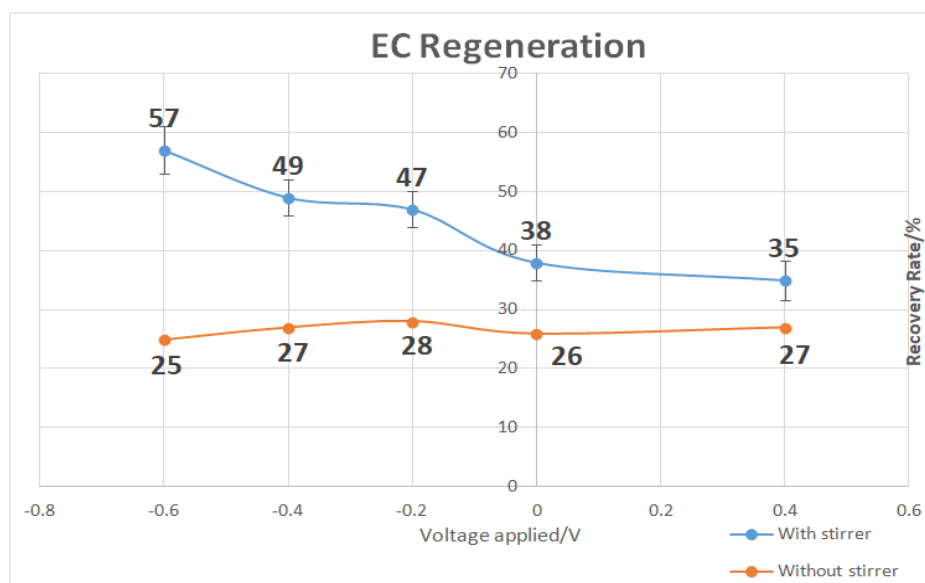


Figure 6. Recovery rate of LDH regenerated at various voltages

3.4 Regeneration through calcination

3.4.1 Effect of calcination as an activation process for newly synthesized films

To investigate temperature suitable for activation of LDHs, effect of calcination on newly synthesized films was investigated. Fresh LDH was heated to high temperature in air for 2 hours for activation. The adsorption capacity increased significantly only when calcination temperature was above 200°C as shown in figure 7, since a new dehydrated phase was formed.¹⁵ Adsorption capacity was subjected to a fourfold increase when films were calcinated at 400°C (Figure 7), reaching a very high adsorption capacity of 418 mg/g which is 60 times than that of activated carbon.⁴ Conditions required for activation were much milder than activated carbon (800-1000°C, inert environment). The activation process is simple, quick and cost effective.

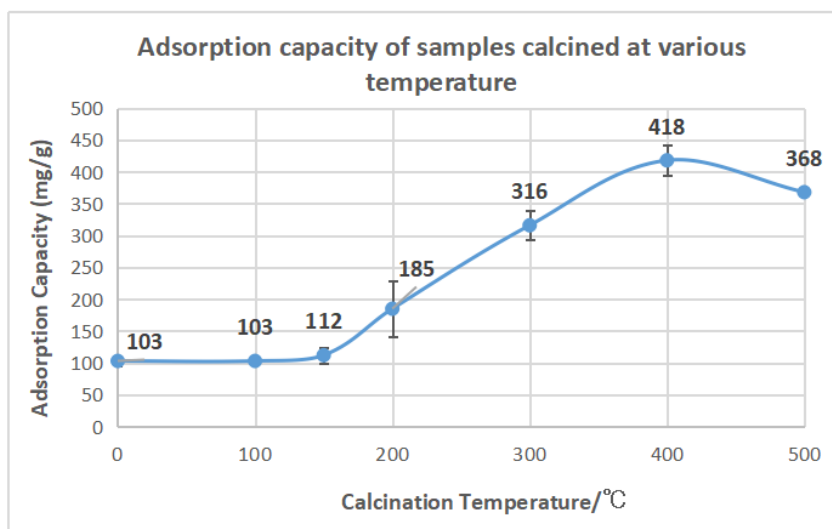


Figure 7. Initial adsorption capacities of LDH activated at various temperature.

As LDH was calcinated at 500°C, high temperature destroyed the layered structure and impeded its ability to recover upon immersion in Congo Red solution,^{16,17} therefore, adsorption capacity decreased. As such, temperatures above 500°C should not be used and are not tested in this work. Activating newly synthesized LDH at 400°C for 2 hours was found to be the optimum conditions as it can greatly boost the initial adsorption capacity, making it a powerful adsorbent in eliminating soluble pollutants from wastewater.

3.4.2 Regeneration of pollutant loaded LDH at various temperatures

After the adsorption tests, LDH films which were fully saturated with pollutants were subsequently regenerated at respective activation temperature (Figure 8).

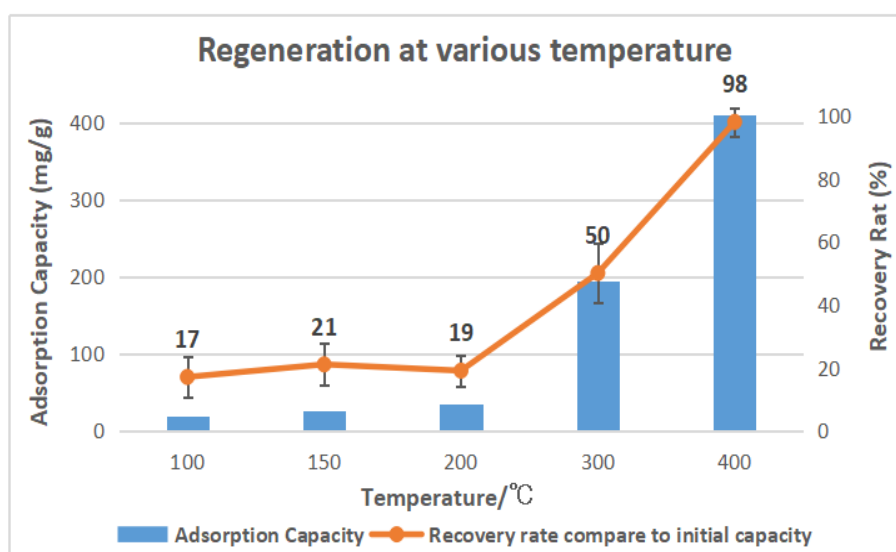


Figure 8. Adsorption capacities and recovery rate of pollutant loaded LDH regenerated at various temperature

As pollutant loaded films were calcinated at temperature ranges from 100 to 200°C, films remained red in color. Hence, recovery rate was very low since films were still fully saturated with Congo Red (10-20%). As films were calcinated at 300°C, they were partially red and an increase in recovery rate was observed. When films were calcinated at 400°C, no trace of redness was observed on the regenerated films and it reached a 98% recovery.

Regeneration mechanism which has never been well understood was identified using FTIR.

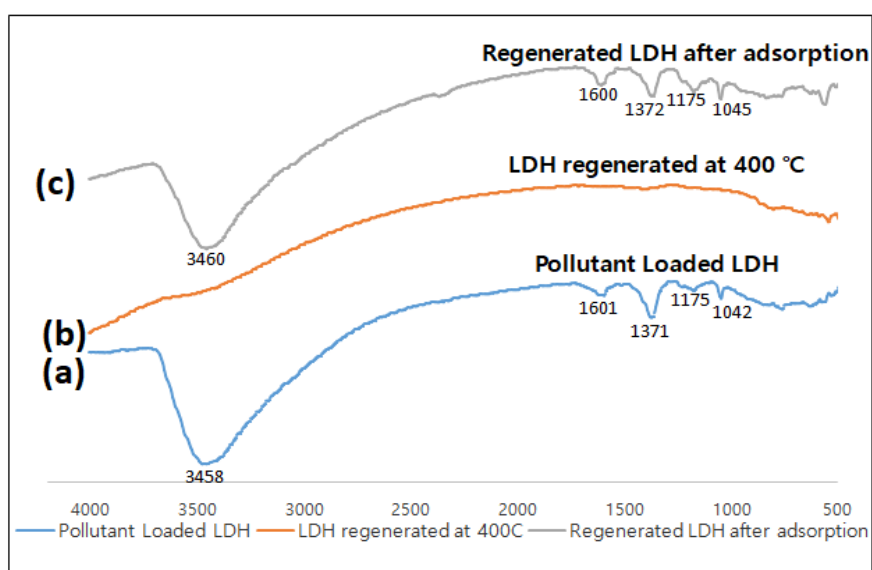


Figure 9. FTIR spectra of (a) pollutant loaded LDH; (b) Regenerated LDH; (c) regenerated LDH after adsorption

Figure 9a shows spectra of pollutant loaded LDH: the broad absorption peak in the uncalcinated LDH spectra between 3031 and 3700 cm^{-1} was due to the structural vibration of OH group in the metal hydroxide layers; The peak at around 1600 cm^{-1} was due to -N=N- stretching and the peaks at 1175 and 1042 cm^{-1} are due to S=O stretching in Congo Red molecule (Figure 9a). After the LDH was regenerated via calcination, the broad peak between 3031 and 3700 cm^{-1} disappeared (Figure 9b), this suggests that the metal hydroxide layers decomposed to a mixed of metal oxide. The peaks at 1175 and 1042 cm^{-1} disappeared, this indicates that the adsorbed pollutant broke down under high temperature (Figure 9b). When the regenerated LDH was immersed into the wastewater (Congo Red solution) again, the broad peak between 3031 and 3700 cm^{-1} appeared again (Figure 9c). This suggests that the metal oxide layers had gained back their original structure of being metal hydroxide. Peaks

which indicate presence of Congo Red appeared again (Figure 9c). It shows that the LDH was capable of adsorbing pollutants while undergoing structural reconstruction (Figure 10).

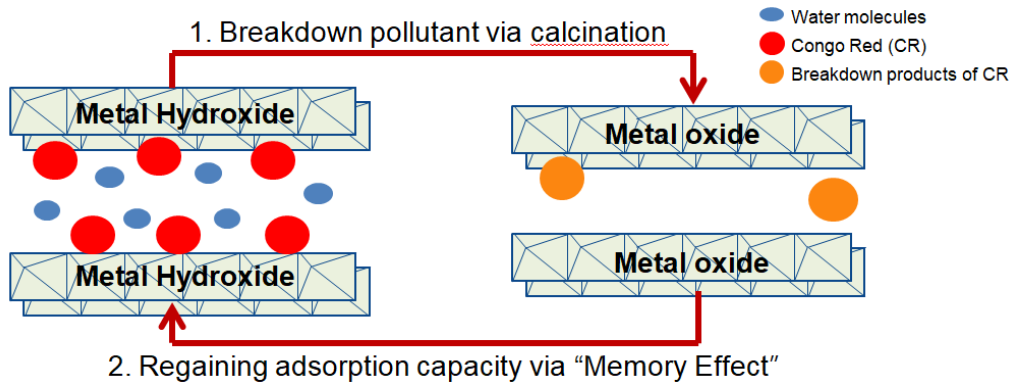


Figure 10. Schematic representation of regeneration mechanism

3.4.3 Successive Regeneration at 400°C

LDH saturated with pollutants was regenerated at 400°C followed by adsorption to test how much capacity is recovered. To investigate the potential reuse at 400°C, this was carried out for multiple cycles.

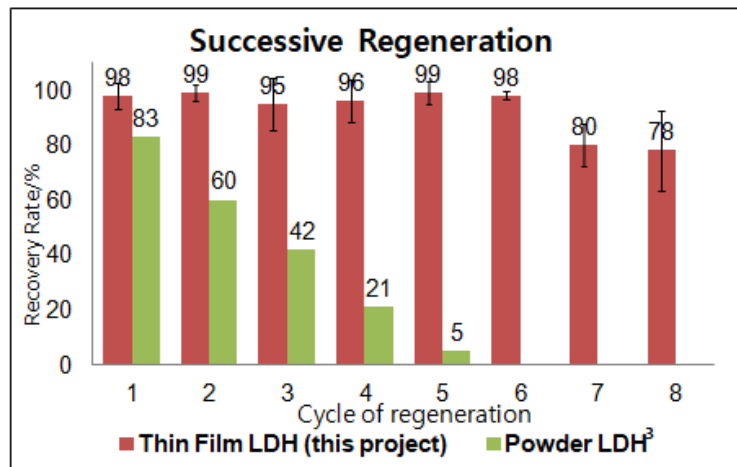


Figure 11. Adsorption capacities and recovery rate of films regenerated at 400° C

Results shows that LDH films can be regenerated without losing much of their capacities for the first six cycles (Figure 11). This indicates that 400°C is a suitable temperature for regeneration. It degrades the intercalated pollutant and triggers memory effect of LDH without destroying its structure. It can also be inferred that minimal peel-off occurs since LDH deposited has good adhesion to the substrate. These are supported by SEM images of film at its 4th cycle of regeneration before and after adsorption. LDH film cracked after

regeneration at 400°C (Figure 12a). After subsequent adsorption, LDH regained its volume and cracks disappeared (Figure 12b).

However, recovery rate started to decrease after the 6th cycle and the capacities of films deviate significantly. This could be due to peel-off of LDH from the substrates. Since each round of calcination causes volume change which led to stress on the LDH, adhesion worsened and LDH peeled off eventually. To verify this, SEM images of film that had undergone 9th cycle calcination are taken. The outer layer surface had similar morphology to nickel substrate calcinated at 400°C which indicates the absence of LDH film (Figure 13). However, LDH deposited in the inner layer surface still remained. This suggests that LDH deposited on the outer layer peels off almost completely since it is subjected to volume change during each round of calcination. As such, adsorption capacity dropped since there was less LDH present. Nevertheless, the sample was still capable of absorbing Congo Red by the LDH adhered to substrate in the inner layer which may experience less stress due to their thinner thickness. Results show significant improvement from work done by Teixeira et al. which showed a loss of capacity each cycle and a recovery rate of less than 5% after 5 cycles (Figure 11).⁸

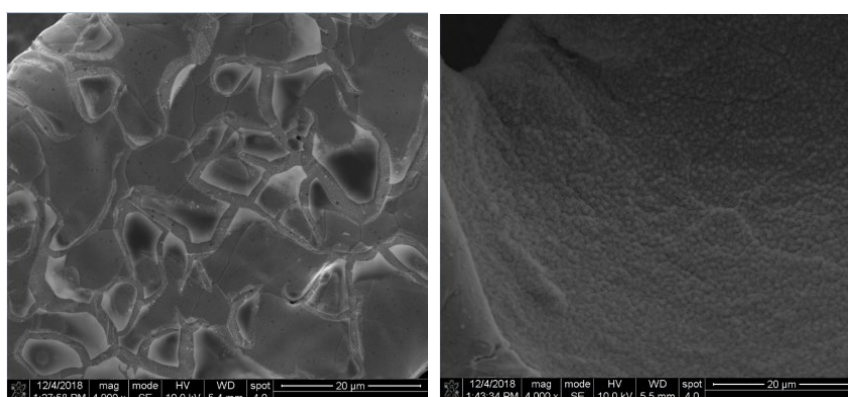


Figure 12. SEM images of (a) Film regenerated at 400°C (before adsorption) and (b) Film regenerated at 400°C (after adsorption) at 4000X magnification

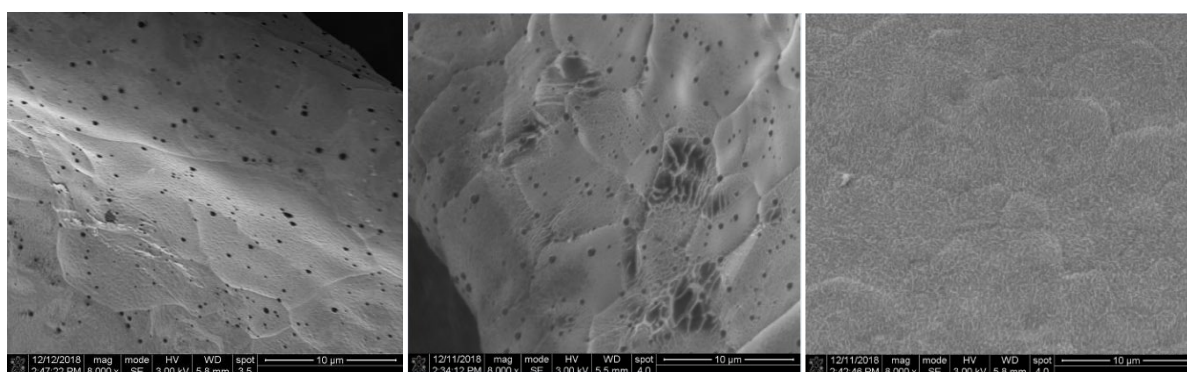


Figure 13. SEM images of (a) Nickel substrate calcinated at 400°C, (b) outer layer of the sample (9th cycle calcination) and (c) inner layer of the sample (9th cycle calcination) at 8000X magnification

4. Conclusion and Future Work

In this work, two regeneration methods were developed which are superior in recycling the high-performance adsorbent LDH. The first is a novel regeneration method which is easy to implement and can thus be used in industry with minimal energy expenditure. Type and concentration could be optimized to further boost the recovery rate. The second is the use of calcination which has shown superior retention of capacity. Since peel-off of adsorbent from the substrate occurs after the 6th cycle, further evaluation can be done to improve the adhesion by the means of fine-tuning ramping temperature.

Research could be done to combine the two regeneration methods to form a hybrid one to boost number of cycles that exhausted LDH could be recycled. Pollutant loaded LDH could be firstly regenerated for multiple cycles via EC regeneration until its recovery capacity is fully exhausted. It could then be transported for regeneration via calcination since it is able to recover the capacity of LDH fully. The multiplier effect of this combination could potentially boosts the number of cycles that LDH could be reused.

Findings of this work greatly improve recovery of pollutant loaded LDH from conventional methods. EC regeneration which is a novel method results in 185% boost in recovery rate and calcination is able to achieve ~100% recovery of exhausted LDH for 6 cycles consecutively which has never been demonstrated before. This allows LDH to be reused with greater ease, thus the adsorption technology in treating wastewater can be more effective and environmentally friendly,

5. Reference List

1. Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: a review. *Advances in colloid and interface science*, 209, 172-184.
2. Gunatilake, S. K. (2015). Methods of removing heavy metals from industrial wastewater. *Methods*, 1(1).

3. Tong, D. S., Zhou, C. H. C., Lu, Y., Yu, H., Zhang, G. F., & Yu, W. H. (2010). Adsorption of acid red G dye on octadecyl trimethylammonium montmorillonite. *Applied Clay Science*, 50(3), 427-431.
4. Gupta, V. K., Carrott, P. J. M., Ribeiro Carrott, M. M. L., & Suhas. (2009). Low-cost adsorbents: growing approach to wastewater treatment—a review. *Critical Reviews in Environmental Science and Technology*, 39(10), 783-842.
5. Goh, K. H., Lim, T. T., & Dong, Z. (2008). Application of layered double hydroxides for removal of oxyanions: a review. *Water research*, 42(6-7), 1343-1368.
6. Khehra, M. S., Saini, H. S., Sharma, D. K., Chadha, B. S., & Chimni, S. S. (2006). Biodegradation of azo dye CI Acid Red 88 by an anoxic-aerobic sequential bioreactor. *Dyes and Pigments*, 70(1), 1-7.
7. Tan, Y. S. (2017). Regeneration of high-performance thin film adsorbent for pollutant removal in wastewater.
8. Teixeira, T. P., Pereira, S. I., Aquino, S. F., & Dias, A. (2012). Calcined layered double hydroxides for decolorization of azo dye solutions: Equilibrium, kinetics, and recycling studies. *Environmental engineering science*, 29(7), 685-692.
9. Ni, Z. M., Xia, S. J., Wang, L. G., Xing, F. F., & Pan, G. X. (2007). Treatment of methyl orange by calcined layered double hydroxides in aqueous solution: adsorption property and kinetic studies. *Journal of Colloid and Interface Science*, 316(2), 284-291.
10. Crepaldi, E. L., Tronto, J., Cardoso, L. P., & Valim, J. B. (2002). Sorption of terephthalate anions by calcined and uncalcined hydrotalcite-like compounds. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 211(2-3), 103-114.
11. Li, M., Farmen, L. M., & Chan, C. K. (2017). Selenium removal from sulfate-containing groundwater using granular layered double hydroxide materials. *Industrial & Engineering Chemistry Research*, 56(9), 2458-2465.
12. You, Y., Vance, G. F., & Zhao, H. (2001). Selenium adsorption on Mg-Al and Zn-Al layered double hydroxides. *Applied Clay Science*, 20(1-2), 13-25.
13. Zhu, M. X., Li, Y. P., Xie, M., & Xin, H. Z. (2005). Sorption of an anionic dye by uncalcined and calcined layered double hydroxides: a case study. *Journal of Hazardous Materials*, 120(1-3), 163-171.

14. Yarger, M. S., Steinmiller, E. M., & Choi, K. S. (2008). Electrochemical synthesis of Zn–Al layered double hydroxide (LDH) films. *Inorganic chemistry*, 47(13), 5859-5865.
15. Stanimirova, T. S., Vergilov, I., Kirov, G., & Petrova, N. (1999). Thermal decomposition products of hydrotalcite-like compounds: low-temperature metaphases. *Journal of Materials Science*, 34(17), 4153-4161.
16. Li, F., & Duan, X. (2006). Applications of layered double hydroxides. In *Layered double hydroxides* (pp. 193-223). Springer, Berlin, Heidelberg.
17. Rocha, J., Del Arco, M., Rives, V., & Ulibarri, M. A. (1999). Reconstruction of layered double hydroxides from calcined precursors: a powder XRD and ^{27}Al MAS NMR study. *Journal of Materials Chemistry*, 9(10), 2499-2503.
18. Yarger, M. S., Steinmiller, E. M., & Choi, K. S. (2008). Electrochemical synthesis of Zn–Al layered double hydroxide (LDH) films. *Inorganic chemistry*, 47(13), 5859-5865.